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TITLE OF THESIS STUDIES ON BROMINATION AND IODINATION
[illegible] THE FREE RADICAL BROMINATION OF ALKYL HALIDES
2) THE REACTION OF tert-BUTYL HYPOCHLORITE WITH IODINE A
WITH METAL IODIDES

UNIVERSITY ALBERTA

DEGREE FOR WHICH THESIS WAS PRESENTED Ph.D.

YEAR THIS DEGREE GRANTED 1974

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NL-91 (10-68)

THE UNIVERSITY OF ALBERTA

STUDIES ON BROMINATION AND IODINATION

1) THE FREE RADICAL BROMINATION OF ALKYL HALIDES

2) THE REACTION OF *tert*-BUTYL HYPOCHLORITE WITH IODINE AND WITH SELECTED METAL IODIDES

by

JEFFREY EDWARD ROWE

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF
DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA

SPRING 1974

THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled

"STUDIES ON BROMINATION AND IODINATION

1) THE FREE RADICAL BROMOINATION OF ALKYL HALIDES

2) THE REACTION OF *tert*-BUTYL HYPOCHLORITE WITH SELECTED METAL IODIDES"

submitted by JEFFREY EDWARD ROWE in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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Supervisor

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External Examiner

November 26th, 1973
Date

ABSTRACT

The rates of the photoinitiated bromination with molecular bromine of a number of substituted n-butanes, 2-methylbutanes and cyclohexanes were determined relative to their parent hydrocarbons. In all cases the alkyl bromides were found to react appreciably faster than the parent hydrocarbons.

The relative rates of the NBS bromination of the same substrates were determined in acetonitrile. The rates of the bromination of the substituted hydrocarbons relative to their parent hydrocarbons were all significantly slower in the NBS reactions than in the reactions with molecular bromine. These differences can be attributed, in part, to the polar effects on the transfer reactions between the substituted alkyl radical and hydrogen bromide.

The differences observed between the two reagents disappeared when the brominations with molecular bromine were carried out at very high bromine concentrations, where the transfer reaction with hydrogen bromide could not compete effectively with the transfer reaction with molecular bromine. This observation further substantiates, at least for high concentrations of NBS in acetonitrile, the mechanism which has been proposed for NBS bromination reactions.

The brominations of 1-chlorobutane and chlorocyclohexane have been studied using both NBS in acetonitrile and molecular bromine as the brominating agents. With

chlorocyclohexane, a considerable difference between the product distribution obtained with these two brominating agents was observed. This difference was explai[illegible] the polar effect on the transfer reaction of the α- an[illegible] chloro alkyl radical with hydrogen bromide.

The reaction of tert-butyl hypochlorite with iodine was studied. The color and the physical properties of the solutions obtained were found to depend upon the composition of the reaction mixture. Hydrolysis of the 3:1 (tert-C_4H_9OCl: I_2) solution indicated that the species present were iodine (III) compounds. The 1:1 and 2:1 solutions were a mixture of iodine (III) species and iodine monochloride, while the 4:1 solution contained iodine (III) species and unreacted hypochlorite. The molecular weights of the species present were determined: the results indicated that the iodine (III) species must be at least partially dimerized. The photoinitiated reaction of the reagents with cyclohexane gave iodocyclohexane and chlorocyclohexane: a subsequent ionic reaction with the iodo cyclohexane led to trans-1,2-dichlorocyclohexane and trans-1-chloro-2-iodo cyclohexane.

The reaction of tert-butyl hypochlorite with silver iodide and mercuric iodide were also studied and a mixture of iodine (I) and iodine (III) species was proposed to explain the observed results. The photoinitiated reaction of the reagents formed with cyclohexane led to iodocyclohexane in yields as high as 87%.

ACKNOWLEDGEMENTS

I would like to thank my supervisor, Dr. Dennis D. Tanner, for his guidance and supervision of this work. I would also like to thank Dr. J. E. Bertie for his helpful discussion of the infrared spectra in Part II, and Dr. Naoto Wada and Mr. Alan G. Ryan for correcting this manuscript.

A special acknowledgement is owed to my wife, Julie, for her constant encouragement.

I wish to thank Mrs. Mary Waters for typing this thesis.

To the Chemistry Department, the National Research Council of Canada and to the Killam Estate (Ottawa) I am indebted for financial support during the course of this work.

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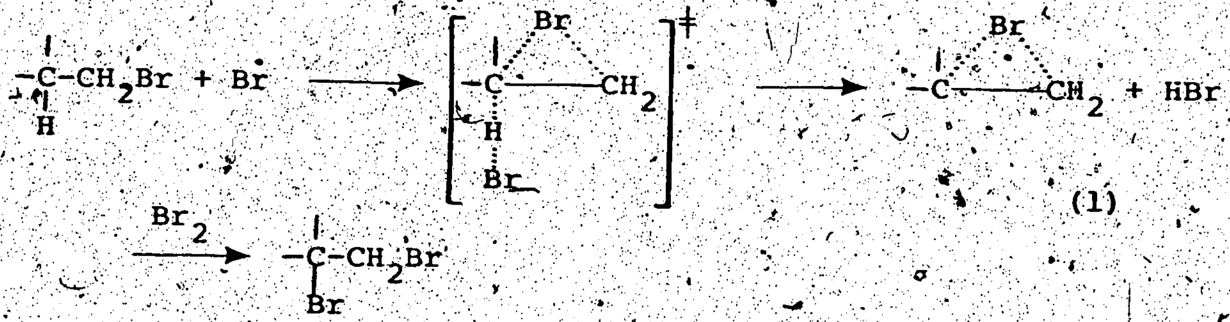
PART ONE

THE FREE RADICAL BROMINATION OF ALKYL HALIDES

INTRODUCTION

The bromination of alkyl halides has received much attention in the chemical literature (1-7). Unlike the brominations of alkyl chlorides and fluorides, which are similar to the brominations of analogous, electronegatively substituted alkanes, the bromination of alkyl bromides appears to be unique (2-7). Anchimeric assistance by the bromine substituent already present in the molecule has been proposed historically to rationalize the anomalous results observed in this system (2-7).



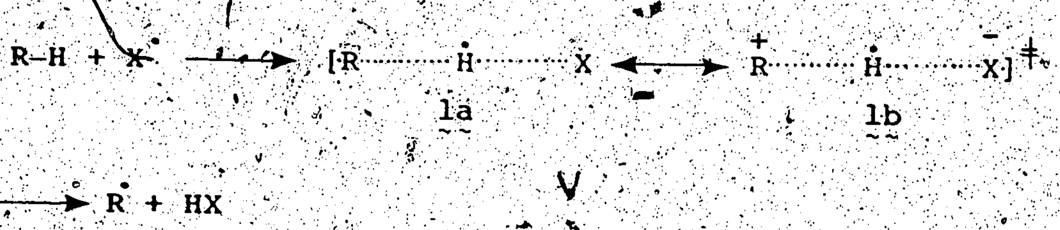
(1)

Three separate lines of evidence have emerged to support this proposal.

(1) The major product from the bromination of alkyl bromides in the liquid phase was the 1,2-dibromide (8). For example, bromination of bromocyclohexane (8) gave a 94% yield of trans-1,2-dibromocyclohexane and the bromination of 1-bromobutane (8) gave 85% 1,2-dibromobutane. This was in direct contrast to the available data for other electronegatively substituted butanes where the β position was found to be de-

activated. A summary of the published data for 1-substituted butanes is given in Table 1. The product distribution for the substituted butanes other than 1-bromobutane has been explained by the influence of polar effects on the radical reactions involved (2,3,12).

Halogen atoms are electrophilic species and would be expected to show increased reactivity at positions in molecules at which electrons are supplied by electron-donating groups, and decreased reactivity as a result of electron-withdrawing substituents. Such a dependence of a radical reaction on polar factors shows that structure 1a cannot be a complete description of the transition state but that there must be a contribution from structure 1b.



$$R{-}H + X\cdot \longrightarrow \left[\underset{\textbf{1a}}{R\cdots\dot{H}\cdots X} \longleftrightarrow \underset{\textbf{1b}}{\overset{+}{R}\cdots\dot{H}\cdots\overset{-}{X}}\right]^{\ddagger} \longrightarrow R\cdot + HX$$

By their inductive effect, halogen or oxygen substituents would be expected to destabilize 1b (this effect would decrease rapidly with the distance from the substituent) leading to the prediction that halogenation β to such substituents would be highly deactivated. This prediction is verified experimentally for the bromination of various substituted butanes (Table 1), except for 1-bromobutane where the stabilization derived from the formation of a bridged bromine radical was thought to counteract the destabilization

TABLE 1

Product Distribution in the Bromination of Selected Substituted Butanes [a]

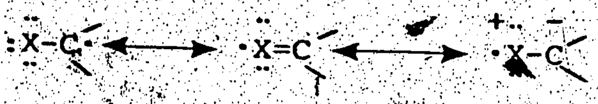
X	CH_3 —	CH_2 —	CH_2 —	CH_2 —	X	Ref.
Cl	–	1.0	0.49	0.44		8
F	0.01	1.0	0.11	0.12		9
COF	–	1.0	0.33	0.42		10
COCl	0.01	1.0	0.42	0.38		10
$OCOCH_3$	0.01	1.0	0.40	0.26		11
CO_2CH_3	0.01	1.0	0.45	0.53		10
Br	–	1.0	5.78	0.06		8

---

[a] Relative to the 1,3-isomer

due to the polar effect.

The situation is a little more complex when considering halogen atom attack α to a halogen substituent. Here the C-H bond is deactivated by the inductive effect of the substituent but the radical formed is stabilized by resonance.

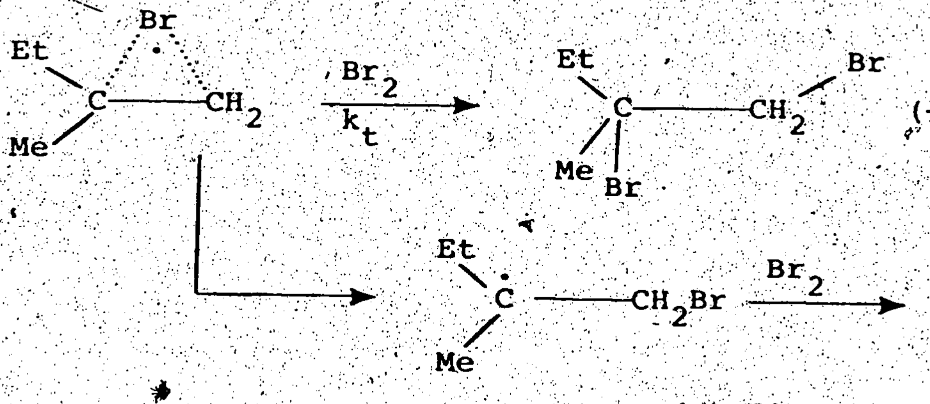


Thus 2-bromo-2-chlorobutane accoun[illegible] for over 92% of the dihalide product from the bromination of 2-chlorobutane (8). Bromination α to a bromine substituent appears to be strongly affected by steric factors, with the bulky bromine substituent hindering further substitution. For example, the rate of introduction of the first bromine atom into the methyl group of 2-methylnaphthalene was 47 times faster than that of the second (13).

(2) The bromination of (+)-1-bromo-2-methylbutane led to the formation of optically active (-)-1,2-dibromo-2-methylbutane as the only observable product (4-6,14,15). This result is in contrast to the earlier result of Brown, Kharasch and Chao (16) who found that the chlorination of optically active 1-chloro-2-methylbutane led to inactive 1,2-dichloro-2-methylbutane.

Skell *et al.* (14) have also studied the bromination of (+)-1-chloro-2-methylbutane and obtained optically active (-)-2-bromo-1-chloro-2-methylbutane as the only monobromide. They proposed a bridged chlorine radical to explain this result although in the case of the bromination of alkyl chlorides, no enhanced yield of the 1,2-dihalide product had previously been reported (for example, see Table 1).

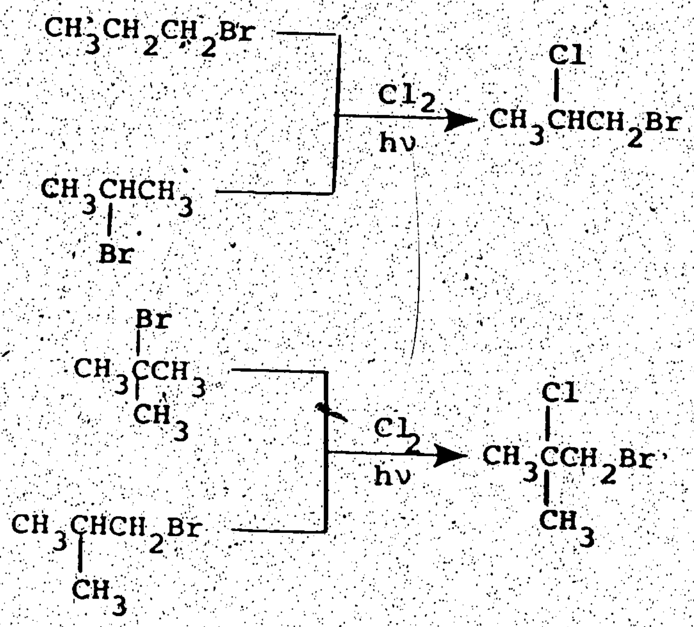
In the bromination of the (+)-1-bromo-2-methylbutane, the optical activity of the product was decreased by using elevated temperatures (>70°), low concentrations of bromine (less than 0.05 M bromine) or N-bromosuccinimide as the brominating agent. As an explanation of these results, Skell (4), suggested that under these conditions the opening of the bridged radical to the classical radical could compete with the transfer of the bridged radical with bromine.



(±)-dibromide

(3) Rearrangement of a bromine substituent to the neighboring carbon has been observed during the chlorination of several alkyl bromides. Thus Skell, Allen and Gilmour (17)

found that the chlorination of 2-bromopropane and 1-bromopropane led to a common product, 1-bromo-2-chloropropane. Similarly, *tert*-butyl bromide and 1-bromo-2-methylpropane were both converted to 1-bromo-2-chloro-2-methylpropane.



Traynham and Hines (18) found 12-15% of the rearranged product, 1-bromo-1-chloromethylcyclohexane, in the chlorination of bromomethylcyclohexane.

All of these lines of evidence have been criticized to some extent in the recent literature and a number of alternative mechanisms to that of anchimeric assistance by the bromine substituent (Reaction (1)) has been proposed to explain the observed results.

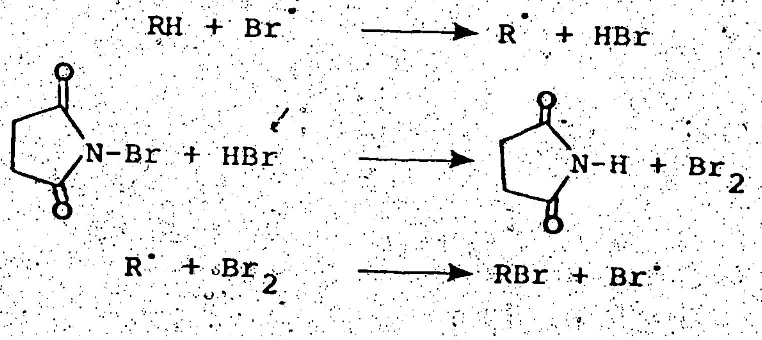
Tanner *et al.* (19) studied the bromination of 1-bromobutane with molecular bromine and reported that the distribution of products was a function of the percentage reaction. At low conversion, the distribution of the dibromides was similar to that found in the bromination of other electronegatively substituted butanes (Table 1). Equilibration of the initially formed radicals with hydrogen bromide was proposed to explain this change in the product distribution with the percentage reaction (19).

$$C_4H_9Br + Br^{\bullet} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C_4H_8\dot{B}r + HBr \qquad (2)$$

$$C_4H_8\dot{B}r + Br_2 \xrightarrow{k_2} C_4H_8Br_2 + Br^{\bullet} \qquad (3)$$

An attempt was made to establish the effect of hydrogen bromide on the product distribution by carrying out the bromination of 1-bromobutane (19,20) and bromocyclohexane (20) with N-bromosuccinimide (NBS). By utilizing the previously established chain mechanism for bromination with NBS (21-23) (Scheme 1), it was anticipated that the hydrogen bromide concentration could be kept low enough to severely limit the reverse reaction.

Scheme 1



This attempt was most successful when the reaction was initiated with azobisisobutyronitrile (AIBN) at 40° in acetonitrile as solvent. The long reaction time required for this reaction (approximately 1000 hours) coupled with the removal of hydrogen bromide by reaction with the NBS should lead to a very low concentration of hydrogen bromide in the reaction medium at any time. The product distribution for the bromination of 1-bromobutane under these conditions is given in Table 2 and that for bromocyclohexane in Table 3. The results for the bromination of 1-bromobutane with NBS in acetonitrile have been confirmed independently by Traynham _et al._ (24).

For the bromination of bromocyclohexane, even at 96% reaction, the β position was the least reactive, whereas with molecular bromine, the relative reactivity at this position was approximately 3.3 times greater than the reactivity at any other position (20). It should be pointed out that no change in the isomer distribution was observed during the bromination of bromocyclohexane with molecular bromine, even at very low percentage reaction (20).

Tedder (25) has studied the vapor phase bromination of a number of haloalkanes in a flow reactor where the reactants and products were in contact with the walls of the vessel and with the product hydrogen bromide for only a very short time. Using this method for the bromination of bromocyclohexane at 110°, the relative reactivity at the β

TABLE 2

Variation of the Isomer Distribution with the Percentage Reaction for the Bromination of 1-Bromobutane with NBS Using AIBN as the Chain Initiator [a,b]

% Reaction	1,4-	1,3-	1,2-	1,1-
	C —	C —	C —	C — Br
9	-	1.00	0.30	0.27
24	-	1.00	0.43	0.28
37	-	1.00	0.84	0.28
57	0.08	1.00	1.37	0.33

---

[a] Taken from Ref. (20).

[b] Peak ratios relative to 1,3-dibromobutane.

TABLE 3

Variation of the Isomer Distribution with the Percentage Reaction for the Bromination of Bromocyclohexane with NBS Using AIBN as Chain Initiator [a,b]

% Reaction	1,1-	*trans*- 1,2-	*trans*- 1,3-	*trans*- 1,4-	*cis*- 1,3-	*cis*- 1,4-
2	0.51	0.22	1.0	0.50	0.71	0.72
36	0.55	0.55	1.0	0.55	0.69	0.77
64	0.50	0.97	1.0	0.60	0.71	0.60
84	0.55	1.21	1.0	0.54	0.71	0.62
96	0.46	1.57	1.0	0.60	0.70	0.62

---

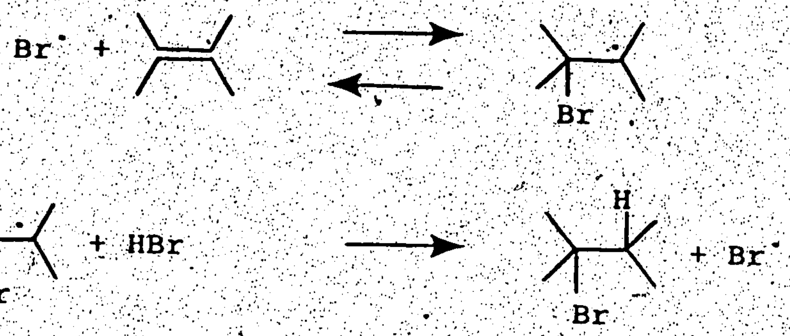
[a] Taken from Ref. (20).

[b] Peak ratios relative to *trans*-1,3-dibromocyclohexane

position was found to be the same as that at the δ position, and somewhat less than that at the α position. (Relative reactivity/H; $\alpha = \beta = \gamma = \delta = 3.2:1.0:0.57:1.0$).

The effect of hydrogen bromide on the bromination of electronegatively substituted alkanes (for example, 1-bromobutane) has been rationalized in the following manner (26). During the initial stage of the reaction, the reversal of the abstraction reaction (k_{-1}) would be unimportant because of the low concentration of hydrogen bromide, and hence the transfer of the bromoalkyl radicals with molecular bromine would reflect the kinetically determined distribution of isomeric radicals. As the reaction proceeds, equilibration of the radicals with hydrogen bromide could occur. It was reasoned that if polar effects determined the kinetic distribution of radical abstraction (k_1), then, by the same token, the reverse transfer reaction with hydrogen bromide (k_{-1}) should be subject to the same polar effects (microscopic reversibility). Therefore, the β radical is not only formed more slowly but likewise reverses more slowly and the 1,2-dibromide is formed since the non-polar bromine molecule is not subject to these polar effects.

A considerable number of precedents exist in the literature for the suggestion that the reverse reaction with hydrogen bromide is important in bromination reactions. It is, after all, the second step in the well-known free radical addition of hydrogen bromide to olefins (27).



Tanner, Mosher and Bunce (28) have studied the vapor phase bromination of deuteriochloroform with molecular bromine in the presence of initially added hydrogen bromide. At the end of the reaction, 65% of the unreacted chloroform was found to contain protium.

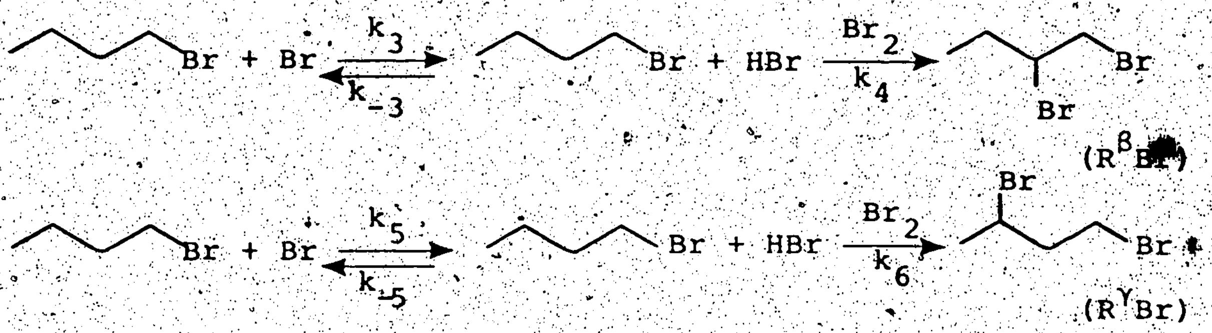
Wiberg and Slaugh (29) have shown that, in measuring the kinetic isotope effect (k_H/k_D) in the bromination of toluenes, low and erratic values were obtained unless the hydrogen bromide formed was continuously removed from the reaction. Several other studies on the bromination of toluenes (21-23) have shown that the kinetic data obtained gave an excellent fit to the Hammett correlation, particularly when σ^+ values were used. The ρ value obtained was found to be dependent upon the $[HBr]/[Br_2]$ ratio. Pearson and Martin (22) have reported that, on increasing the $[Br_2]/[HBr]$ ratio, the ρ value changed from -1.07 to -1.36 at 80°. The latter figure was very similar to that obtained from N-bromosuccinimide brominations (-1.46) at the same temperature. Both these experimental observations have been explained by suggesting an important reverse reaction with hydrogen bromide. Anderson <u>et al</u>.

(30) have demonstrated in kinetic studies the hydrogen bromide inhibition for the bromination of toluene in the vapor phase.

Recently two communications (24,31) have appeared questioning the previously reported result (19), that in the bromination of 1-bromobutane with molecular bromine, at less than 30% reaction, the ratio of the 1,2-/1,3-dibromobutane was less than unity. Both groups have noted a change in the product distribution with the percentage reaction, although the effect was nowhere near as great as was previously reported (19). If one examines the data of Skell and Shea (31), the ratio of 1,2-/1,3-dibromobutane at complete reaction was 6.3 while at low conversion, it was 3.6. Likewise, in this laboratory, in a reinvestigation of the bromination of 1-bromobutane, the previous observation that the ratio of 1,2-/1,3-dibromobutane was less than unity at low percentage reaction could not be repeated (26).

Ashton, Tedder and Walton (32) have published a study of the vapor phase bromination of 1-bromobutane with molecular bromine at 100°. These workers have found, in agreement with the previous report (19), a change in the product distribution as the reaction progressed. The ratio of 1,2-/1,3-dibromobutane changed from 0.28 after 10 minutes reaction time to 2.20 after 120 minutes. Addition of hydrogen bromide was found to change drastically the product distribution so that, after 10 minutes reaction time, the ratio of 1,2-/1,3-dibromobutane was 6.77. The formation of 1,2-dibromobutane was explained by assuming elimination of a bromine atom to form the olefin (1-butene, a product in the reaction) followed by the addition of bromine to the double bond.

The following reaction sequence has been proposed (26) to account for the formation of the two major products, 1,2-dibromobutane and 1,3-dibromobutane (≥96% of total product (26)) in the photobromination of 1-bromobutane with molecular bromine.

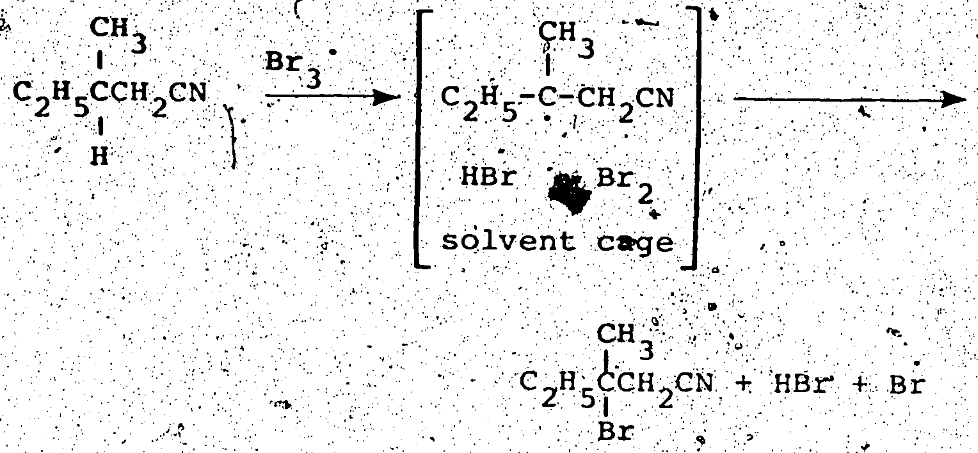


The relative rate of production of the two dibromides is given by the equation (4).

$$\frac{d[R^\beta Br]/dt}{d[R^\gamma Br]/dt} = \frac{k_3}{k_5} \cdot \frac{k_4}{k_{-3}} \cdot \frac{k_{-5}}{k_6} \left[\frac{1 + \frac{k_6}{k_{-5}} \frac{[Br_2]}{[HBr]}}{1 + \frac{k_4}{k_{-3}} \frac{[Br_2]}{[HBr]}}\right] \qquad (4)$$

This expression has been evaluated by carrying out the bromination of perdeuterio-1-bromobutane in the presence of excess bromine and hydrogen bromide. The following relative rate constants were determined under these conditions: $k_3/k_5 = 9.41$; $k_4/k_{-3} = 30.1$; $k_6/k_{-5} = 4.1$ (26). The observation that the ratio of rate constants for transfer with bromine and with hydrogen bromide of the β radical (k_4/k_{-3}) was greater than the same ratio for the γ radical (k_6/k_{-5}) is consistent with the concept that polar effects are operating in the reaction between a polar radical and hydrogen bromide, while no such interaction takes place with the non-polar bromine molecule. Following this line of reasoning, the polar effects at the β position must be much greater than those at the γ position. The difference in the ratio of the rate constants can also be ascribed to anchimeric assistance in the abstraction of the β hydrogen, leading to a bridged radical which would reverse with hydrogen bromide more slowly than the unbridged γ radical.

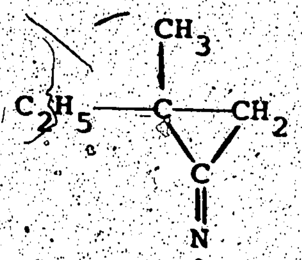
Haag and Heiba (33) have criticized the evidence for the bridged radical derived from the bromination of (+)-1-bromo-2-methylbutane. They examined the liquid phase bromination of (+)-3-methylvaleronitrile, a reaction which they claim proceeded with high selectivity at the tertiary carbon to yield (+)-3-bromo-3-methylvaleronitrile. Since they believed neighboring group participation leading to a bridged cyano radical was most unlikely, an alternate explanation was proposed. It was suggested that the abstracting species was $Br_3\cdot$, and that the resulting radical underwent a cage reaction with bromine before rotation could occur.



$$C_2H_5\underset{\displaystyle H}{\overset{\displaystyle CH_3}{C}}CH_2CN \xrightarrow{Br_3\cdot} \left[\begin{array}{c} C_2H_5\text{-}\underset{\cdot}{\overset{\displaystyle CH_3}{C}}\text{-}CH_2CN \\ HBr \quad Br_2 \\ \text{solvent cage} \end{array}\right] \longrightarrow C_2H_5\underset{\displaystyle Br}{\overset{\displaystyle CH_3}{C}}CH_2CN + HBr + Br \qquad (5)$$

The recombination of geminately caged radicals without the loss of optical activity has been the subject of a number of reports in the literature. For example, Bartlett and McBride (34) have reported the decomposition of *meso*- and *dl*-azobis-3-methyl-2-phenyl-2-butane in a glass matrix at 77°K and observed 100% stereospecificity in the products. The cage coupling products obtained from the decomposition of optically active 1,1'-diphenyl-1-methylazomethane were formed with a net retention of configuration (35).

The suggestion by Haag and Heiba that bridged cyano radicals can be excluded *a priori* is not altogether reasonable. Such a radical would be an imidyl radical 2 and these radicals have received some attention as reaction intermediates (36-38). For example, participation of a bridged cyanide group in 3 has been proposed in the rearrangement which takes place in the hypoiodite reaction of 20-hydroxy-20-cyano steroids to give 18-cyano-20-keto steroids (38).



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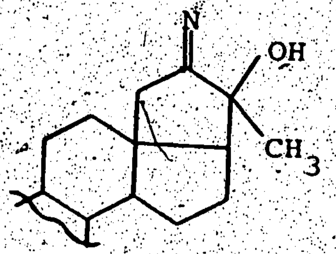

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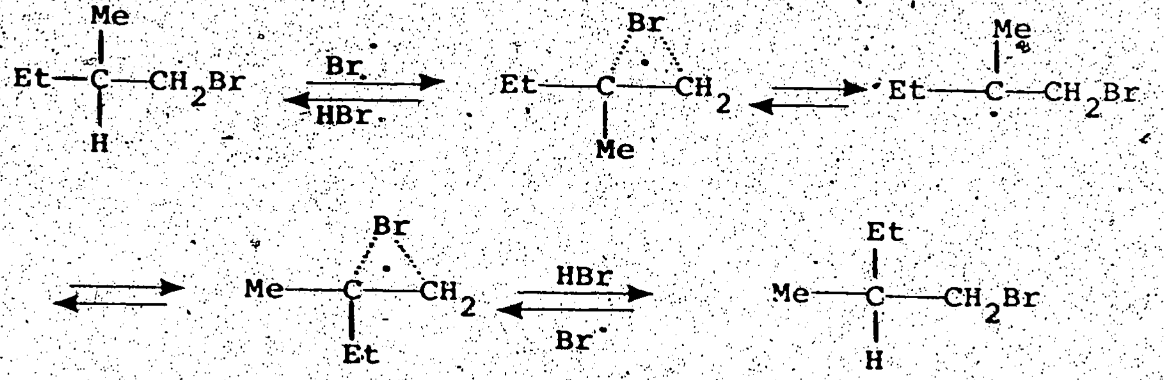
The bromination of (+)-3-methylvaleronitrile has been reinvestigated in this laboratory (39). When molecular bromine was used as the brominating agent, (+)-2-bromo-3-methylvaleronitrile was obtained in greater than 90% yield. The bromination was also carried out with a heterogeneous mixture of NBS and bromine (RCN:NBS:Br_2 ~ 6:4:1) in carbon tetrachloride as solvent. Under these conditions, optically inactive 3-bromo-3-methylvaleronitrile was the major product (2-bromo-:3-bromo-:4-bromo- = 4.7:85.1:10.2). The other two bromocyanides, 2-bromo- and 4-bromo-3-methylvaleronitrile, were found to be optically active. As a result of this investigation, the possibility that the rotation observed by Haag and Heiba (33) in the bromination of (+)-3-methylvaleronitrile was caused by small amounts of (+)-2-bromo- and (+)-4-bromo-3-methylvaleronitrile in the 3-bromo-3-methylvaleronitrile prepared, cannot be ignored.

The bromination of (+)-1-bromo-2-methylbutane with molecular bromine has been reinvestigated by Tanner, Yabuuchi and Blackburn (40). They found that the product, 1,2-dibromo-2-methylbutane, was optically active with a specific rotation in good agreement with the value reported by Skell et al. (14). The unreacted starting material was recovered, and was found to have racemized to a small extent (3-7%) during the reaction. If the bridged radical is the first formed intermediate, then this racemization observed cannot be explained by transfer of the open radical with hydrogen bromide; but if one adheres to the principle of microscopic reversibility, the racemization must be explained by transfer with the bridged radical to give back starting material (40).

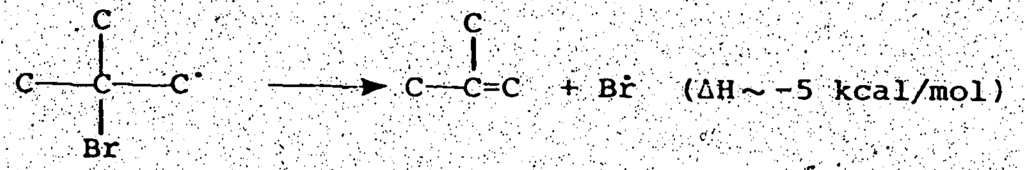


The mechanism proposed by Haag and Heiba (33) (reaction (5)) could equally well explain the observed results. If atom transfer of the tertiary radical with hydrogen bromide occurred at a rate comparable with molecular rotation in the solvent cage, then some racemized starting material would result. If transfer with bromine, within the solvent cage, takes place at a rate faster than molecular rotation, then active dibromide would be formed.

Tanner et al. (40) have also studied the bromination of (+)-1-fluoro-2-methylbutane and (+)-2-methylbutyl acetate. In both these experiments, the reisolated starting materials were substantially racemized, 86-88% in the case of 1-fluoro-2-methylbutane and 44% for 2-methylbutyl acetate. These results indicate that the reversal of the initial abstraction reaction was very important in these two systems. Not surprisingly, the 1-fluoro-2-bromo-2-methylbutane product was found to be optically inactive.

In a recent publication, Shea and Skell (41) have reported the bromination of (+)-1-bromo-2-methylbutane (13.2 mmol, $[\alpha]^{27}_{D}$ + 3.99° neat) with bromine (4.0 mmol) in the presence of deuterium bromide (57 mmol) in trichlorofluoromethane as solvent. They found that the recovered monobromide contained 51.8% d_1 and was only about 1% racemized. The implication from this experiment is that the radical retained its stereochemistry outside the solvent cage and the authors interpreted this observation as good evidence in favor of a bridged bromine radical.

Haag and Heiba (42) have reinvestigated the chlorination of tert-butyl bromide with tert-butyl hypochlorite. Previously the rearranged 1-bromo-2-chloro-2-methylpropane (17) had been reported to be the exclusive product. Haag and Heiba carried out the reaction at -78° in carbon disulfide as solvent. Under these conditions both the rearranged and unrearranged products were present. Moreover the proportion of the unrearranged product 2-bromo-1-chloro-2-methylpropane, increased with increasing hypochlorite concentration and reached about 30% in 2.5 M tert-butyl hypochlorite. These authors suggested that the rearranged product could be adequately explained by a facile elimination of a bromine atom from the intermediate β-bromoalkyl radical to give the olefin.



$$C{-}\overset{\overset{C}{|}}{\underset{\underset{Br}{|}}{C}}{-}C^{\bullet} \longrightarrow C{-}\overset{\overset{C}{|}}{C}{=}C + Br^{\bullet} \quad (\Delta H \sim -5\ \text{kcal/mol})$$

This reaction is exothermic and should have a relatively low activation energy. It would therefore be fast even at -78°. Evidence for this suggestion was obtained by carrying out the reaction in the presence of allene. Allene is an excellent scavenger for bromine atoms, and was found under these conditions to give bromochloropropenes in 42% yield (based on tert-butyl bromide reacted) at the expense of the rearranged product.

A similar elimination-readdition mechanism was proposed to account for the high yield of 1,2-dibromides in the bromination of alkyl bromides (19). To test this suggestion, the bromination of 1-bromobutane was carried out using isotopically enriched bromine (3.97% bromine-79; 96.03% bromine-81) (40). If the reaction proceeded via olefin formation, it was anticipated that some enrichment of the bromine-81 in the dibromide product would be observed. On the other hand, if the mechanism involved a bridge or a direct substitution reaction, the product must contain 27.3% bromine-79 and 72.7% bromine-81. Mass spectral analysis of the recovered dibromide showed a ratio of 27.4/72.6 for $^{79}Br/^{81}Br$. This means that either the β-bromoalkyl radical does not eliminate a bromine atom to give the olefin, or, if the elimination-readdition mechanism was operative, the original bromine never became free to mix with the bulk of the bromine in the solution. This result was recently confirmed by Bruylants et al. (43) who have studied the bromination of 1-bromobutane labelled with bromine-82. After dehydrobromination of the 1,2-dibromobutane produced with sodium hydroxide, the activity of the products, 1- and 2-bromobutene, was measured. 10% of the bromine-82 was found in the 2-bromobutene and the remaining 90% in the 1-bromobutene.

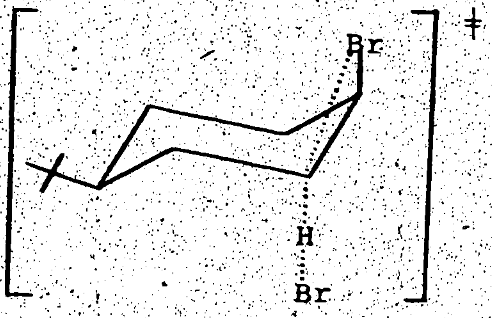
Skell (4-6) has long proposed the idea of anchimeric assistance by a neighboring bromine substituent in the abstraction of a hydrogen atom by a bromine atom. A critical test for this postulate would be a study of the relative kinetics of the reaction. If the assistance is large enough to overcome the normal polar effects, then the bromination of an alkyl bromide would be expected to proceed at a faster rate than the bromination of the parent hydrocarbon which in turn should react faster than the other negatively substituted alkanes, where polar effects would lead to deactivation (Table 1). Such a test for this mechanism has received relatively little study.

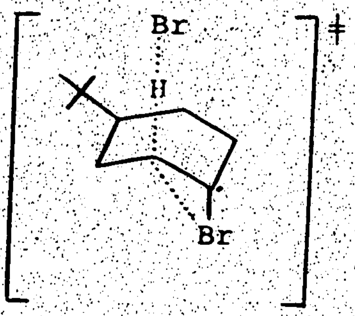
Skell (4-6,31) has studied the relative rates for bromination of *cis* and *trans*-1-bromo-4-*tert*-butylcyclohexane.

cis

trans

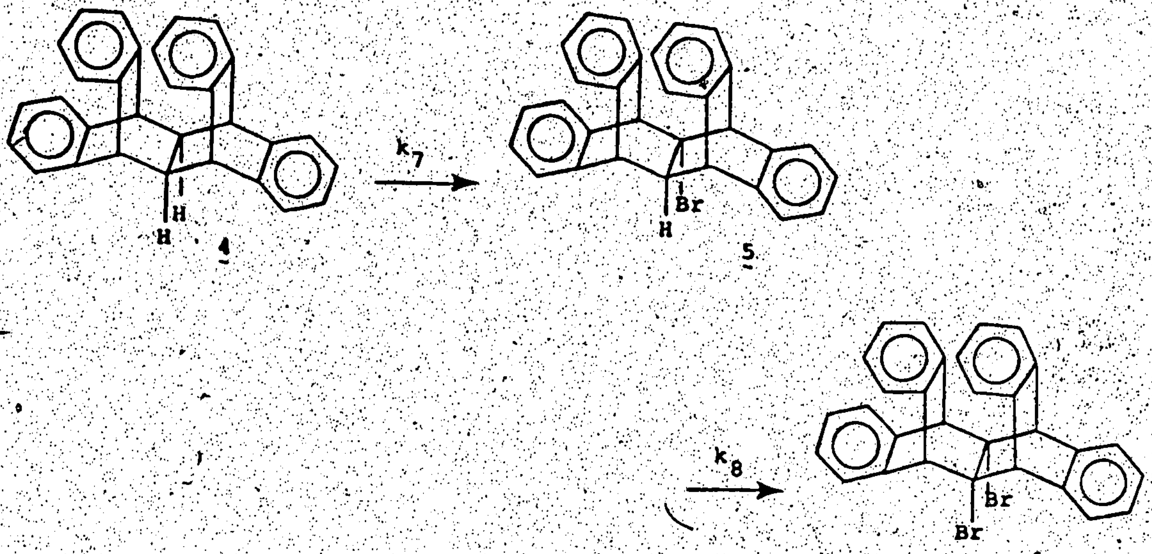
In competitive bromination experiments, $k_{cis}/k_{trans} > 15$ was obtained. Furthermore the *cis* isomer gave a single product, *cis*-1-*trans*-2-dibromo-4-*tert*-butylcyclohexane, while the bromination of the *trans* isomer led to a mixture of isomeric dibromides. These results were interpreted as good evidence for anchimeric assistance. In the *cis* isomer, the bromine substituent is in an ideal geometric arrangement to assist in the abstraction of the 2-axial hydrogen. In the case of the trans isomer, the trans di-axial arrangement of hydrogen and bromine could only be obtained after conversion of the chair cyclohexane into the higher energy boat form.





However, for the same reason, elimination of a bromine atom from the radical derived from the cis compound to give the olefin would be expected to be much faster than the elimination of a bromine atom from the radical derived from the trans compound. This elimination of a bromine atom from the β radical, together with a facile reversal of the initial abstraction reaction at the other positions, could possibly explain the faster rate of the cis-compound, and the unique product from this isomer.

Cristol, Imhoff and Lewis (44) have reported a study on the bromination of janusene (5,5a,6,11,11a,12-hexahydro-5,12:6,11-di-o-benzenonaphthacene, 4).



They found that k_8/k_7 was 1.4 at 72°. Since there are two reactive hydrogens in 4 and only one in 5, then, compared with hydrogen, bromine activates the β hydrogen by a factor of 2.8. At 12°, similar data led to a factor of 5.2.

A competitive photobromination between 5a-chlorojanusene and janusene at 72° revealed that chlorine, unlike a bromine substituent, had a deactivating effect upon the β hydrogen compared with hydrogen ($k_9/0.5k_7 = 0.5$).

The removal of a hydrogen atom from 5a-bromojanusene cannot proceed *via* a bridged bromine radical as the *anti* configuration of 5 would have prohibitively high strain energy. These authors suggested that the enhanced reactivity could be explained by a *syn* hyperconjugative electron delocalization in the *syn* bromo radical and in the transition state leading to it.

Recently Skell and Shea (31) communicated preliminary results on the competitive photobromination of a number of substrates. The β hydrogens of 1-bromobutane reacted 2.5 times faster than, and the γ hydrogens 0.37 times as fast as, the secondary hydrogens in propane at 30°. Similar data for 1-chlorobutane indicated that the β hydrogens reacted 0.09 times as fast (at 60°) and the γ hydrogens 0.25 times as fast (at 30°) as the secondary hydrogens in propane. The tertiary hydrogen in 1-bromo-2-methylpropane reacted 8 times faster than the tertiary hydrogen in 2-methylbutane indicating considerable apparent acceleration.

The aim of the present investigation was to expand greatly this kinetic approach in order to test the various mechanisms proposed for the bromination of alkyl bromides and chlorides. Substituted butanes, cyclohexanes, and 2-methylbutanes were chosen for study since previous investigations had determined a considerable amount of data about these compounds including in most cases the nature of the products. It was proposed to study the competitive kinetics both under normal bromination conditions ($R_1H:R_2H:Br_2 \sim 1:1:1$), and by utilizing the NBS method developed in a previous study (20) ($R_1H:R_2H:NBS \sim 1:1:8$ - AIBN 1% of the brominating agent), a method where the hydrogen bromide concentration was kept to a minimum. In this manner, it was hoped that any contribution to the overall reaction from anchimeric assistance or from the reverse reaction with hydrogen bromide would be readily discernible from the kinetic data obtained (45).

Another method for limiting the effect of the reverse reaction with hydrogen bromide would be to carry out the competitive kinetics with a large excess of bromine and thereby to increase the rate of the forward reaction to brominated products. Pearson and Martin (22) have reported that the ρ value obtained from the bromination of substituted toluenes was dependent on the $[Br_2]/[HBr]$ ratio. They interpreted this as being due to a restricted reverse reaction with hydrogen bromide at higher bromine concentrations. Competitive reactions, in several suitable cases (i.e. where the reactants were stable) in the presence of high bromine concentrations, were carried out and the results compared with those from other methods (45).

The determination of the relative kinetics has found extensive use in the study of free-radical reactions (21-23, 46).

$$R_1H + X^{\cdot} \underset{k_{-10}}{\overset{k_{10}}{\rightleftarrows}} R_1^{\cdot} + HX \xrightarrow[X_2]{k_{11}} R_1X + X^{\cdot} \qquad (6)$$

$$R_2H + X^{\cdot} \underset{k_{-12}}{\overset{k_{12}}{\rightleftarrows}} R_2^{\cdot} + HX \xrightarrow[X_2]{k_{13}} R_2H + X^{\cdot} \qquad (7)$$

Integration of the rate expressions (see Appendix A) gives

$$\frac{k_{10}}{k_{12}} = \frac{\log \dfrac{[R_1H]_o}{[R_1H]_f}}{\log \dfrac{[R_2H]_o}{[R_2H]_f}} \qquad (8)$$

The ratio of the rate constants (k_{10}/k_{12}) can only be computed by equation (8) if the abstraction reactions (k_{10}) and (k_{12}) are irreversible. If appreciable reversal of the abstraction reactions occurs then equation (9) must be used to evaluate the relative rates (k_{10}/k_{12}).

$$\frac{d\ \ln(R_1H)/dt}{d\ \ln(R_2H)/dt} = \frac{k_{10}}{k_{12}} \left[\frac{1 + k_{-12}[HBr]/k_{13}[Br_2]}{1 + k_{-10}[HBr]/k_{11}[Br_2]} \right] \qquad (9)$$

The integration of equation (9) represents a much more formidable challenge and only in the limiting case where (9) reduces to (8) (no reversal) can it be readily evaluated. The relative rates for bromination with molecular bromine ($R_1H:R_2H:Br_2 \sim 1:1:1$) were computed using equation (8) even though the reversal of the abstraction reaction has been demonstrated to be an important process (22,26,28,29,40,41). They should therefore be regarded as apparent relative rates.

RESULTS

I. Photobromination of Mixtures of Substrates with Molecular Bromine ($R_1H:R_2H:Br_2 \sim 1:1:1$)

The rates of bromination of cyclohexane relative to its bromo- and chloro- derivatives, n-butane, 1-chlorobutane and 1-bromobutane; and of 2-methylbutane relative to its 1-chloro-, 1-bromo- and 1-fluoro- derivatives were determined by competitive bromination using a 1:1:1 mol ratio of the two substrates to molecular bromine ($R_1H:R_2H:Br_2$).

The reactions were carried out in sealed degassed Pyrex ampoules which were irradiated at 40° in a water bath. A Rayonet merry-go-round apparatus was used to ensure uniform irradiation of all ampoules in any experiment. The irradiation was continued until the bromine color disappeared.

The rates were computed by determining the area ratios by gas, liquid partition chromatography (glpc) of the two hydrocarbons to Freon 112, the internal standard, both before and after the reaction. Experimentally this was accomplished by sealing an aliquot of the initial hydrocarbon/Freon 112 solution in a Pyrex ampoule. This solution and the brominated solutions were then analysed by glpc at the same time. The relative rate constants obtained in this manner are given in Table 4.

TABLE 4

Relative Kinetics for the Bromination with Molecular Bromine at 40° ($R_1H:R_2H:Br_2 \sim 1:1:1$).

R_1H	R_2H	k_{R_1H}/k_{R_2H} [a,b]
n-Butane	Cyclohexane	1.08 ± 0.07 (4)
1-Chlorobutane	Cyclohexane	0.80 ± 0.07 (4)
1-Bromobutane	Cyclohexane	3.66 ± 0.28 (4)
Chlorocyclohexane	Cyclohexane	1.48 ± 0.05 (4)
Bromocyclohexane	Chlorocyclohexane	4.36 ± 0.14 (4)
1-Chloro-2-methylbutane	2-Methylbutane	1.90 ± 0.08 (4)
1-Bromo-2-methylbutane	1-Chloro-2-methylbutane	8.60 ± 1.50 (4)
1-Fluoro-2-methylbutane	1-Chloro-2-methylbutane	0.13 ± 0.01 (4)

---

[a] The errors indicated are average deviations from the mean.

[b] Number of experiments is given in parentheses.

II. AIBN Initiated Bromination of Substrates with N-Bromosuccinimide ($R_1H:R_2H:NBS \sim 1:1:8$)

The same competitive reactions as for the molecular bromine experiments were carried out in homogeneous acetonitrile solutions at 40°. Mixtures consisting of a 1:1:8 mo ratio of $R_1H:R_2H:NBS$, Freon 112 as the internal standard, and a catalytic amount of azobisisobutyronitrile (AIBN) (1 mol.% based on the brominating agent) were placed in sealed, degassed Pyrex ampoules. The reactions were carrie out in the dark for an appropriate period of time (~800 hours). (At this temperature, AIBN has a half-life of approximately 700 hours (47)). The data obtained are given in Table 5.

One further point, which will be discussed in more detail later, should be mentioned. The material balances obtained in the NBS brominations were generally poor, i.e. the amount of active bromine that was consumed during the reaction could not be accounted for by analysis of the substrate bromination products. For the AIBN initiated reactions, the material balances obtained in this way were only 10-30%. Somewhat better material balances were obtained in the photoinitiated reactions with NBS (25-60%), N-bromotetramethylsuccinimide and the hydantoins to be discussed later.

TABLE 5

Relative Kinetics for the AIBN Initiated Bromination with NBS at 40° ($R_1H:R_2H:NBS \sim 1:1:8$)

R_1H	R_2H	k_{R_1H}/k_{R_2H} [a,b]
1-Chlorobutane	Cyclohexane	0.15 ± 0.02 (6)
1-Bromobutane	Cyclohexane	0.28 ± 0.03 (6)
n-Butane	Cyclohexane	0.48 ± 0.06 (6)
Chlorocyclohexane	Cyclohexane	0.21 ± 0.02 (4)
Bromocyclohexane	Chlorocyclohexane	1.37 ± 0.16 (4)
1-Chloro-2-methylbutane	2-Methylbutane	0.27 ± 0.04 (4)
1-Bromo-2-methylbutane	1-Chloro-2-methylbutane	6.2 ± 0.5 (4)
1-Fluoro-2-methylbutane	1-Chloro-2-methylbutane	0.14 ± 0.1 (3)

---

[a] The errors indicated are average deviations from the mean

[b] The number of experiments is given in parentheses.

III. Photoinitiated Bromination of Substrates with NBS ($R_1H:R_2H:NBS \sim 1:1:8$)

Reaction mixtures consisted of a 1:1:8 mol ratio of $R_1H:R_2H:NBS$ in acetonitrile as solvent. The degassed solutions were sealed in Pyrex ampoules and were irradiated at 40° in a water bath for a time sufficient to ensure at least 10% reaction of each substrate. The results are given in Table 6.

IV. Photoinitiated Bromination of Substrates with Several N-Bromoimides in Acetonitrile at 40° ($R_1H:R_2H:SBr \sim 1:1:8$)

The reactions were carried out in the same manner as the NBS brominations in acetonitrile and the results are given in Table 7. Included in the Table are two NBS brominations with initially-added molecular bromine ($R_1H:R_2H:NBS:Br_2 \sim 1:1:8:0.4$).

V. Photoinitiated Bromination of Substrates with High Concentrations of Molecular Bromine

The reaction mixtures, consisting of ratios of $R_1H:R_2H:Br_2$ varying from 1:1:5 to 1:1:100, with Freon 112 as the internal standard, were placed in Pyrex ampoules, degassed and sealed. The ampoules were irradiated at 40.0° for a time sufficient to ensure at least 10% reaction of each substrate. Before analysis by glpc, the

TABLE 6

Relative Reactivities for the Photoinitiated Bromination with NBS at 40° ($R_1H:R_2H:NBS \sim 1:1:8$)

R_1H	R_2H	k_{R_1H}/k_{R_2H} [a,b]
1-Bromobutane	Cyclohexane	0.58 ± 0.10 (2)[c]
Chlorocyclohexane	Cyclohexane	0.23 ± 0.02 (6)
Bromocyclohexane	Chlorocyclohexane	1.79 ± 0.17 (6)
1-Chloro-2-methylbutane	2-Methylbutane	0.29 ± 0.02 (4)
1-Bromo-2-methylbutane	1-Chloro-2-methylbutane	5.5 ± 0.5 (4)
1-Fluoro-2-methylbutane	1-Chloro-2-methylbutane	0.23 ± 0.02 (2)

---

[a] The errors are average deviations from the mean.

[b] The number of experiments is given in parentheses.

[c] Result by Y. Kosugi.

TABLE 7

Relative Reactivities for the Photoinitiated Bromination with Several N-Bromoimides at 40° ($R_1H:R_2H:SBr \sim 1:1:8$)

R_1H	R_2H	Reagent[c]	k_{R_1H}/k_{R_2H}[a,b]
Chlorocyclohexane	Cyclohexane	A	0.23 ± 0.02 (6)
		B	0.14 ± 0.02 (2)
		C	0.43 ± 0.01 (3)
		D	0.18 ± 0.01 (2)
		E	0.29 ± 0.02 (3)
Bromocyclohexane	Chlorocyclohexane	A	1.80 ± 0.20 (6)
		B	1.58 ± 0.05 (3)
		C	1.87 ± 0.03 (3)
		D	1.88 ± 0.09 (2)
1-Bromobutane	Cyclohexane	E	0.32 ± 0.02 (2)

---

[a] The errors are average deviations from the mean.

[b] The number of experiments is given in parentheses.

[c] A, NBS (from Table 6); B, N-bromotetramethylsuccinimide; C, 1,3-Dibromo-5,5-dimethylhydantoin; D, 1-Bromo-3,5,5-trimethylhydantoin; E, NBS-Br_2 ($R_1H:R_2H:NBS:Br_2 \sim 1:1:8:0.4$).

excess bromine was destroyed by ice-cold sodium bisulfite and the organic layer extracted with Freon 113 or o-dichlorobenzene.

The stability of the substrates in the presence of excess bromine in the dark was checked both with and without added hydrogen bromide. 1-Bromobutane and chlorocyclohexane were stable in the presence of hydrogen bromide (approximately equal to the concentration produced in the reaction) and a hundred fold excess of molecular bromine in the dark. Bromocyclohexane was found to be unstable in the presence of high concentrations of bromine in the dark.

The results from this study are given in Table 8.

VI. Photoinitiated Bromination of Substrates with N-Bromotetramethylsuccinimide in Carbon Tetrachloride at 40°.

The relative rates of two pairs of substrates using N-bromotetramethylsuccinimide in carbon tetrachloride were determined. This brominating agent was chosen because of its much greater solubility in the solvent than NBS itself (0.16 M *versus* 0.006 M (15)). The results are given in Table 9. In the ir spectrum of the reaction mixture, an absorption at 2240 cm^{-1} attributable to an isocyanate (48) could be detected.

TABLE 8

Relative Reactivities for the Photoinitiated Bromination with Excess Molecular Bromine at 40°.

R_1H	R_2H	$R_1H:R_2H:Br_2$	k_{R_1H}/k_{R_2H} [a,b]
1-Bromobutane	Cyclohexane	1:1:1	3.7 ± 0.3 (4)
		1:1:5[c]	1.61 ± 0.12 (3)
		1:1:20[c]	1.06 ± 0.04 (2)
		1:1:100[c]	0.52 ± 0.01 (2)
Chlorocyclohexane	Cyclohexane	1:1:1	1.48 ± 0.05 (4)
		1:1:6	1.02 ± 0.07 (3)
		1:1:20	0.68 ± 0.02 (2)
		1:1:40	0.56 ± 0.04 (2)
		1:1:100	0.36 ± 0.03 (3)
Bromocyclohexane	Chlorocyclohexane	1:1:1	4.4 ± 0.1 (4)
		1:1:5	2.7 ± 0.2 (3)

---

[a] The errors are average deviations from the mean.

[b] The number of experiments is given in parentheses.

[c] Results of Y. Kosugi.

TABLE 9

Relative Reactivities for the Photoinitiated Bromination with N-Bromotetramethylsuccinimide in Carbon Tetrachloride at 40° ($R_1H:R_2H:SBr \sim 1:1:8$)

R_1H	R_2H	k_{R_1H}/k_{R_2H} [a,b]
1-Bromobutane	Cyclohexane	3.17 ± 0.13 (2)
Chlorocyclohexane	Cyclohexane	1.55 ± 0.10 (2)

---

[a] The errors are standard deviations from the mean.

[b] The number of experiments is given in parentheses.

VII. Brominations in Methylene Chloride as Solvent at 40°.

Two competitions were studied in methylene chloride using several different brominating conditions.

Brominations with molecular bromine ($R_1H:R_2H:Br_2 \sim 1:1:1$) were carried out in a manner similar to that described previously. At the end of the reaction, approximately 60% of the initial bromine appeared as mono-brominated products and another 30% as bromodichloromethane.

Utilizing a method described by Skell (4,6,49), the competitions were determined by the photolysis of a homogeneous solution of the two substrates, NBS and molecular bromine in methylene chloride ($R_1H:R_2H:NBS:Br_2 \sim 1:1:1:0.07$). Approximately 70% of the initial active bromine could be accounted for at the end of the reaction, 30% of this as bromodichloromethane.

An attempt was made to measure the relative rates of the two substrates in the photoinitiated bromination with NBS in methylene chloride, a solvent in which NBS has a low solubility* (0.29 M (15)) ($R_1H:R_2H:NBS \sim 1:1:5.5$). The values of the relative rates thus obtained were not very reproducible, as has been previously reported for this solvent (21). At the end of the reaction, approximately 70% of the active bromine which could be accounted for, appeared as bromodichloromethane.

The results are given in Table 10.

TABLE 10

Relative Rates for the Photoinitiated Brominations in Methylene Chloride at 40°

R_1H	R_2H	Reagent[c]	k_{R_1H}/k_{R_2H} [a,b]
Chlorocyclohexane	Cyclohexane	A	1.44 ± 0.08 (3)
		B	1.32 ± 0.08 (4)
		C	0.7 ± 0.2 (3)
Bromocyclohexane	Chlorocyclohexane	A	3.2 ± 0.3 (3)
		B	2.90 ± 0.05 (2)
		C	2.5 ± 0.7 (3)

---

[a] The errors are standard deviations from the mean.

[b] The number of experiments is given in parentheses.

[c] A, $R_1H:R_2H:Br_2 \sim 1:1:1$; B, $R_1H:R_2H:NBS:Br_2 \sim 1:1:1:0.07$; C, $R_1H:R_2H:NBS \sim 1:1:5.5$.

VIII Bromination of Chlorocyclohexane with Molecular Bromine and with NBS at 40°.

The bromination of chlorocyclohexane was studied using three different brominating conditions:-

(A) Photoinitiated bromination with molecular bromine (mol ratio $C_6H_{11}Cl:Br_2 \sim 5:1$) in Freon 112.

(B) Photoinitiated bromination with NBS in acetonitrile (mol ratio $C_6H_{11}Cl:NBS \sim 1:3$). The reactions were stopped after varying reaction times to determine any changes in [illegible] distribution as the reaction progressed.

(C) AIBN initiation of NBS bromination in acetonitrile (mol ratio $C_6H_{11}Cl:NBS \sim 1:1.5$; AIBN, 1% based upon NBS). The reaction was stopped at an early stage to determine the initial product distribution.

The results from this study are given in Table 11.

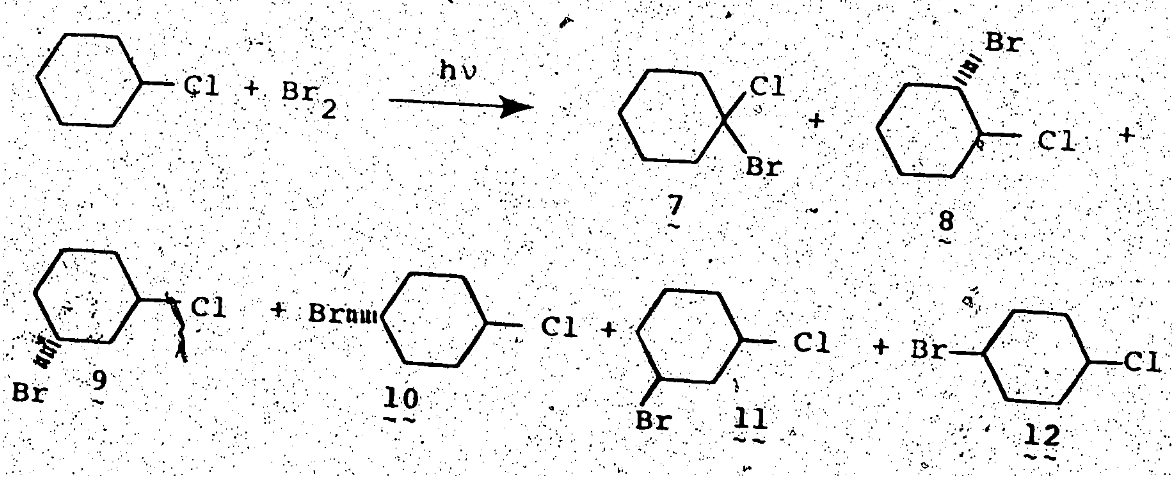


TABLE 11

Isomer Distribution in the Bromination of Chlorocyclohexane at 40°.[a,b]

Brominating conditions	% reaction[c]	7	8	9	10	11	12
NBS/CH_3CN/hν	1.4	1.73	1.0	2.49	1.29	1.71	1.59
	3.0	2.39	1.0	2.56	1.34	1.65	1.68
	18.3	4.94	1.0	1.65	0.85	1.05	1.03
	29.9	5.92	1.0	1.24	0.71	0.89	0.77
NBS/AIBN/CH_3CN[d]	5.5	1.44	1.0	2.32	1.15	1.28	1.36
Br_2/hν[d,e]	100	8.12	1.0	0.46	0.25	0.43	0.26

---

[a] Values are mol ratios relative to trans-1-bromo-2-chlorocyclohexane (8) and are the averages of duplicate analyses of each reaction mixture.

[b] The material balance for the cyclohexanes was 96-100% in all reactions.

[c] Percentage conversion of chlorocyclohexane.

[d] Average of two separate experiments.

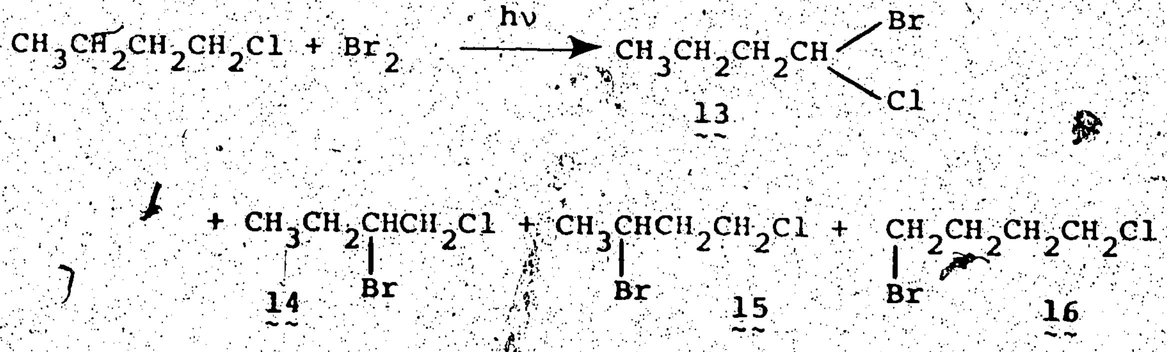
[e] Plus 6.2% dibromochlorocyclohexanes. The material balance for bromine was 99%.

The products were collected by preparative glpc. Products **8**, **9**, **10**, **11**, and **12** all gave molecular ions in the mass spectrum corresponding to $C_6H_{10}BrCl$ and were identified by a comparison of their spectra (ir, nmr) with the data available in the literature. No product assignable to cis-1-bromo-2-chlorocyclohexane was found.

1-Bromo-1-chlorocyclohexane had a refractive index in agreement with the value in the literature. Hydrolysis with barium carbonate gave cyclohexanone and dehydrohalogenation with potassium hydroxide in ethanol gave 1-chlorocyclohexene and a small amount of another product which from the nmr of the reaction mixture appeared to be 1-bromocyclohexene.

IX Bromination of 1-Chlorobutane with Molecular Bromine and with NBS at 40°

The bromination of 1-chlorobutane was carried out using the same brominating conditions outlined previously for the bromination of chlorocyclohexane. The results are given in Table 12.



$$CH_3CH_2CH_2CH_2Cl + Br_2 \xrightarrow{h\nu} CH_3CH_2CH_2CH\begin{matrix}Br\\Cl\end{matrix}$$

13

$$+ CH_3CH_2\underset{Br}{CH}CH_2Cl + CH_3\underset{Br}{CH}CH_2CH_2Cl + \underset{Br}{CH_2}CH_2CH_2CH_2Cl$$

14 **15** **16**

TABLE 12

Isomer Distribution in the Bromination of 1-Chlorobutane at 40° [a,b]

Brominating conditions	% reaction[c]	13	14	15	16	poly-bromide
NBS/CH_3CN/hν	1.0	0.23	0.28	1.0	0.086	
	4.0	0.28	0.35	1.0	0.056	
	11.0	0.28	0.40	1.0	0.026	~0.05
NBS/AIBN/CH_3CN[d]	5.0	0.27	0.32	1.0	0.11	
Br_2/hν[d,e]	100	0.52	0.57	1.0	0.007	~0.08

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[a] Values are mol ratios relative to 3-bromo-1-chlorobutane (15) and are the averages of duplicate analyses of each reaction mixture.

[b] The material balance for the butanes was 96-101% in all reactions.

[c] Percentage conversion of n-C_4H_9Cl.

[d] Average of two separate experiments.

[e] The material balance for bromine was 97-100%.

The reactions with molecular bromine were carried out with a 9.5:1.0 mole ratio of $\underline{n}$-C_4H_9Cl to Br_2. At lower ratios of $\underline{n}$-C_4H_9Cl to Br_2 substantial amounts of dibromochlorobutanes were obtained along with altered ratios of the mono-bromochlorobutanes.

The products were collected by preparative glpc and were identified from their mass and nmr spectra and by the agreement between the refractive indexes obtained and the literature values.

The product distribution in the bromination with molecular bromine was very similar to that previously reported by Thaler (8).

DISCUSSION

Photobromination of Mixtures of Substrates with Molecular Bromine ($R_1H:R_2H:Br_2 \sim 1:1:1$)

A superficial examination of the results obtained from the competitive brominations of the halogenated alkanes (Tables 13-15) indicates that with the exception of 1-chlorobutane and 1-fluoro-2-methylbutane all of the substituted alkanes react at faster rates than their unsubstituted parent hydrocarbons.

The values listed in Tables 13-15, however, were determined using equation (8), which assumes an irreversible abstraction process. The relative reactivities calculated using this expression are therefore only apparent relative rates if there is significant reversal, and do not necessarily reflect the true kinetic values.

Competitive Bromination of Mixtures of Substrates with NBS ($R_1H:R_2H:NBS \sim 1:1:8$)

The relative kinetics using NBS as the brominating agent and either photochemical or AIBN initiation in acetonitrile as solvent are given in Tables 13-15.

The results indicate that, in all cases, the rates of NBS bromination of the halogenated alkanes relative to the parent hydrocarbons are significantly lower than the values obtained from the bromination with molecular

TABLE 13

A Comparison of the Relative Rates of Bromination of Cyclohexane and Substituted Cyclohexanes with NBS and Molecular Bromine at 40°

Conditions	Substituent		
	H	Cl	Br
Br_2/hν	1.00	1.48	6.45
NBS/CH_3CN/hν	1.00	0.23	0.41
NBS/CH_3CN/AIBN	1.00	0.21	0.29
$R_1H:R_2H:Br_2$, 1:1:5.5/hν	1.00	1.02	2.75
$R_1H:R_2H:Br_2$, 1:1:100/hν	1.00	0.36	-

TABLE 14

A Comparison of the Relative Rates of Bromination of 2-Methylbutane and 1-Substituted-2-methylbutanes with NBS and Molecular Bromine at 40°

Conditions	Substituent			
	H	Cl	Br	F
$Br_2/h\nu$	1.00	1.9	16.3	0.24
$NBS/CH_3CN/h\nu$	1.00	0.29	1.61	0.066
$NBS/CH_3CN/AIBN$	1.00	0.27	1.67	0.038

TABLE 15

A Comparison of the Relative Rates of Bromination of Butane and 1-Substituted Butanes with NBS and Molecular Bromine at 40°

Conditions	Substituent		
	H	Cl	Br
$Br_2/h\nu$	1.00	0.74	3.4
$NBS/CH_3CN/AIBN$	1.00	0.31	0.58

bromine. The relative rates of bromination with NBS of the 1-substituted butanes and the monosubstituted cyclohexanes are all slower than the parent hydrocarbons as would be predicted from a consideration of the polar effects of the substituent on a hydrogen abstraction by an electrophilic bromine atom. Only in the case of 1-bromo-2-methylbutane, where the rate is lowered by a factor of 10 by bromination with NBS rather than with molecular bromine, is the relative rate of bromination with NBS slightly larger (1.68) than for the parent hydrocarbon.* It must be pointed out that in this case, if neighboring group participation were operative, the assistance would be required to help the abstraction of a tertiary hydrogen β to a bromine substituent, an energetically less useful process than the assisted abstraction of a secondary hydrogen which is not seen.

Although AIBN initiation of NBS brominations is a well established method (22), the exact mechanism of the initiation step is not known. A number of possibilities have been suggested by Martin and Pearson (22) which fit the experimental rate expressions established by Dauben and Youngman (50).

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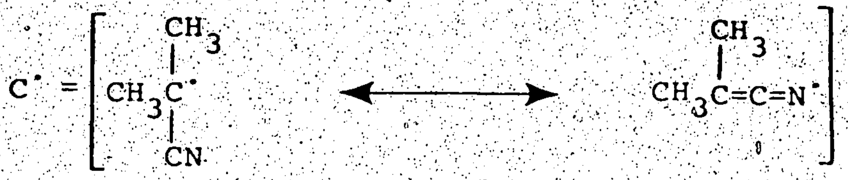
* Since the NBS bromination only approximates reactions carried out in the absence of hydrogen bromide (20), small amounts of residual reversal between the alkyl radicals and hydrogen bromide may explain the small amount of enhancement found in this case.

The first possibility, outlined in Scheme 2, assumes that NBS always contains a small amount of molecular bromine.

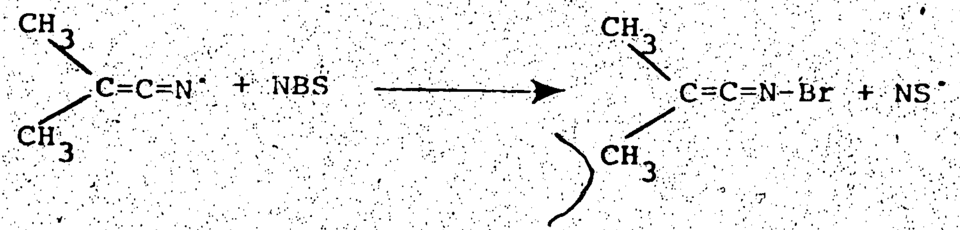
SCHEME 2

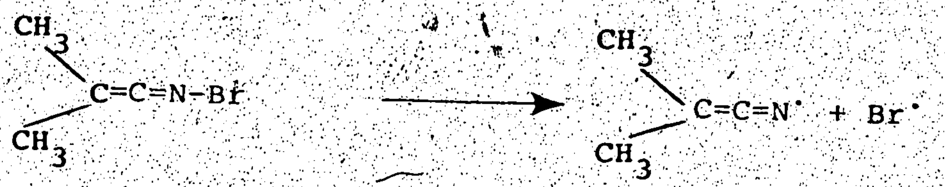
$$\mathrm{AIBN} \longrightarrow 2\mathrm{C}^{\bullet} + \mathrm{N_2}$$
$$\mathrm{C}^{\bullet} + \mathrm{Br_2} \longrightarrow \mathrm{CBr} + \mathrm{Br}^{\bullet}$$
$$\mathrm{RH} + \mathrm{Br}^{\bullet} \longrightarrow \mathrm{R}^{\bullet} + \mathrm{HBr}$$
$$\mathrm{HBr} + \mathrm{NBS} \longrightarrow \mathrm{NSH} + \mathrm{Br_2}$$
$$\mathrm{R}^{\bullet} + \mathrm{Br_2} \longrightarrow \mathrm{RBr} + \mathrm{Br}^{\bullet}$$



$$\mathrm{C}^{\bullet} = \left[\mathrm{CH_3}\overset{\mathrm{CH_3}}{\underset{\mathrm{CN}}{\mathrm{C}^{\bullet}}} \longleftrightarrow \mathrm{CH_3}\overset{\mathrm{CH_3}}{\mathrm{C}}\mathrm{{=}C{=}N}^{\bullet}\right]$$

Attack of an initiator fragment at an α hydrogen of NBS could afford bromine atoms and acrylyl isocyanate in a concerted or stepwise process. Another possibility would involve the abstraction of bromine from NBS by the 2-cyanopropyl radical, forming an N-bromoketeneimine which might then liberate bromine atoms by spontaneous decomposition or as a result of attack by another radical.

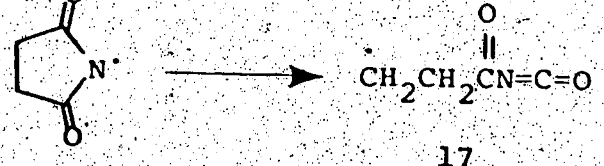




In the study of the relative rates of bromination of the substituted alkanes with NBS in acetonitrile, generally poor material balances were obtained, i.e. the amount of active bromine that was consumed during the reaction could not be accounted for by the analysis of the substrate bromination products.

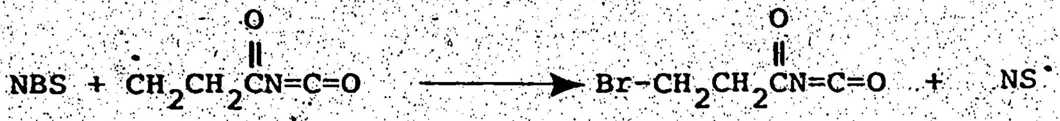
The active bromine presumably could have been taken up by an acid catalysed bromination of the solvent, since small amounts of hydrogen bromide have been shown to catalyze the reaction of bromine with acetonitrile (51). However, no bromoacetonitrile could be detected by glpc analysis of the reaction mixtures (51).

An alternative route for the disappearance of NBS exclusive of the bromination of the solvent or the substrates, is the well-established β-scission reaction in the chain decomposition of the reagent (48,52).



(NS·)

17

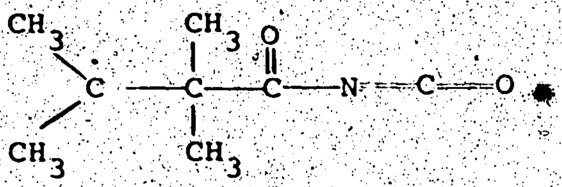


$$\text{NBS} + \dot{\text{C}}\text{H}_2\text{CH}_2\overset{\text{O}}{\overset{\|}{\text{C}}}\text{N=C=O} \longrightarrow \text{Br-CH}_2\text{CH}_2\overset{\text{O}}{\overset{\|}{\text{C}}}\text{N=C=O} + \text{NS}^{\cdot}$$

Under the reaction conditions which were used to carry out the competitive brominations, a strong band at 2340 cm^{-1} in the ir (acetonitrile), characteristic of an isocyanate (48), was detected (51). Any isocyanate produced would be quantitatively removed by the treatment with aqueous thiosulfate prior to analysis. The observation of this side reaction presented the possibility that the results of the competitive bromination reactions using NBS were influenced by radical intermediates other than bromine atoms.

The mechanism for NBS bromination (Scheme 1), which is generally accepted to proceed <u>via</u> a bromine atom chain, was established independently by three groups of workers (21-23) in 1963. The reactivity of the NBS reagent and that of molecular bromine (in the absence of reversal) were found to be the same for the abstraction of benzylic hydrogens of substituted toluenes (21-23). It is not inconceivable, however, as has recently been suggested by Traynham (24), that the mechanism may not be the same for the energetically less favorable bromination of the substituted alkanes.

The reactivity observed in the NBS reactions was shown not to be due to a carbon-centered radical arising from the β scission of a succinimidyl radical by comparing the reactivity of NBS and N-bromotetramethylsuccinimide. In one case β scission of the succinimidyl radical would lead to the primary carbon-centered radical **17** while in the other case, it would lead to the tertiary radical **18**. These two radicals would be expected to show different reactivities.



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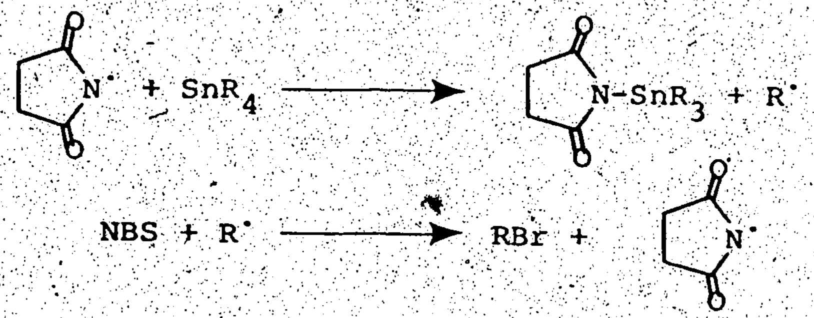
An examination of the data in Table 7 indicates that these two reagents, 1,3-dibromo-5,5-dimethylhydantoin and 1-bromo-3,5,5-trimethylhydantoin all react with quite similar reactivities.

Until 1963, when the studies on toluene were published (21-23), NBS brominations were generally accepted to proceed *via* a succinimidyl radical chain (53).

After the acceptance of the bromine atom chain for NBS brominations, interest in succinimidyl radicals lagged, until fairly recently when a renewed interest has become apparent in the literature. Davies, Roberts and Smith (54,55) have found that N-bromosuccinimide reacts with tetraalkyltins by a radical chain mechanism to give the corresponding alkyl halide and N-trialkylstannylsuccinimide. A mechanism was proposed which involved attack by a succinimidyl radical at the metal center, although no distinction could be made between a stepwise or synchronous process.



As an argument in support of the bromine atom chain, Walling et al. (21) suggested that the N-H bond of succinimide was too weak ($D(CH_2CO)_2N-H \sim 74$ kcal/mol) for the succinimidyl radical to be a candidate for the hydrogen-abstracting species. One recent estimate (56) now suggests that the strength of this bond may be as high as 100 kcal/mol , quite sufficient for ~~the~~ reaction with most C-H bonds to be exothermic. Perkins et al. (57) in a recent study, claim [illegible] uncovered evidence for a free-radical hydrogen transfer between succinimidyl radicals derived from the thermal decomposition of tert-butyl succinimideperoxycarboxylate and toluene.

As a result of this evidence, the possibility that in acetonitrile, particularly at the early stages of the reaction, succinimidyl radicals were doing the abstraction of hydrogen, with a changeover to a bromine atom chain as the reaction progressed, could not be ignored.

A comparison of the reactivity of four N-bromo reagents; NBS, N-bromotetramethylsuccinimide, 1,3-dibromo-5,5-dimethylhydantoin and 1-bromo-3,5,5-trimethylhydantoin, is made in Table 7. It is apparent that although the relative rates were not identical, quite similar reactivities were observed. Since the reactivity of NBS has been shown to vary with reaction time (19,20) the agreement obtained can be regarded as quite acceptable. Thus within the experimental limitations, all the N-bromo brominating agents show the same reactivity, that of the bromine atom, unless fortuitously all these structurally different reagents have nitrogen radicals which all show the same selectivity.

The probability of a mixed chain, abstraction by both succinimidyl radicals and bromine atoms, in the NBS brominations of unreactive substrates would be rather low if an appreciable amount of molecular bromine was present throughout the reaction. When the relative rates of bromination of cyclohexane relative to chlorocyclohexane or 1-bromobutane were determined using a homogeneous acetonitrile solution of the two substrates, molecular bromine and NBS ($R_1H:R_2H:NBS:Br_2 \sim 1:1:8:0.4$), the same relative rates were obtained as for NBS brominations (see Table 7). These results together with the results from the N-bromo brominating agents discussed earlier, can be taken as good evidence for a radical chain involving bromine atoms.

Competitive Brominations of Mixtures of Substrates with High Concentrations of Molecular Bromine

The alternative method of limiting the influence of the transfer reaction of alkyl radicals with hydrogen bromide upon the overall reaction, was to carry out the brominations in the presence of high concentrations of molecular bromine. Competitive transfer reactions having similar rate constants, k_t and $k_{t'}$, can be affected by changing the concentration of the transfer agents so that either path can become dominant.

$$R^{\cdot} + HBr \xrightarrow{k_t} RH + Br^{\cdot}$$

$$R^{\cdot} + Br_2 \xrightarrow{k_{t'}} RBr + Br^{\cdot}$$

Several examples of the competitive reactions which showed large differences between the results obtained from molecular bromine (1:1:1) bromination and from NBS bromination, were carried out using large excesses of molecular bromine. The relative rates of these substrates obtained in the presence of increasing amounts of molecular bromine changed progressively from the values determined for low concentrations of bromine (1:1:1) to the values obtained in the NBS reactions (see Table 8).

In the case of bromocyclohexane, the value obtained with NBS could not be achieved by increasing the concentration of molecular bromine since it was found that at the concentrations of bromine necessary to reach this limit, bromocyclohexane was not stable.

The observation that the relative rates of bromination of the substrates using high concentrations of molecular bromine are similar to the values obtained with NBS in acetonitrile is strong support for the proposal that both reactions proceed <u>via</u> a mechanism which involves the same abstracting species.

It is apparent from the results for the bromination with the N-bromo reagents that the solvent, acetonitrile, plays an important role in the reaction. When two competitions were carried out using N-bromotetramethylsuccinimide in carbon tetrachloride, the values obtained were similar to those found in the bromination with molecular bromine (Table 9), while use of the same reagent in acetonitrile gave values similar to those obtained in the bromination with NBS in that solvent.

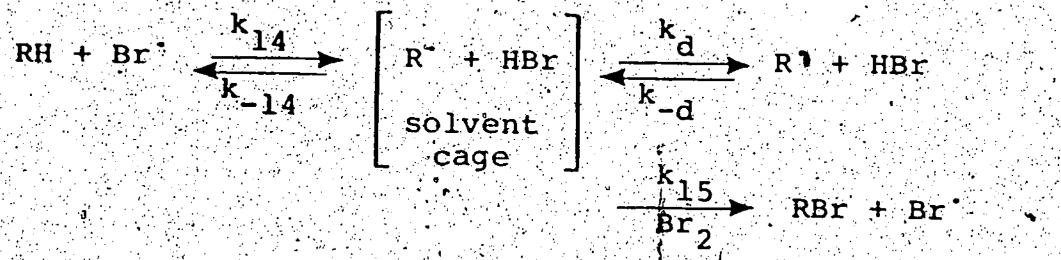
The values obtained with NBS in methylene chloride, although not very reproducible, appeared to be closer to those obtained with molecular bromine than with NBS in in acetonitrile. Brominations with a mixture of bromine and NBS in methylene chloride were reproducible and gave values similar to those for molecular bromine bromination, while comparable reactions in acetonitrile gave values similar to NBS alone in that solvent.

A reasonable proposal to account for the role of the solvent, acetonitrile, would be the formation of a complex with the hydrogen bromide as soon as it is formed, which would thus minimize the reversal of the abstraction reaction. This suggestion is supported by the observation that acetonitrile readily forms complexes with hydrogen halides of varying compositions (for a review of this reaction see (58,59)) and such complexes have been proposed as intermediates in a number of reactions (e.g. the Gattermann and Hoesch reactions (58)). For example, a solid complex, $CH_3CN:2HBr$, mp 83-85°, is formed reversibly from acetonitrile and hydrogen bromide and has been characterized by Janz and Danyluk (60).

This proposal has the merit that it enables the results from both the excess bromine and the NBS in acetonitrile reactions to be adequately rationalized. In one case (excess bromine), the reverse reaction is limited by increasing the concentration of the transfer reagent, bromine, and thereby increasing the rate of the reaction leading to brominated products at the expense of the transfer with hydrogen bromide leading to starting material. In acetonitrile on the other hand, the transfer with hydrogen bromide is limited by the formation of a stable complex between the solvent and the hydrogen bromide, and subsequently the destruction of the hydrogen bromide by the NBS.

The possibility still exists that, even in the absence of significant reversal with external hydrogen bromide, the apparent kinetic reactivity of the bromine atom in solution may be affected by reversal with the hydrogen bromide formed within the solvent cage (Scheme 3). The reversal reaction within the solvent cage

SCHEME 3



(k_{-14}), competitive with diffusion (k_d), will be subject to the same kinetic influences as are seen with external hydrogen bromide.

If, however, significant cage reversal with hydrogen bromide does occur in the brominations using molecular bromine, then this type of process is also possible in the NBS brominations. However, as suggested earlier, acetonitrile, by complexing with hydrogen bromide, may slow down the reversal reaction, even within the solvent cage. It is noteworthy that, by using high concentrations of molecular bromine, comparable to those used in this work, Hammond (61) was able to scavenge cyanopropyl radicals from the solvent cage in the decomposition of AIBN.

Bromination of 1-Chlorobutane and Chlorocyclohexane

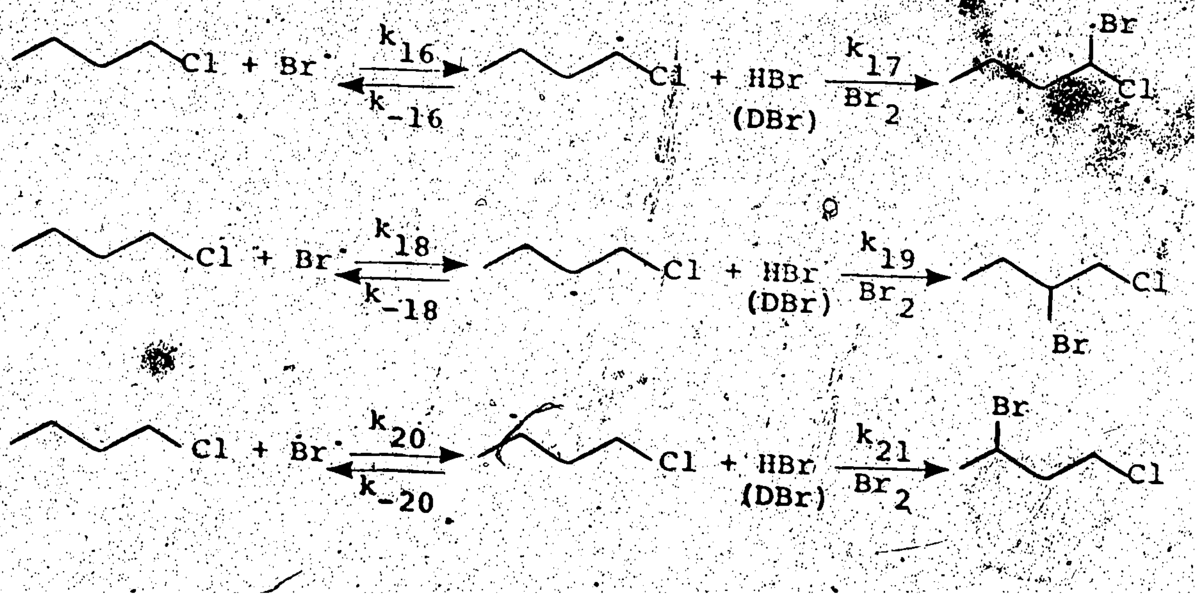
The rates of bromination of 1-bromobutane and bromocyclohexane relative to their parent hydrocarbons were significantly different depending upon whether the brominating agent was NBS or molecular bromine (Tables 13-15). Earlier studies (19,20) had shown that these changes in rate corresponded to significant changes in the product distribution under the various brominating conditions

The relative rates of bromination of the alkyl chlorides were also found to depend upon the brominating agent used (Tables 13-15). For example, the rate of bromination of chlorocyclohexane relative to cyclohexane ($k_{C_6H_{11}Cl}/k_{C_6H_{12}}$) changed from 0.21 in the AIBN initiated NBS brominations to 1.48 in photolytic brominations with molecular bromine.

It is apparent from the results in Tables 11-12 that the product distribution in the bromination of 1-chlorobutane and chlorocyclohexane also changed depending on the brominating conditions.

In 1-chlorobutane, the change in the product distribution (Table 12) was small, corresponding to the small change in the rate observed (Table 15). The 1- and 2-positions were slightly more deactivated in the brominations with NBS in acetonitrile than in the reaction with molecular bromine. The amount of the 1-bromo-4-chlorobutane was greatly enhanced in the bromination with NBS when the reaction was stopped at an early stage. Traynham *et al.* (24) have noted a similar increase in the amount of 1,4-dibromobutane in the bromination of 1-bromobutane with NBS under similar conditions.

In an attempt to determine the ratios of the rate constants for transfer with bromine and with hydrogen bromide in the bromination of 1-chlorobutane, perdeuterio-1-chlorobutane has been brominated in the presence of excess bromine and hydrogen bromide (62).



Preliminary results indicate that $k_{17}/k_{-16} = 1.95$, $k_{19}/k_{-18} = 2.61$ and $k_{21}/k_{-20} = 0.715$ (62). These ratios of rate constants are consistent with the small change observed in the product distribution on changing the brominating agent from molecular bromine to NBS in acetonitrile. Interestingly, about 2.2% of the deuterium in the δ position was exchanged during the reaction even though no 1-bromo-4-chlorobutane was observed (62).

In the case of chlorocyclohexane, a large change in the product distribution was observed (Table 11). In Table 16, the relative reactivities per hydrogen in the various positions are given and compared with the literature values for the bromination and chlorination of chlorocyclohexane and bromocyclohexane.

The fact that no <u>cis</u>-1-bromo-2-chlorocyclohexane was observed in these reactions is not surprising. The <u>trans</u>-1,2-/<u>cis</u>-1,2-ratio is greater than 10 in the chlorinations and brominations of all the cyclopentyl and cyclohexyl halides so far [illegible]igated. Even the chlorination of fluorocyclohexane led to a <u>trans</u>-1,2-/<u>cis</u>-1,2-ratio of >40 (65). This so-called "<u>trans</u> effect" (66) has been explained in the literature by (a) a steric interaction between the substituent and the incoming halogen molecule (66,67), (b) a dipole-dipole interaction in the transition state for the reaction of a halogen molecule with the cycloalkyl radical (66, 67), (c) the formation of a bridged radical (6), and

TABLE 16

The Relative Reactivities per Hydrogen in the Halogenation of $C_6H_{11}X^a$

X	Reagent	α	β	γ	δ
Br^b	Cl_2	0.40	0.20	0.91	1.0
Br^c	Molecular Br_2	0.34	3.26	0.52	1.0
Cl^b	Cl_2	0.36	0.44	0.79	1.0
Cl	NBS-AIBN at 5% reaction	1.15	0.20	0.72	1.0
Cl	NBS at 1.4% reaction	1.20	0.17	0.73	1.0
Cl	NBS at 30% reaction	8.03	0.34	0.73	1.0
Cl	Molecular Br_2	31.5	0.97	0.87	1.0
Cl^d	Br_2-vapor phase-100°	27.5	0.79	0.76	1.0
Cl^e	Br_2-flow reactor-110°	3.78	0.77	0.65	1.0

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[a] Values were calculated for β, γ, and δ positions using combined yields of *cis* and *trans*-dihalides.

[b] Taken from Ref. (63).

[c] Taken from Ref. (20).

[d] Taken from Ref. (64).

[e] Taken from Ref. (25).

(d) a very unsymmetrical interaction between the filled P-atomic orbitals of the substituent halogen and the half-filled π-orbital of the radical (25,65,68).

Tedder et al. (64) have recently reported the vapor phase bromination of chlorocyclohexane with molecular bromine. The isomer distributions found were in reasonable agreement with the results obtained in this work with molecular bromine in the liquid phase (Table 16). Tedder et al. (25) have also studied the vapor phase bromination of chlorocyclohexane with molecular bromine in a flow reactor where the reactants and products were in contact with the walls of the vessel and with the hydrogen bromide produced for only a very short time. Using this method, a product distribution very similar to that found using NBS as the brominating agent in acetonitrile (at low percentage reaction) was observed (Table 16).

The changes in the product distribution in the alkyl bromides were rationalized by considering the polar effects of the substituents (20,26). The same reasoning can be applied to the bromination of 1-chlorobutane and chlorocyclohexane, where the abstraction at the 1- and 2-positions in particular are subject to polar deactivation both in the abstraction step and in the reaction with hydrogen bromide. Transfer with the non-polar bromine rather than the polar hydrogen bromide would be favored and result in an increase of the bromination products in these two positions (the observed result). In the bromination with NBS, however, NBS is reacting via the accepted bromine atom chain; its main function is to remove the hydrogen bromide formed in the first step and thus to minimize the reverse reaction.

Mechanistic Conclusions

The observation that the relative rates of bromination of the substrates using very high concentrations of molecular bromine are the same as, or approximate, the values obtained with NBS in acetonitrile is strong support for the proposal that both reactions proceed via a mechanism which involves the same abstracting species (i.e. a bromine atom). This conclusion is further substantiated by the observation that NBS reactions in acetonitrile with initially added molecular bromine led to the same relative rates as in the absence of the molecular bromine.

The solvent, acetonitrile, appears to play an important role in the reaction. A mechanism has been proposed whereby the acetonitrile forms a complex with the hydrogen bromide as soon as it formed, and thus minimizes the reversal of the abstraction reaction.

The observation that with the exception of 1-bromo-2-methylbutane the bromination of the substituted hydrocarbons with NBS in acetonitrile, and, in the two cases where the substrates were stable, with very high concentrations of molecular bromine, were slower than the parent hydrocarbons further demonstrates the retarding effect of a neighboring bromine or chlorine substituent and argues against the concept of anchimeric assistance by a bromine substituent. In the case of 1-bromo-2-methylbutane the rate of the bromination reaction relative to 2-methylbutane is lowered by a factor of 10 by bromination with NBS in acetonitrile rather than with molecular bromine.

The much faster rate of bromination of the substituted alkanes under "normal" brominating conditions compared with the reactions with NBS in acetonitrile is consistent with the reversal of the initial abstraction reaction. The reaction of a radical with hydrogen bromide must be subject to the same polar effects as are present in the initial hydrogen abstraction by the bromine atom (microscopic reversibility). The polar carbon-centered radical will thus be deactivated to the reversal of the initial abstraction reaction, but should react in a manner unaffected by polar interactions with the non-polar bromine molecule to give the bromination products. Alternatively, a non-polar carbon-centered radical will, in addition to transferring with bromine to form products, reverse "normally" (not subject to polar interactions) with hydrogen bromide and return to starting material. If the energetics of the reaction are only subject to polar effects then the net result of this sequence of reactions is an apparent increase in the rate of the reaction of the polar molecule compared with the non-polar molecule (parent hydrocarbon).

EXPERIMENTAL

I. Materials.

1-Bromobutane, bromocyclohexane, 1-chlorobutane and chlorocyclohexane were commercially available chemicals. They were purified by washing with concentrated sulfuric acid and with water, drying over anhydrous sodium sulfate and fractional distillation.

Carbon tetrachloride (Fisher Scientific Co., "Spectranalysed" reagent) was distilled from phosphorus pentoxide. Freon 112 (1,2-difluoro-1,1,2,2-tetrachloroethane) was obtained from P.C.R. Inc. and distilled prior to use, bp 89.5-90.0°/700mm. No impurities were detected by glpc. Freon 113 (1,1,2-trichloro-1,2,2-trifluoroethane; Matheson of Canada, Ltd.) was used as supplied. Acetonitrile was purified by the method of O'Donnell et al. (69), dried by distillation from calcium hydride and stored in a dry box.

Cyclohexane and n-butane were Phillips research grade chemicals and were used as supplied. Spectroquality 2-methylbutane (Matheson, Coleman and Bell) was distilled before use.

1-Bromo-2-methylbutane, bp 117-119°/705mm, n_D^{20} 1.4455 (Lit. (70) bp 121.6°/760mm, n_D^{20} 1.4451) was prepared by the method of Crombie and Harper (71) from phosphorus tribromide and 2-methylbutanol.

1-Chloro-2-methylbutane, bp 96.5°/695mm, n_D^{20} 1.4126

(Lit. (16) bp 100.5°/760mm, n_D^{20} 1.4124) was prepared from the corresponding alcohol by treatment with thionyl chloride and pyridine (16).

1-Fluoro-2-methylbutane was prepared by the method of Tanner, Yabuuchi and Blackburn (40). A suspension of 2-methylbutyl tosylate (23.4g, 0.0966 mol) and excess potassium fluoride (30.5g, 0.526 mol) were heated to 100° in diethylene glycol (30.0g) under constant mechanical stirring. The fluoride (7.60g, 87%) was distilled from the reaction mixture at a slightly reduced pressure and was collected in a receiver flask cooled in a dry ice-acetone bath. The crude fluoride was treated with concentrated sulfuric acid to remove any olefin formed and was then washed with 10% sodium bicarbonate solution and water. After drying over anhydrous sodium sulfate, the fluoride was further purified by preparative glpc using a 20 ft. x 0.25 in. column packed with 15% diethylene glycol succinate (DEGS) on chromosorb W-AW, nmr (CCl_4) τ 8.92-9.17 (6H, 4-H and 2-CH_3), 8.0-9.0 (3H, multiplet, 2- and 3-H), 5.42 and 6.22 (2H, doublet of doublets, 1-H split by 1-F ($J_{H,F}$ = 48.0 Hz) and by 2-H ($J_{H,H}$ = 5.8 Hz)).

trans-1-Bromo-2-chlorocyclohexane was prepared by adding a suspension of NBS (25.0g, 0.14 mol) in chloroform (40 ml) in portions to a solution of cyclohexene (12.3 g, 0.15 mol) in chloroform (60 ml). Through this mixture anhydrous hydrogen chloride was passed (72). A colorless liquid was obtained by fractional distillation, bp 64°/1mm, n_D^{25} 1.5173 (Lit. (72), bp 76.5-77°/9mm, n_D^{25} 1.5173).

Bromine was washed with concentrated sulfuric acid and distilled from phosphorus pentoxide and/or molecular sieve type 4A prior to use.

N-Bromosuccinimide (NBS) was purified by rapid recrystallization from hot water and dried in a vacuum desiccator over phosphorus pentoxide; iodometric titration showed its purity to be always > 98%. 1,3-Dibromo-5,5-dimethylhydantoin, 100% pure by titration, was obtained from Arapahoe Chemicals and used without further purification.

Tetramethylsuccinimide was prepared by the method of Bickel and Waters (73) from AIBN as a colorless crystalline solid, mp 188-189° (Lit. (73) mp 187-188°). The tetramethylsuccinimide (8.00g, 0.0516 mol) was dissolved in a solution of sodium bicarbonate (4.34g, 0.0516 mol) in water (530 ml). The resulting solution was cooled to 4° in an ice bath, bromine (8.80g, 0.055 mol) was added dropwise with constant stirring. N-Bromotetramethylsuccinimide was collected as a colorless crystalline compound, 11.4g (94%) and was purified by sublimation at 140°/1mm. Iodometric titration showed its purity to be 98-100%.

1-Bromo-3,5,5-trimethylhydantoin, 99.5% pure by titration was prepared from 5,5-dimethylhydantoin (74). In the bromination of the 3,5,5-trimethylhydantoin, the same procedure as that described previously for N-bromotetramethylsuccinimide was used (22).

II. Methods and Procedures

General Procedures for Reactions

Reaction ampoules were made of Pyrex tubes joined to 10/30 joints. The ampoules were cleaned with chromic acid solution, water, concentrated ammonium hydroxide and distilled water, then oven-dried at 120°. In subdued light, the reactants, solvents and an internal standard were placed in the ampoules and then degassed by three cycles of freeze-thaw at ca. 10^{-5} mm. After degassing the ampoules were sealed under vacuum, allowed to thaw and then equilibrate at the desired temperature. The ampoules were irradiated with incandescent tungsten lamps placed at a distance of three to four inches from the ampoules for an appropriate reaction time. Ampoules were kept in the dark by wrapping in aluminum foil.

Gas Liquid Partition Chromatography (glpc)

For glpc analyses, two instruments we[illegible] used: (1) Carlo Erba Fractovap Model GV and (2) Varian Aerograph Model 1520. The columns used are specified in the individual experiments. All compounds studied were stable on the columns used.

Analyses were carried out in duplicate. Peak areas were calculated by multiplying the peak height by the peak width at one-half the peak height or by means of a disc or electronic integrator. The methods used were consistent with each other. Calibration curves (see Appendix B) were constructed to convert the area ratios of the products relative to Freon 112, the internal standard, into mol ratios. Where quoted, the experimental uncertainties are average deviations from the mea value obtained from several reactions. Retention time comparison and peak enhancement refer to the addition of authentic material to a portion of the sample and reanalysis by glpc.

Spectral Measurements

Infrared spectra (ir) were recorded on either a Perkin Elmer Model 421 or a Perkin Elmer Model 337 recording spectrophotometer. The nmr spectra are proton spectra. Chemical shifts are expressed in τ units and are relative to tetramethylsilane (TMS, $\tau = 10.00$). The spectra were obtained on either a Varian Associates A-60, A-56/60A or HA-100 high resolution nmr spectrophotometer. The mass spectra were obtained on a Metropolitan Vickers MS2 or on an A.E.I. MS12 mass spectrometer.

Physical Constants

All melting points and boiling points are uncorrected. Melting points were obtained using a Reichert melting point apparatus. Refractive indexes were measured on a Bausch and Lomb refractometer.

III. Competitive Bromination with Molecular Bromine ($R_1H:R_2H:Br_2 \sim 1:1:1$)

The reaction mixtures consisted of an approximately 1:1:1 mol ratio of $R_1H:R_2H:Br_2$ in Freon 112 as solvent. The Freon 112 served as the internal standard.

A solution of the two substrates in Freon 112 was first prepared: a typical solution contained cyclohexane (0.4432g, 5.276×10^{-3} mol) and chlorocyclohexane (0.5906g, 4.984×10^{-3} mol) in Freon 112 (5 ml). An aliquot (1 ml) of this solution was added by means of a pipet to a Pyrex tube containing a known amount of bromine (e.g. 0.129g, 8.06×10^{-4} mol). Another aliquot (1 ml) was added to a Pyrex tube without bromine. The resulting solutions (1 ml) were degassed by the freeze-thaw method and sealed under vacuum. The reaction tubes were irradiated at 40.0 ± 0.1° with 2 x 200-W incandescent lamps until all the bromine color disappeared.

The brominated solutions and the initial hydrocarbon/Freon 112 solution were analysed by glpc on either a

10% diethylene glycol succinate (DEGS) on Diatoport, 30 ft. x 0.25 in. or on a 20% diisodecylphthalate (DIDP) on Chromosorb W-AW, 12 ft. x 0.25 in. glass column. The results obtained are given in Table 4.

IV Competitive Bromination with Succinimides and Hydantoins in Acetonitrile as Solvent

All reactions were carried out in homogeneous acetonitrile solutions. Reaction mixtures, consisting of a 1:1:8 mol ratio of $R_1H:R_2H$:brominating agent and an internal standard, were degassed and sealed under vacuum in Pyrex ampoules. Thermal reactions contained a catalytic amount of AIBN (1 mol % based on the brominating agent) and were carried out at 40.0 ± 0.5° in the dark for an appropriate period of time (~800 hours). Photolytic experiments were conducted at 40.0 ± 0.1° by irradiation with either one 60-W or two 40-W incandescent lamps for a time sufficient to ensure at least 10% reaction for each component.

A typical reaction mixture was prepared in the following manner. Initially solutions of NBS (3.793g, 2.131×10^{-2} mol) in acetonitrile (50 ml), and cyclohexane (0.0634g, 7.55×10^{-4} mol) and chlorocyclohexane (0.1007 g, 8.49×10^{-4} mol) in Freon 112 (2 ml), were prepared. Aliquots of the acetonitrile solution (3 ml; NBS, 1.28×10^{-3} mol) and the Freon 112 solution

(0.4 ml; cyclohexane, 1.51 x 10^{-4} mol and chlorocyclohexane, 1.70 x 10^{-4} mol) were added by means of a pipet to the Pyrex reaction tube. Another aliquot of the Freon 112 solution (0.5 ml) was added to a second Pyrex tube. The resulting solutions were degassed by the freeze-thaw method and sealed under vacuum.

After reaction, the organic reactants and products were separated from the unreacted brominating agent either by vacuum distillation or by destruction of the brominating agent with aqueous potassium iodide acidified with mineral acid, followed by extraction with Freon 113 or o-dichlorobenzene. Control experiments indicated that both procedures gave > 98% recovery of substrates and internal standard. In either case, the amount of brominating agent remaining was determined by titration with standard sodium thiosulfate solution. The same glass glpc columns were used as outlined previously for the molecular bromine brominations. In the typical experiment with chlorocyclohexane and cyclohexane, after irradiation with two 40-W incandescent lamps for four hours, 18.6% (2.38 x 10^{-4} mol) of the NBS had been consumed: 43.9% (6.63 x 10^{-5} mol) of the cyclohexane and 13.0% (2.21 x 10^{-5} mol) of the chlorocyclohexane had reacted leading to a relative rate of 0.241. The results are given in Tables 5-7.

The material balances obtained in these brominations were generally poor, i.e. the amount of active bromine that was consumed during the reaction could not be accounted for by the analysis of the substrate bromination products. In the AIBN initiated reactions, the material balances obtained were only 10-30%. Somewhat better material balances were obtained in the photoinitiated reactions with NBS (25-[illegible]5%), N-bromotetramethylsuccinimide (25-40%), 1-bromo-3,5,5-trimethylhydantoin (25-40%) and 1,3-dibromo-5,5-dimethylhydantoin (50-65%).

Two competitions were carried out in the same manner as the photoinitiated reactions with NBS in acetonitrile except that they contained intially added molecular bromine ($R_1H:R_2H:NBS:Br_2 \sim 1:1:8:0.4$). The material balance for the active bromine in these experiments was 55-65%. The results are included in Table 7.

V. Competitive Bromination with Excess Molecular Bromine

The reaction mixtures, degassed and sealed in Pyrex tubes, consisted of ratios of $R_1H:R_2H:Br_2$ varyi~~ng from~~ 1:1:5 to 1:1:100 with Freon 112 as the internal standard. The procedure was similar to that described previously for the bromination using a mol ratio of molecular bromine to substrates of 1:1:1. The tubes were irradiated at 40 ± 0.1° until at least 10% of each substrate had reacted. The excess bromine was destroyed with ice-cold aqueous sodium bisulfite. The organic substrates were extracted with a suitable solvent (Freon 113 or o-dichlorobenzene), washed once with cold water and dried over anhydrous sodium sulfate. The solutions were analysed by glpc on a 10% DEGS on Diatoport, 30 ft. x 0.25 in. glass column. The results are given in Table 8.

The stability of the substrates, in excess bromine in the dark, was checked both with and without added hydrogen bromide. Bromocyclohexane was found to be unstable in the presence of a 100-fold mol excess of molecular bromine in the dark; after approximately the same reaction time as in the photoinitiated experiments, 20% of the bromocyclohexane had reacted. The other substrates, 1-bromobutane (45) and chlorocyclohexane were stable to equivalent amounts of hydrogen bromide and a 100-fold mol excess of molecular bromine.

VI. Competitive Bromination with N-Bromotetramethylsuccinimide in Carbon Tetrachloride as Solvent

The reaction mixtures were prepared from solutions of the brominating agent in carbon tetrachloride and the two substrates in Freon 112 in the manner described previously for the reactions in acetonitrile. The reaction tubes were irradiated at 40.0 ± 0.1° with two 40-W incandescent lamps for a time sufficient to ensure at least 10% reaction of each component. After the destruction of any excess brominating agent with aqueous, acidified potassium iodide, the brominated solutions and the initial hydrocarbon/Freon 112 solution were analyzed by glpc on a 10% Carbowax 20M TPA on Chromosorb P-AW, 20 ft. x 0.25 in. glass column. The results are given in Table 9.

An ir spectrum of one of the brominated solutions was determined before destruction of the brominating agent. A strong absorption at 2240 cm^{-1} characteristic of an isocyanate was observed (48).

VII. Competitive Brominations in Methylene Chloride as Solvent

Solutions of the two substrates in Freon 112 were prepared in the usual manner. Three different brominating conditions were employed using methylene chloride as the solvent.

(a) Molecular bromine brominations were carried out as follows: a solution of bromine in methylene chloride was prepared and aliquots of this solution and the Freon 112 solution were added by means of a pipet to a Pyrex ampoule such that the reaction mixtures consisted of approximately a 1:1:1 mol ratio of $R_1H:R_2H:Br_2$. After degassing and sealing under vacuum, the reaction tubes were irradiated in a water bath at 40.0 ± 0.1° with a 200-W incandescent lamp until all the bromine color disappeared. The solutions were analysed on the same columns as described previously (see sec. III). Approximately 60% of the initial bromine appeared as mono-brominated products and another 30% as bromodichloromethane.

) The competitions were determined by the photolysis of a homogeneous solution of the two substrates, NBS and molecular bromine in methylene chloride (R_1H: R_2H:NBS:Br_2 ~ 1:1:1:0.07). Solutions of NBS (0.15-0.20 M) in methylene chloride and bromine in methylene chloride were prepared. Aliquots of these solutions and the Freon 112 solution of the substrates were taken so as to make up the required composition. After degassing and sealing under vacuum, the ampoules were irradiated at 40.0 ± 0.1° until all the bromine color disappeared. The solutions were analysed by glpc. Approximately 60-70% of the initial active bromine could be accounted for at the end of the reaction, 70% of this as monobrominated products and another 30% as bromodichloromethane.

) The photoinitiated bromination of the two substrates with NBS in a homogeneous methylene chloride solution was attempted (R_1H:R_2H:NBS ~ 1:1:5.5). The ampoules containing the reaction solutions were prepared in the usual manner and irradiated with a 200-W incandescent lamp at 40.0 ± 0.1°. The organic reactants and products were separated from the brominating agent by vacuum distillation and the NBS remaining determined by titration with standard sodium thiosulfate. At the end of the reaction, 15-40% of the initial active bromine could be accounted for, 60-70% of this as bromodichloromethane and the remainder as monobrominated products. The results are given in Table 10.

VIII. Bromination of Chlorocyclohexane

Bromination of Chlorocyclohexane with NBS

All reactions were carried out in homogeneous acetonitrile solutions. The AIBN initiated reactions employed a mol ratio of chlorocyclohexane to NBS of 1:1.5 (AIBN: 1% based on NBS). These reactions were carried out at 40.0 ± 0.5° in the dark for an appropriate period of time (> 100 hours). In the photoinitiated experiments, the solutions consisted of a 1:3 mol ratio of chlorocyclohexane to NBS. The reactions were conducted in a Pyrex water bath at 40.0 ± 0.1° by irradiation with one 200-W incandescent lamp. The ampoules from these experiments were [illegible]ed from the bath after varying reaction times and the NBS remaining determined by iodometric titration.

A typical reaction mixture contained chlorocyclohexane (4.21×10^{-4} mol), Freon 112 [illegible] $\times 10^{-3}$ mol) and NBS (1.26×10^{-3} mol) in acetonitrile (2 ml). After titration with sodium thiosulfate, the organic products were extracted with Freon 113 (2 ml) and the reaction mixtures were analysed by glpc on a 10% DEGS on Chromosorb W-AW, 20 ft. x 0.25 in. glass column. The results are given in Table 11.

The six bromochlorocyclohexanes were collected by preparative glpc on the DEGS column. The first product eluted was 1-bromo-1-chlorocyclohexane 7, n_D^{25} 1.5076 (Lit. (75) n_D^{25} 1.5081). The nmr spectrum (CCl_4 solution) showed two unresolved absorptions at τ 7.62 (4H) and at τ 8.35 (6H) (cf. 1,1-dibromocyclohexane (76), τ 7.52 (4H), τ 8.35 (6H)). Hydrolysis with barium carbonate (72) gave cyclohexanone, identified by its retention time on the DEGS column and from its mass and ir spectra which were identical with those obtained from an authentic sample. Dehydrohalogenation with potassium hydroxide in ethanol gave 1-chlorocyclohexene, identified from its spectral properties (ir and mass spectra) which were identical to those of authentic 1-chlorocyclohexene and by its retention time on the DEGS column. A small amount of another product, presumably 1-bromocyclohexene, was also observed. Molecular ions at m/e 160 and 162 were present in the mass spectrum with the intensities expected for C_6H_9Br.

The second product eluted was shown to be *trans*-1-bromo-2-chlorocyclohexane 8 by a comparison of its glpc retention time, mass, nmr and ir spectra with those obtained from an authentic sample. The mass spectra obtained for the other four bromochlorocyclohexanes all had molecular ions at m/e 196, 198 and 200 with the intensities expected for $C_6H_{10}BrCl$.

Peak 3 corresponded to *trans*-1-bromo-3-chlorocyclohexane 9, nmr ($CDCl_3$) τ 7.8 - 8.4 (6H, multiplet), 7.67 (2H, triplet, 2-H, $J_{H,H}$ = 5.5 Hz), 5.54 (2H, multiplet, 1-H and 3-H) [Lit. (77) (CCl_4) τ 7.68 (2H, triplet, 2-H, $J_{H,H}$ = 5.5 Hz), 5.58 (2H, multiplet, 1-H and 3-H)]. The ir spectrum (CS_2) in the region 2700 - 3100 cm^{-1} was identical with the spectrum published by Van Dort and Havinga (78).

Peak 4 was assigned to *trans*-1-bromo-4-chlorocyclohexane 10. It was a colorless solid, mp 99.5 - 100.0° (Lit. (79) mp 102°), nmr ($CDCl_3$) τ 7.95 - 8.40 (4H, multiplet), 7.45 - 7.90 (4H, multiplet), 5.50 - 6.00 (2H, multiplet, 1-H and 4-H) [Lit. (77) (CCl_4) τ 5.50 - 6.10 (2H, multiplet, 1-H and 4-H).

Peak 5 corresponded to *cis*-1-bromo-3-chlorocyclohexane 11, nmr ($CDCl_3$) τ 7.50 - 8.80 (7H, multiplet), 7.21 (1H, doublet of septuplets, 2-H, $J_{H,H}$ = 1.9 Hz, $J_{H_2,H_2'}$ = 13 Hz), 5.90 - 6.40 (2H, multiplet, 1-H and 3-H) [Lit. (77) (CCl_4) τ 7.21 (1H, doublet of septuplets, 2-H, $J_{H,H}$ = 1.9 Hz, $J_{H_2,H_2'}$ = 13 Hz), 6.25 (2H, multiplet, 1-H and 3-H). The ir spectrum (CS_2) in the region 2700 - 3100 cm^{-1} was identical with the published spectrum (78).

Peak 6 was assigned to *cis*-1-bromo-4-chlorocyclohexand **12**, nmr (CDCl$_3$) τ 7.55 - 8.20 (8H, multiplet), 5.80 (2H, multiplet, 1-H and 4-H) [Lit. (77) (CCl$_4$) τ 5.90 (2H, multiplet, 1-H and 4-H). The ir spectrum was identical to the previously reported spectrum (80).

Bromination of Chlorocyclohexane with Molecular Bromine

The reaction mixtures consisted of a 1:5 mol ratio of bromine to chlorocyclohexane in a Freon 112 solution. The Freon 112 served also as the internal standard. A typical reaction mixture, containing chlorocyclohexane (2.58 x 10^{-3} mol), Freon 112 (5.54 x 10^{-3}) and bromine (5.00 x 10^{-4} mol) in a Pyrex ampoule, was degassed and sealed under vacuum. After equilibration at 40° in a Pyrex water bath, the ampoules were irradiated with one 200-W incandescent lamp until all the bromine color disappeared. The brominated solutions were analysed by glpc on a 10% DEGS on Diatoport, 30 ft. x 0.25 in. glass column. Six bromochlorocyclohexanes were found in the ratio of 8.12:1.0:0.46:0.25:0.43:0.26. By a comparison of their glpc retention times, mass and ir spectra the products were shown to be identical to the products described previously in the bromination with NBS. Several products with higher retention times, corresponding to dibromochlorides, were also observed (6.2%

of the total product). Ions (M^+-Br) were observed in the mass spectrum at m/e 195, 197 and 199 with the intensities expected for $C_6H_9BrCl^+$. The results are given in Table 11.

IX Bromination of 1-Chlorobutane

Bromination of 1-Chlorobutane with Molecular Bromine

The reaction mixtures consisted of a 1:9.5 ± 0.5 mol ratio of bromine to 1-chlorobutane, and Freon 112 as the internal standard. A typical reaction mixture, containing 1-chlorobutane (6.09×10^{-3} mol), Freon 112 (2.85×10^{-3} mol) and bromine (6.06×10^{-4} mol), was degassed and sealed in a Pyrex ampoule. The reactions were carried out in the same manner described previously for the bromination of chlorocyclohexane, and the brominated solutions were analysed on the same DEGS column. Four bromochlorobutanes were found in the ratio 0.52:0.57:1.0:0.007. The compound corresponding to peak 1 did not have a molecular ion, but those corresponding to peaks 2-4 had molecular ions at m/e 170, 172 and 174 with the intensities expected for C_4H_8BrCl. Several products with higher retention times corresponding to dibromochlorobutanes were observed (3.6% of the total product). The compound corresponding to peak 5 had molecular ions at m/e 248, 250, 252 and 254 with the intensities expected for $C_4H_7Br_2Cl$, while those from peaks 6-8 had ions at M^+-Br (169, 171 and 173) corresponding to $C_4H_7BrCl^+$. The results obtained are given in Table 12.

Peak 1 corresponded to 1-bromo-1-chlorobutane **13**, η_D^{20} 1.4678 (Lit. (8) η_D^{20} 1.4680), nmr (CCl_4) τ 9.03 (3H, triplet, 4-H), 8.1-8.8 (2H, multiplet, 3-H), 7.73 (2H, quadruplet, 2-H), 4.28 (1H, triplet, 1-H).

Peak 2 was assigned to 2-bromo-1-chlorobutane **14**, η_D^{20} 1.4802 (Lit. (8) η_D^{20} 1.4800), nmr (CCl_4) τ 8.92 (3H, triplet, 4-H), 7.5 - 8.5 (2H, multiplet, 3-H), 5.7 - 6.6 (3H, multiplet, 1-H and 2-H).

Peak 3 corresponded to 3-bromo-1-chlorobutane **15**, η_D^{20} 1.4789 (Lit. (8) η_D^{20} 1.4782), nmr (CCl_4) τ 8.23 (3H, doublet, 4-H), 7.83 (2H, quadruplet, 2-H), 6.32 (2H, triplet, 1-H), 5.70 (1H, multiplet, 3-H). Peak 4 was assigned to 1-bromo-4-chlorobutane **16** by a comparison of its glpc retention time and mass spectrum with those from the authentic compound.

Bromination of 1-Chlorobutane with NBS

All reactions were carried out in homogeneous acetonitrile solutions in the manner described previously for the NBS bromination of chlorocyclohexane. The products were analysed on a 10% DEGS on Chromosorb W-AW, 20 ft. x 0.25 in. glass column. By a comparison of their glpc retention times and mass spectra the products were shown to be identical to the products described previously in the bromination with molecular bromine. The results obtained are given in Table 12.

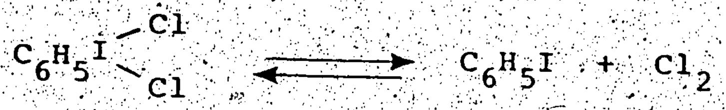
PART TWO

THE REACTION OF *tert*-BUTYL HYPOCHLORITE WITH IODINE AND WITH SELECTED METAL IODIDES

INTRODUCTION

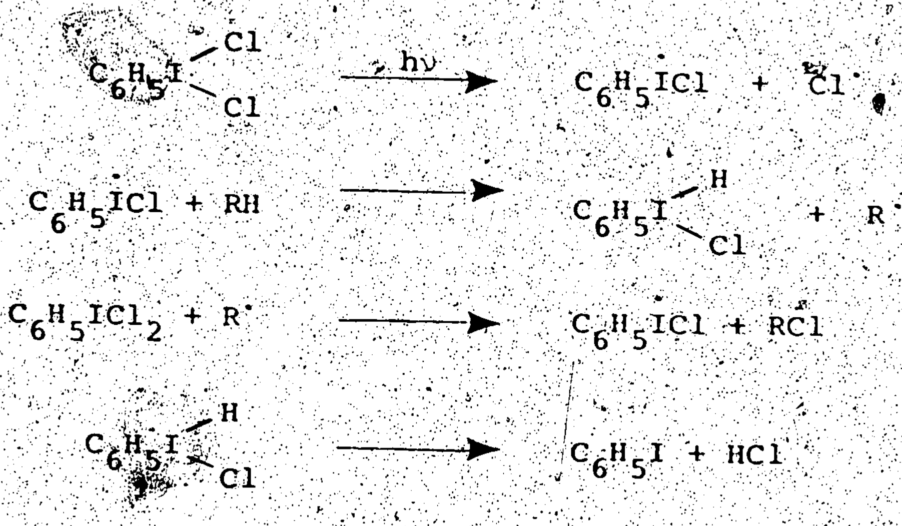
The photochemical reactions of several aryl iodine (III) chlorides (81-84) and a reagent which can be considered formally to be *tert*-butyl hypoiodite (85) have received some attention in the recent literature.

Iodobenzene dichloride is a crystalline compound which decomposes slowly on standing to iodobenzene and chlorine (86).



$$C_6H_5ICl_2 \rightleftharpoons C_6H_5I + Cl_2$$

The photochemical reactions of this reagent have been studied and as a result of the very high selectivity observed (primary : secondary : tertiary = 1:21:368), a radical chain involving abstraction by an iodonyl radical was proposed (81,82).



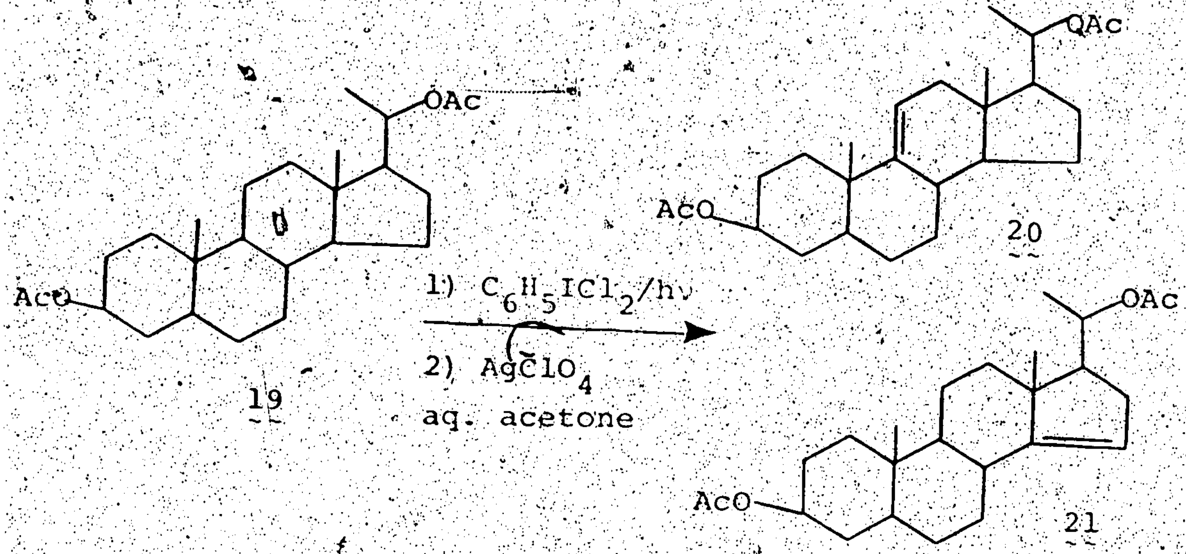
$$C_6H_5ICl_2 \xrightarrow{h\nu} C_6H_5\dot{I}Cl + Cl^{\cdot}$$

$$C_6H_5\dot{I}Cl + RH \longrightarrow C_6H_5I(H)Cl + R^{\cdot}$$

$$C_6H_5ICl_2 + R^{\cdot} \longrightarrow C_6H_5\dot{I}Cl + RCl$$

$$C_6H_5I(H)Cl \longrightarrow C_6H_5I + HCl$$

Breslow (87) has recently made use of this highly selective radical to selectively introduce double bonds into the steroid ring system. For example, **19** reacted with iodobenzene dichloride photochemically to give a mixture of chlorides. Treatment with an aqueous acetone solution of silver perchlorate gave a 75% yield of mono-olefins, which were an approximately 1:1 mixture of **20** and **21**, with only minor traces of other products. Presumably the 9-



and 14-chlorides were intially formed by the selective free radical reaction and gave on the elimination of hydrogen chloride, the observed olefins.

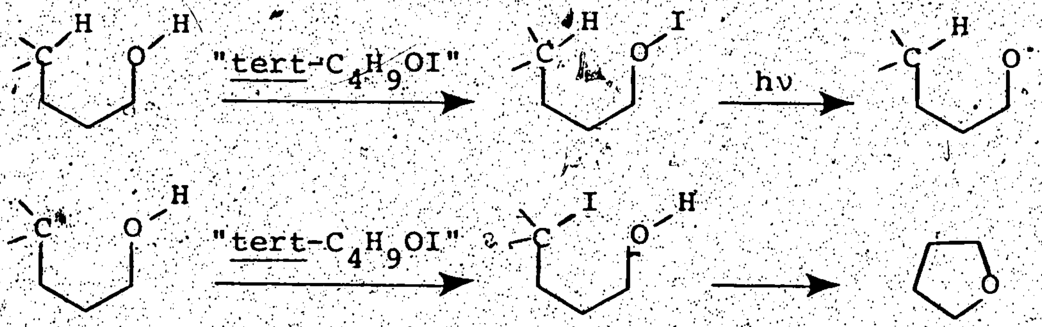
Iodobenzene tert-butoxychloride (IBBC) has been prepared, by the oxidation of iodobenzene with tert-butylhypochlorite, as a pale yellow solid, (84). IBBC reacted photochemically with hydrocarbons to yield alkyl chlorides. A high selectivity was again observed (primary : secondary : tertiary = 1:13:144). The fact that this selectivity was lower than that observed for iodobenzene dichloride suggests that the IBBC reaction proceeded at least partly *via* a mixed chain with some abstraction by chlorine atoms or by *tert*-butoxy radicals (or both) as well as abstraction by the iodonyl radical (84).

Recently, in connection with another study, Walling and Kjellgren (88) described a reaction between potassium *tert*-butoxide and iodine. The resulting solutions were found to retain their oxidising power for some time. When two mol of the butoxide were treated with one mol of iodine, the purple iodine color almost completely disappeared and a tan precipitate formed which, on drying, was shown to be a mixture of potassium iodide and potassium iodate.

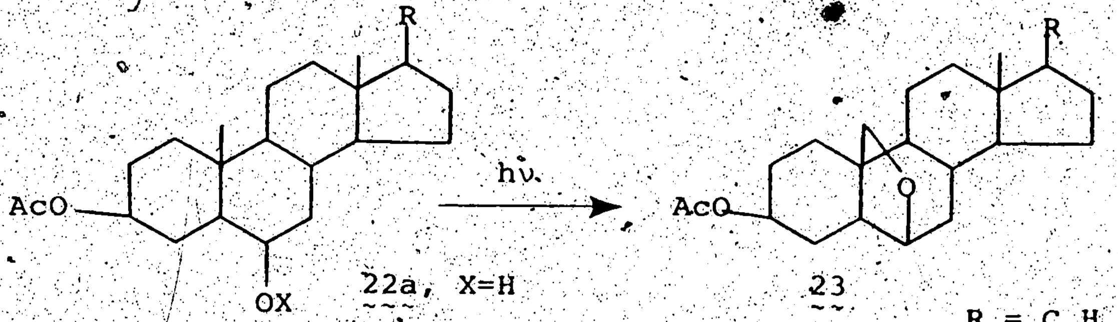
Some time ago, Walling and Jacknow (89), in a study on the chlorination of toluenes with *tert*-butylhypochlorite, found that the reaction was catalysed by AIBN and retarded by hydroquinone, *p*-cresol and oxygen. However iodine, normally an efficient radical scavenger, was found to accelerate the reaction. Although no explanation was offered to account for this observation, it seems reasonable to suggest that the *tert*-butylhypochlorite reacted with iodine to produce a species which reacted with toluene faster than *tert*-butyl hypochlorite itself.

Barton and Akhtar (90) prepared solutions of "*tert*-butyl hypoiodite" by both the reaction of *tert*-butyl hypochlorite with iodine and the reaction of potassium *tert*-butoxide with iodine. In both methods, an excess of iodine was used. This reagent was employed to prepare steroid hypoiodites which could be used as intermediates in the Barton reaction (Scheme 4).

SCHEME 4



For example, the hypoiodite **22b** was formed from the steroid by treatment with a solution of "*tert*-butyl hypoiodite". On irradiation, the 6,19-oxide **23** was obtained in 60-80% yield. Such reactions of steroid hypoiodites



22a, X=H
22b, X=I
23
R = C_8H_{17}

have been the subject of a number of investigations and have been reviewed previously (38,91). In most of this work, the steroid hypoiodites were prepared by reaction with either lead tetraacetate and iodine or mercuric oxide and iodine, and not from "*tert*-butyl hypoiodite".

Barton, Beckwith and Goosens (92) used "*tert*-butyl hypoiodite" to prepare N-iodoamides. Suitably substituted

N-iodoamides on photolysis underwent a 1,5 hydrogen transfer analogous to the hypoiodites described previously (Scheme 4). Intramolecular ring closure gave imino lactones which on hydrolysis yielded lactones.

Solutions of "*tert*-butyl hypoiodite" prepared by the reaction of potassium *tert*-butoxide with iodine have been used for the photochemical decarboxylation of acids (93). In general, a carboxylic acid, irradiated at room temperature in benzene with the reagent, afforded a high

$$\text{"}\underline{\text{tert}}\text{-}C_4H_9OI\text{"} + RCO_2H \longrightarrow RCO_2I + \underline{\text{tert}}\text{-}C_4H_9OH$$

$$RCO_2I \xrightarrow{h\nu} RCO_2^{\cdot} + I^{\cdot}$$

$$RCO_2^{\cdot} \longrightarrow R^{\cdot} + CO_2$$

$$R^{\cdot} + RCO_2I \longrightarrow RI + RCO_2^{\cdot}$$

yield of carbon dioxide and a good yield of the corresponding iodide. For example, at 20°, cyclohexane carboxylic acid gave a 70% yield of iodocyclohexane and a 90% yield of carbon dioxide (93).

A preliminary report on the use of "*tert*-butyl hypoiodite" for the free radical iodination of alkanes has been published by Tanner and Gidley (85). In this study, the reagent was prepared by reacting *tert*-butyl hypochlorite with mercuric iodide. In further work (94,95), other metal iodides (notably silver iodide) were utilized leading to essentially the same results.

Carbon tetrachloride or Freon 113 solutions of the reagent, upon irradiation with hydrocarbon substrates, gave, in some limited cases, preparatively useful yields of iodinated hydrocarbons (Table 17). The iodination failed with compounds containing tertiary hydrogens; neither iso-butane nor 2,3-dimethyl butane gave detectable amounts of tertiary iodides. When the reaction with iso-butane was carried out with initially added tert-butyl iodide, more of the alkyl iodide was found to react than the hydrocarbon substrate. This high reactivity of the tertiary halide explains the absence of tertiary iodination products, which must be consumed on formation faster than the unreacted substrate.

For n-butane, the selectivity was found to be approximately primary : secondary (per H), 1:29. This selectivity is very similar to that observed in the abstraction reactions of iodobenzene dichloride (81) (primary : secondary, 1:21) but is appreciably higher than the selectivity reported for tert-butoxy radicals (primary : secondary, 1:8) (89).

On the basis of this selectivity data, a radical chain mechanism was proposed for the photoinitiated iodination whereby the iodonyl radical was the abstracting species. A similar mechanism has been proposed for the free radical chain halogenation of alkanes with iodobenzene dichloride (81,82).

TABLE 17

Photoinitiated Reaction of "tert-C_4H_9OI" with Hydrocarbons (85)

Hydrocarbon	Product	Yield (%)[a]
Neopentane	Neopentyl iodide	34
n-Butane	2-Iodobutane (95 ± 3%) 1-Iodobutane (5 ± 3%)	39
Cyclohexane	Iodocyclohexane	71
Toluene	Benzyl iodide	38

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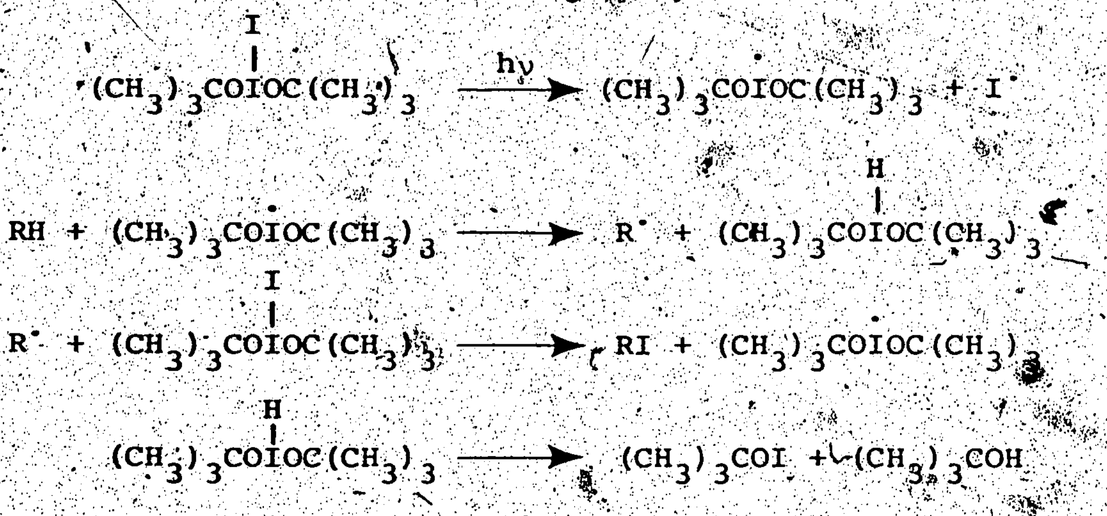
[a] (mol/mol "tert-C_4H_9OI") x 100



$$(CH_3)_3CO\overset{I}{I}OC(CH_3)_3 \xrightarrow{h\nu} (CH_3)_3CO\overset{\bullet}{I}OC(CH_3)_3 + I^{\bullet}$$

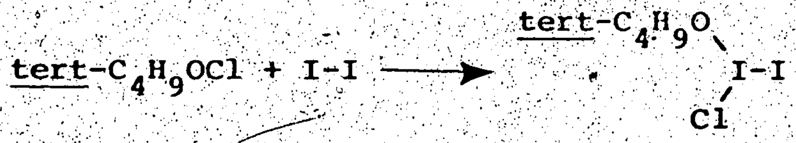
$$RH + (CH_3)_3CO\overset{\bullet}{I}OC(CH_3)_3 \longrightarrow R^{\bullet} + (CH_3)_3CO\overset{H}{I}OC(CH_3)_3$$

$$R^{\bullet} + (CH_3)_3CO\overset{I}{I}OC(CH_3)_3 \longrightarrow RI + (CH_3)_3CO\overset{\bullet}{I}OC(CH_3)_3$$

$$(CH_3)_3CO\overset{H}{I}OC(CH_3)_3 \longrightarrow (CH_3)_3COI + (CH_3)_3COH$$

The photoinitiated decomposition of "tert-butyl hypoiodite" has been studied (94,95) (Table 18). Several other minor products (≤2%) were not identified (94,95). The products found in the decomposition of "tert-butyl hypoiodite" (Table 18) are analogous to those found by Walling and Padwa in the photoinitiated decomposition of tert-butyl hypochlorite (96).

The reactions of tert-butyl hypochlorite (84) or chlorine (81,86) with iodobenzene and the reaction of excess chlorine with molecular iodine (97) all led to iodine (III) compounds. A reaction of tert-butyl hypochlorite with iodine or with metal iodides leading to analogous species can be proposed.



$$\underline{tert}\text{-}C_4H_9OCl + I\text{-}I \longrightarrow \underset{Cl}{\overset{\underline{tert}\text{-}C_4H_9O}{I}}\text{-}I$$

In order to investigate this proposal as part of a continuing study of iodine (III) compounds (81,83,84) and

TABLE 18

Photoinitiated Decomposition of "*tert*-Butyl Hypoiodite" at 40°

Product	Yield (%)[a]
Acetone	55
Iodomethane	55
tert-Butyl alcohol	2[illegible]
1-Iodo-2-methyl-2-propanol	2.8
Isobutylene oxide	3.3
1-Iodo-2-propanone	3
Iodine	11

---

[a] (mol/mol "*tert*-C_4H_9OI") x 100

"*tert*-butyl hypoiodite" (85,94,95), the reaction of *tert*-butyl hypochlorite with iodine was chosen for further study. Barton has previously used the reagent prepared *via* this reaction for the synthesis of hypoiodites (90), N-iodoamides (92) and for the decarboxylation of acids (93) but has given little consideration to the reactions involved in the preparation of, and to the nature of, the reagent. As part of this investigation, further work on the reaction of *tert*-butyl hypochlorite with metal iodides was also undertaken.

RESULTS AND DISCUSSION

I. Reaction of tert-Butyl Hypochlorite with Iodine

In Barton's earlier work (90,92) with this reaction, excess iodine was used, leading to purple solutions of the reagent and iodine in the solvent (usually benzene). If, on the other hand, the ratio of the hypochlorite to iodine was increased, successive changes in the appearance of the solutions occurred until at 4:1 (tert-$C_4H_9OCl:I_2$) a green-yellow solution containing unreacted hypochlorite was formed. (At 4:1, the nmr indicated the appearance of a second absorption at τ 8.69 characteristic of the tert-butyl protons in the hypochlorite and in the ir, the characteristic O-Cl stretching vibration at 692 cm^{-1} (98) was apparent). A summary of these color changes together with the nmr data in carbon tetrachloride is given in Table 19.

A similar series of reactions occurred when iodine monochloride was used in place of iodine and this data is also included in the Table.

The 1:1 solution had an absorption maximum in the visible region at 505 mμ. This represents a very slight shift from the position of the maximum for iodine in carbon tetrachloride at 515 mμ. It is well known that the absorption maximum for iodine shifts to shorter wavelengths in complexing solvents (99,100) and the small shift observed here can be readily explained by a solvent

TABLE 19

The Reaction of *tert*-Butyl Hypochlorite with Iodine and with Iodine Monochloride - Physical Appearance of the Solutions and nmr Data

Ratio	Color of Solution	nmr Data[a]
tert-C_4H_9OCl	yellow-green	8.69
tert-$C_4H_9OCl:I_2$	red-purple	8.53
2 *tert*-$C_4H_9OCl:I_2$	orange	8.50
3 *tert*-$C_4H_9OCl:I_2$	yellow	8.52
4 *tert*-$C_4H_9OCl:I_2$	yellow-green	8.54 8.69 (Ratio 5.7:1.0)
tert-$C_4H_9OCl:ICl$	orange-yellow	8.51
2 *tert*-$C_4H_9OCl:ICl$	yellow	8.54 8.69 (Ratio 3.6:1.0)

---

[a] Singlets for *tert*-butyl protons in τ.

effect due to the addition of the *tert*-butoxy moiety to the carbon tetrachloride solvent. If the extinction coefficient is assumed to remain constant, then the amount of unreacted iodine is approximately 30% of the initial concentration.

Similar reasoning can be applied to the 2:1 (*tert*-$C_4H_9OCl:I_2$) solution, which has a maximum in the visible region at 452 mμ, only a slight shift from the position of the maximum of iodine monochloride (ICl) in carbon tetrachloride at 460 mμ. If the absorption at 452 mμ is indeed due to ICl and the extinction coefficient remains constant, then the concentration is approximately 45% of the initial iodine concentration.

The 3:1 solution indicated a very weak absorption in the region of 450 mμ (too small to measure), while the 4:1 solution did not have an absorption maximum in this region.

Silver salts of carboxylic acids and iodine in the ratio 3:2 react to form iodine (III) tricarboxylates (101,102). These iodine tricarboxylates have a marked sensitivity to water and undergo hydrolysis *via* the

$$3RCO_2Ag + 2I_2 \longrightarrow I(OCOR)_3 + 3AgI$$

following sequence of reactions (101,102).

$$I(OCOR)_3 + 3H_2O \longrightarrow [I(OH)_3] + 3RCO_2H$$

$$5[I(OH)_3] \longrightarrow 3HIO_3 + I_2 + 6H_2O$$

Iodic acid reacts with iodide ion according to the following reaction:

$$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$$

This leads to the prediction that the ratio of the iodine formed in the initial hydrolysis reaction to the iodine released by the oxidation of the iodide ion should be 1:9.

Trivalent iodine compounds are probable products from the reaction of tert-butyl hypochlorite with iodine and a similar sequence of reactions with water would be expected. The 3:1 solution was chosen for careful study, since in this solution, unreacted iodine, iodine monochloride and tert-butyl hypochlorite appeared from the spectroscopic data to be absent or almost absent. Indeed when the 3:1 solution was shaken with water, a purple iodine color was immediately apparent in the carbon tetrachloride layer and the ratio of the initial iodine concentration produced from the hydrolysis reaction, to the iodine released by the oxidation of iodide ions was found experimentally to be 1.0:9.3 ± 0.8. On evaporation to dryness, the aqueous layer yielded a colorless crystalline compound which had an equivalent weight by titration with standard sodium thiosulfate of 58.6 ± 0.5 (Theoretical for HIO_3 is 58.6). The ir spectrum was identical to that from authentic iodic acid. These results can be taken as good evidence that iodine (III) species were present in the 3:1 solution. If, for example, an iodine (V) species had been present and had undergone an equivalent series of reactions with water, the ratio of iodine to iodine released by the oxidation of iodide ions would have been 1:20, while a monovalent species would lead to a ratio of 1:1.5. Both these values are substantially different from the value obtained here.

The hydrolysis of the 2:1 solution was performed, leading to a ratio of 1.0:5.4. Iodine monochloride is also hydrolysed by water (103,104), causing in the case of the 2:1 solution, more iodine to be formed in the initial hydrolysis reaction than in the 3:1 solution.

$$ICl + H_2O \longrightarrow IOH + HCl$$

$$5IOH \longrightarrow HIO_3 + 2I_2$$

Evaporation of the aqueous phase to dryness again led to iodic acid.

The data obtained from the ir spectra in the 250-720 cm^{-1} region using carbon tetrachloride as solvent (cesium bromide cells) are given in Table 20.

TABLE 20

Data from the Infrared Spectra (240-720 cm^{-1}) in Carbon Tetrachloride

Composition	ir Absorption Bands (cm^{-1})^{a}
tert-C_4H_9OH	346 (w), 426 (w), 466 (m)
(*tert*-$C_4H_9O)_2$	355 (m), 428 (w), 466 (s), 536 (m)
tert-C_4H_9OCl	345 (m), 398 (w), 455 (m), 692 (s)
ICl	375 (s)
tert-$C_4H_9OCl + I_2$	283 (s), 340 (s), 355 (sh), 385 (m), 468 (m), 604 (s)
2 *tert*-$C_4H_9OCl + I_2$	285 (s), 338 (s), 355 (sh), 385 (m), 469 (m), 604 (s)
3 *tert*-$C_4H_9OCl + I_2$	265-308 (s), 350-360 (w), 384 (m), 469 (m), 600 (s)
4 *tert*-$C_4H_9OCl + I_2$	~280 (s), ~300 (sh), 348-360 (w), 384 (m), 469 (m), 600 (s), 692 (w)
tert-C_4H_9OCl + ICl	280-310 (s), 350-385 (w), 385 (m), 460 (sh), 468 (m), 602 (s)
2 *tert*-C_4H_9OCl + ICl	~280 (s), ~298 (sh), 346-358 (w), 384 (m), 468 (m), 600 (s), 692 (w)
tert-C_4H_9OCl + AgI	283 (w), 347 (w), 382 (m), 458 (m), 603 (s)
tert-$C_4H_9OK + I_2$	346 (w), 382 (m), 459 (m), 603 (s)
Iodobenzene Dichloride^{b}	~250 (s), ~278 (s), 454 (m)

---

[a] w = weak, m = medium, s = strong, sh = shoulder

[b] Nujol mull using CsI plates: 220 - 600 cm^{-1}

The strong unresolved absorptions in the 260-340 cm^{-1} region can be assigned at least in part to I-Cl stretching vibrations. The I-Cl stretching vibration for iodine monochloride in carbon tetrachloride is at 375 cm^{-1} but shifts to lower wave numbers in complexing solvents (355 cm^{-1} in benzene (105)) and in complexes with amines (106) (292 cm^{-1} in the pyridine-ICl complex (106)). It is noteworthy that absorptions [illegible] this region were entirely absent in the solution from the reaction of potassium *tert*-butoxide with iodine, where no chlorine was present. The absorptions at 340 and 338 cm^{-1} respectively in the 1:1 and the 2:1 solutions can tentatively be assigned to iodine monochloride. In a solution of *tert*-butyl alcohol and iodine monochloride (1.75:1.0) in carbon tetrachloride, the I-Cl stretching vibration shifted from its position in pure carbon tetrachloride (375 cm^{-1}) to 343 cm^{-1}. A small shift of the absorption maximum in the visible spectrum to 455 mμ was also observed.

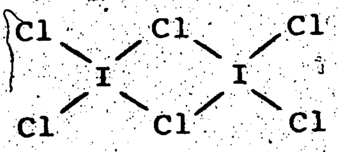
The strong absorptions at 602 ± 2 cm^{-1} can be assigned to an O-I stretching mode. The absence of the characteristic O-Cl stretching mode in *tert*-butyl hypochlorite at 692 cm^{-1} (98), except under conditions where excess hypochlorite was present, (*tert*-$C_4H_9OCl:I_2$, 4:1; *tert*-$C_4H_9OCl:ICl$, 2:1) should be pointed out.

The other three absorptions in the 340-500 cm^{-1}

region are also apparent in the spectra of tert-butyl alcohol, tert-butyl hypochlorite and di-tert-butyl peroxide and have not been further assigned.

The average molecular weights of the species obtained in these reactions have been determined using the cryoscopic method (107,108), in this case, by the freezing point of a benzene solution. The data are given in Table 21.

From the spectral data, the 3:1 solution appears to represent a situation of complete reaction in that unreacted iodine, iodine monochloride and tert-butyl hypochlorite were absent or almost absent. This observation, together with the more extensive data obtained for this solution, enable a number of possible structures to be proposed. The following information must be accounted for: (a) the 3:1 mol ratio of the reactants, (b) the presence of iodine (III) species, (c) the presence of both O-I and I-Cl stretching modes in the ir spectrum, and (d) the molecular weight obtained in a benzene solution. In the light of this information, the following possible structures can be proposed, although no unique structure will explain all of the data.



(Molecular weight, 466.5)

$(\textit{tert}\text{-}C_4H_9O)_3I$

24

(Molecular weight, 346.3)

TABLE 21

Average Molecular Weights of the Species Present - Determined from the Depression of the Freezing Point of Benzene Solutions

	Composition	Molecular Weight[a]	Corrected Molecular Weight
	tert-$C_4H_9OCl + I_2$	360 ± 5	430[b]
2	*tert*-$C_4H_9OCl + I_2$	470 ± 20	670[c]
3	*tert*-$C_4H_9OCl + I_2$	440 ± 20	
4	*tert*-$C_4H_9OCl + I_2$	345 ± 10	420[d]

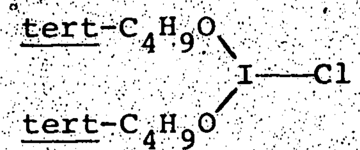
---

[a] Average of two independent experiments.

[b] Corrected for unreacted molecular iodine (35%)

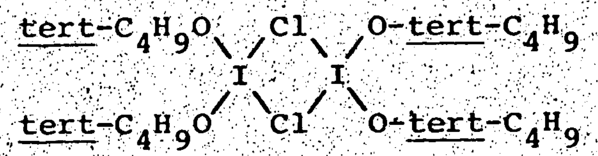
[c] Corrected, assuming the absorption at 405 mμ was due to iodine monochloride (56% based on initial iodine).

[d] Corrected for unreacted *tert*-butyl hypochlorite (13.3%).



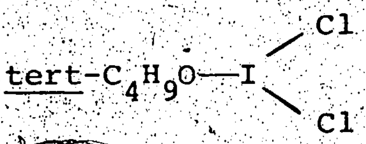
25

(Molecular weight, 308.6)



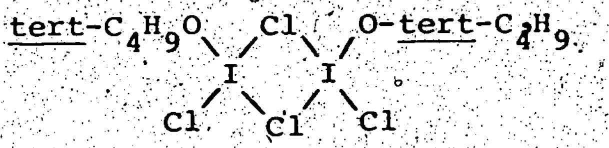
26

(Molecular weight, 617.2)



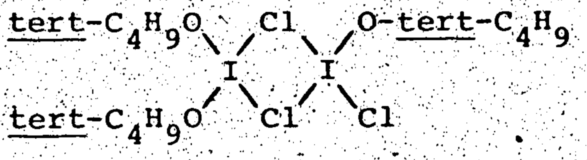
27

(Molecular weight, 270.9)



28

(Molecular weight, 541.9)



29

(Molecular weight, 579.5)

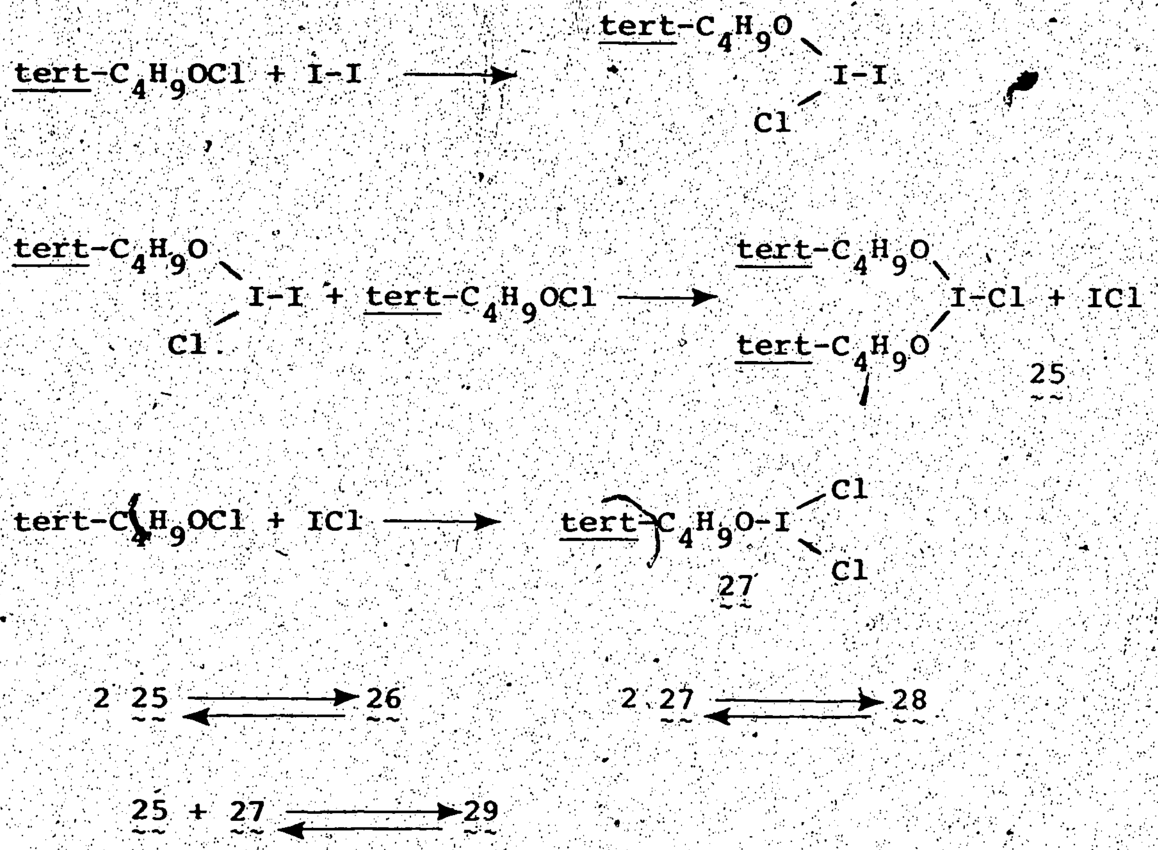
Iodine trichloride exists in the solid state as a flat dimer I_2Cl_6 (109,110), the stucture of which has been established by x-ray studies (109). In solution, it dissociates into iodine monochloride and chlorine (110,111) with the expected absorption maxima at 460 mμ and 332 mμ in the visible-uv spectrum (CCl_4) (111). The 4:1 solution did not absorb in the region of 450 mμ, and the 3:1 solution had only a trace of absorption in the same region. For this reason, both iodine trichloride and iodine monochloride can be ruled out as important components of these two solutions.

Iodine (III) tri-tert-butoxide 24 is more difficult to rule out conclusively. Intuitively, it does not fit in with the stoichiometry of the reaction. If in the 3:1 solution, iodine trichloride, iodine monochloride and molecular chlorine are absent and 24 is present, then the chlorine from the tert-butyl hypochlorite cannot be explained. Species 24 is also a possible product from the reactions of tert-butyl hypochlorite with the metal iodides or from the reaction of potassium tert-butoxide with iodine. After these reactions, the nmr spectra showed that the tert-butyl protons had shifted upfield from their position in tert-butyl hypochlorite (τ 8.70) to τ 8.80-8.85, while after the reactions of tert-butyl hypochlorite with iodine, they had shifted downfield to τ 8.50-8.55 (Table 19), indicating some differences in the species obtained.

Species 25-29 remain as possible structures for the products from the reaction of 3 mol of tert-butyl hypochlorite with 1 mol of iodine.

The following sequence of reactions can be proposed as a possible explanation of the reactions involved (Scheme 5).

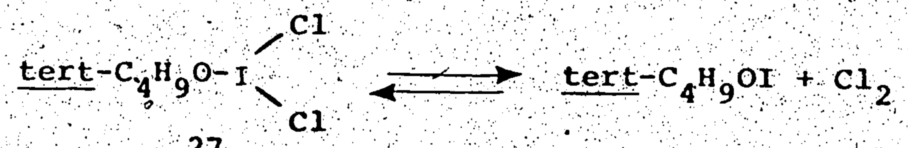
SCHEME 5



The presence of iodine monochloride in the 2:1 solution has been inferred from the visible spectrum of the solution. Indeed, iodine monochloride was found to react rapidly with *tert*-butyl hypochlorite (1:1) to give a solution which had very similar properties in the nmr, ir and visible spectra to the solution formed from the reaction with iodine at 3:1. The main difference was in the ir spectrum where the absorption assigned to I-Cl stretching vibrations was slightly broader in the solution from the reaction with iodine (3:1) extending to 270 cm^{-1}, presumably due to species **25** and/or **26**. A solution of 2 *tert*-$C_4H_9OCl:ICl$ indicated the presence of unreacted hypochlorite both in the nmr and ir spectra (Tables 19 and 20). The molecular weight of the 2:1 solution has been corrected for iodine monochloride and a value of 670 obtained. If the proposed mechanism is correct, then the iodine (III) species must be present mainly as the dimer **26** (molecular weight, 617.2).

The molecular weight of the 3:1 solution is surprisingly much lower than the corrected molecular weight of the 2:1 solution. It is perhaps informative that the average molecular weight of a mixture (1:1) of the dimer **26** and the monomer **27** would be 444, very close to the experimental value in the 3:1 solution.

The spectral evidence indicates that the stoichiometry of the reaction is only approximately 3 *tert*-$C_4H_9OCl:I_2$. The integration of the nmr spectrum of the 4:1 solution gave the ratio of the reagent to unreacted hypochlorite as 5.7:1.0. The ir spectrum of this solution also showed differences in the 270-300 cm^{-1} region to the 3:1 solution (Table 20). These observations require that the species present in the 3:1 solution react further with the hypochlorite. A possible sequence of reactions is as follows:

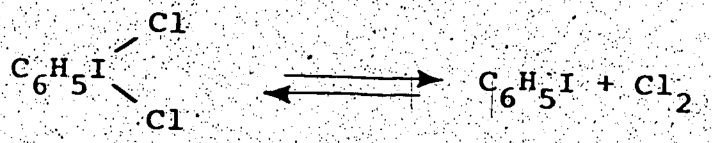


$$\textit{tert}\text{-}C_4H_9O\text{-}ICl_2 \rightleftharpoons \textit{tert}\text{-}C_4H_9OI + Cl_2 \quad (10)$$

27

25

Equation (10) is analogous to the decomposition reactions of iodobenzene dichloride (86) and iodine trichloride (110).

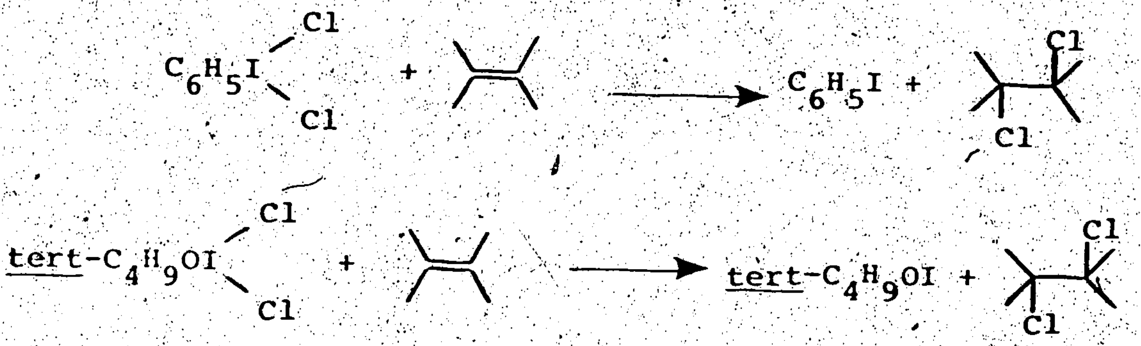


Some experimental evidence is available to support the suggestion that molecular chlorine is formed. In the ir spectrum, a weak, broad absorption for the Cl-Cl stretching vibration centered at 531 cm^{-1} in benzene has been reported (112). A very weak absorption at approximately 530 cm^{-1} in the ir was observed in the 4:1 solution using this solvent. The Raman spectrum of this solution also had a broad unresolved absorption at 530 cm^{-1} ($^{35}Cl_2$, 532.1; $^{35}Cl^{37}Cl$, 525.0 (113)) which was not apparent in the other solutions.

The green-yellow color of the solution supports this conclusion. The fact that there is no absorption maximum in the region of 330 mμ is not surprising as all the solutions investigated absorb strongly in the uv region, sufficient to mask any absorption due to molecular chlorine (λ max. 332 mμ, ε 99 (111)).

Reactions with Cyclohexene

An attempt was made to trap any free halogen present in these solutions by reaction with cyclohexene. The solutions were stirred in the dark for 10 minutes and then quenched by the addition of aqueous acidified potassium iodide solution. The iodide formed was determined by titration with sodium thiosulfate. Although these results (Table 22) are consistent with the mechanism suggested, they do not represent definitive evidence for the presence of iodine monochloride in the 1:1 and the 2:1 solutions and chlorine in the 4:1 solution. Iodine (III) halides would also be expected to add to the double bond of the olefin. For example, 27, analogous to the reaction of iodobenzene dichloride (83), could be expected to add to the olefin to give the dichloride.



27

Another possible route to the dichloride is *via* an ionic "dark" reaction with the initially formed *trans*-1-chloro-2-iodocyclohexane. This compound reacts

TABLE 22

Reactions of "*tert*-Hypoiodite" with Cyclohexene in Carbon Tetrachloride at 0°C[a]

Initial *tert*-C_4H_9OCl	Initial I_2	*trans*-$C_6H_{10}Cl_2$	*trans*-$C_6H_{10}ICl$	I_2 equivalent remaining
6.00	6.00	-	6.24	0.938
6.00	3.00	0.145	5.66	2.01
9.01	3.00	1.40	5.61	3.80
12.0	3.00	2.81	4.27	2.74

---

[a] mol x 10^4

rapidly with iodine trichloride in the dark to give the dichloride.

It is noteworthy that little or no dichloride is formed in the reactions with the 1:1 or 2:1 solutions. This eliminates molecular chlorine as a possible product in these solutions.

Some dichloride is formed from the 3:1 solution. This is consistent with the formation of **27** by reaction of *tert*-butyl hypochlorite with the iodine monochloride present in the 2:1 solution. As suggested earlier, the dichloride could possibly be formed by a subsequent ionic reaction, but the reacting species cannot be present in the 1:1 or 2:1 solutions, as little or no dichloride was formed in these reactions.

The much greater amount of dichloride formed in the 4:1 solution is consistent with the formation of molecular chlorine in this solution.

Reactions with Cyclohexane and Iodocyclohexane

"*tert*-Butyl hypoiodite" formed by the reaction of the hypochlorite with metal iodides has in some limited cases led to preparatively useful yields of alkyl iodides on irradiation with hydrocarbons (Table 17) (85). In order to determine the potential of the reagent formed by the reaction with iodine, the reaction with cyclohexane was chosen for study. The reactions were carried out in sealed, degassed Pyrex ampoules at 40° by irradiation with two 200-W tungsten lamps. The results of this investigation are given in Table 23 together with the results from the reaction with iodine monochloride and iodine trichloride.

The reaction with cyclohexane is catalysed by light. When ampoules were wrapped in aluminum foil to keep out any light but were in other respects subject to the same conditions as in the photoinitiated experiments (reaction time, temperature), no products were observed with iodine monochloride or iodine trichloride at 10°, and only a trace of chlorocyclohexane was observed with the 3:1 (*tert*-$C_4H_9OCl:I_2$) solution at 40°. These results can be taken as good evidence that the initial reaction to give either iodocyclohexane or chlorocyclohexane proceeded *via* a radical mechanism.

The results with iodine trichloride were very similar to the published results of Huyser and coworkers (114). They proposed a radical chain mechanism involving abstraction by both $\dot{I}Cl_2$ and the chlorine atom (114).

[illegible]$_6H_{12} + \dot{I}Cl_2 \longrightarrow C_6\dot{H}_{11} + ICl + HCl$

$$C_6\dot{H}_{11} + ICl_3 \longrightarrow C_6H_{11}Cl + \dot{I}Cl_2$$

$$C_6\dot{H}_{11} + ICl \longrightarrow C_6H_{11}I + Cl^{\bullet}$$

$$C_6H_{12} + Cl^{\bullet} \longrightarrow C_6\dot{H}_{11} + HCl$$

TABLE 23

Photoinitiated Reactions of "*tert*-Butyl Hypoiodite", Iodine Monochloride and Iodine Trichloride with Cyclohexane

Initial Concentrations[a]			Products[a]					
ICl_n	*tert*-C_4H_9OCl	I_2	$C_6H_{11}Cl$	$C_6H_{11}I$	*trans*-$C_6H_{10}Cl_2$	*trans*-$C_6H_{10}ClI$	I_2 remaining	HX
	3.00	2.99[b]	0.473	0.216	-	2.10	1.79	0.30
	6.00	3.00[b]	1.28	0.172	trace	3.30	1.64	0.510
	9.01	3.00[b]	2.92	0.451	0.240	3.[illegible]	1.46	0.736
	9.01	2.26[b]	3.95	0.669	0.323	2.18	0.998	[illegible].721
13.3[c]			1.05 ±0.02	0.415 ±0.002	1.58 ±0.08	1.69 ±0.03	5.62 ±0.10	6.36 ±0.20
19.5[d]			[illegible] ±0.05	1.05 ±0.06	7.43 ±0.05	4.33 ±0.02	7.09 ±0.13	3.20 ±0.10

[a] In mol x 10^4

[b] At 40°

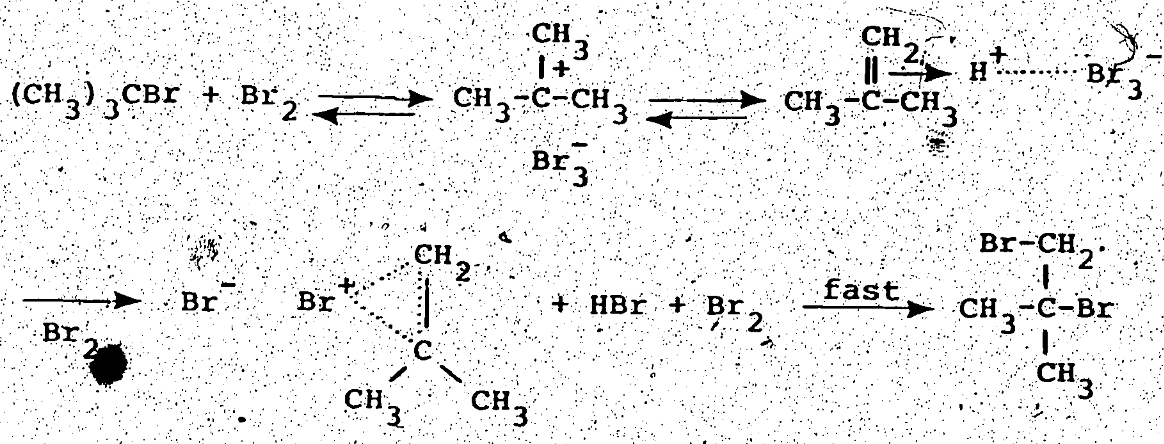
[c] n=1; at 10°

[d] n=3; at 10°

To explain the dihalide products, they proposed an acid catalysed dehydrohalogenation followed by addition to the olefin formed. In this study, both iodocyclohexane and chlorocyclohexane were shown to be stable in the presence of hydrogen chloride in concentrations similar to those expected from the reaction, and an alternative explanation for the formation of the dihalides was sought.

Keefer and Andrews (115,116) some time ago found that iodine monochloride reacted with alkyl iodides _via_ an ionic reaction. For example, _tert_-butyl iodide reacted with iodine monochloride by a reaction which even in dilute solutions at 25° was too rapid for kinetic study with a spectrophotometer and led to _tert_-butyl chloride and the iodochloride.

Russell and Brown (117) have investigated a similar reaction between bromine and tertiary bromides. _tert_-Butyl bromide and 2-bromo-2,3-dimethylbutane were found to react with bromine in the dark to give the corresponding dibromides. In a kinetic study with _tert_-butyl bromide the reaction was found to exhibit third-order kinetics (second order in bromine) and the following mechanism was proposed.



Keefer and Andrews proposed almost the same mechanism on the basis of similar kinetic data.

These earlier studies suggest that in the reaction with cyclohexane (Table 23), the iodocyclohexane formed in the initial radical reaction reacted further by an ionic "dark" reaction to yield chlorocyclohexane and the dihalides. The results of a study of the reaction of "*tert*-butyl hypoiodite", iodine monochloride and iodine trichloride with iodocyclohexane in the dark are given in Table 24.

These results (Tables 23 and 24) demonstrate that the reaction of the three halogenating agents with cyclohexane proceed initially *via* a radical reaction to the monohalides and subsequently by an ionic mechanism to the dihalides. This dual mechanism is similar to Russell and Brown's proposal (117) for the bromination of isobutane and 2,3-dimethyl butane.

Although the mechanism for the radical stage of the reaction with "*tert*-butyl hypoiodite" has not been

TABLE 24

"Dark" Reaction of "*tert*-Butyl Hypoiodite", Iodine Monochloride and Iodine Trichloride with Iodocyclohexane

ICl_n	Initial Concentrations[a]			Products[a]					
	tert-C_4H_9OCl	I_2	$C_6H_{11}I$	$C_6H_{11}Cl$	$C_6H_{11}I$	*trans*-$C_6H_{10}Cl_2$	*trans*-$C_6H_{10}ClI$	I_2	HX
	3.00	3.00[b]	12.1	0.314	9.22	trace	2.87	2.70	-
	6.00	2.99[b]	12.1	0.745	5.96	0.0312	5.81	3.43	-
	27.0	9.04[b]	36.2	3.86	8.88	0.236	23.6	11.5	-
	12.0	3.00[b]	24.1	1.68	12.3	0.433	9.96	4.23	-
13.6[c]			26.0	2.38 ±0.17	19.0 ±0.02	0.342 ±0.006	5.58 ±0.43	8.33 ±0.07	4.66 ±0.07
25.0[d] ±1.6			51.8	17.2 ±0.5	12.0 ±2.0	10.0 ±1.0	10.8 ±0.2	25.6 ±1.7	22.5 ±1.5

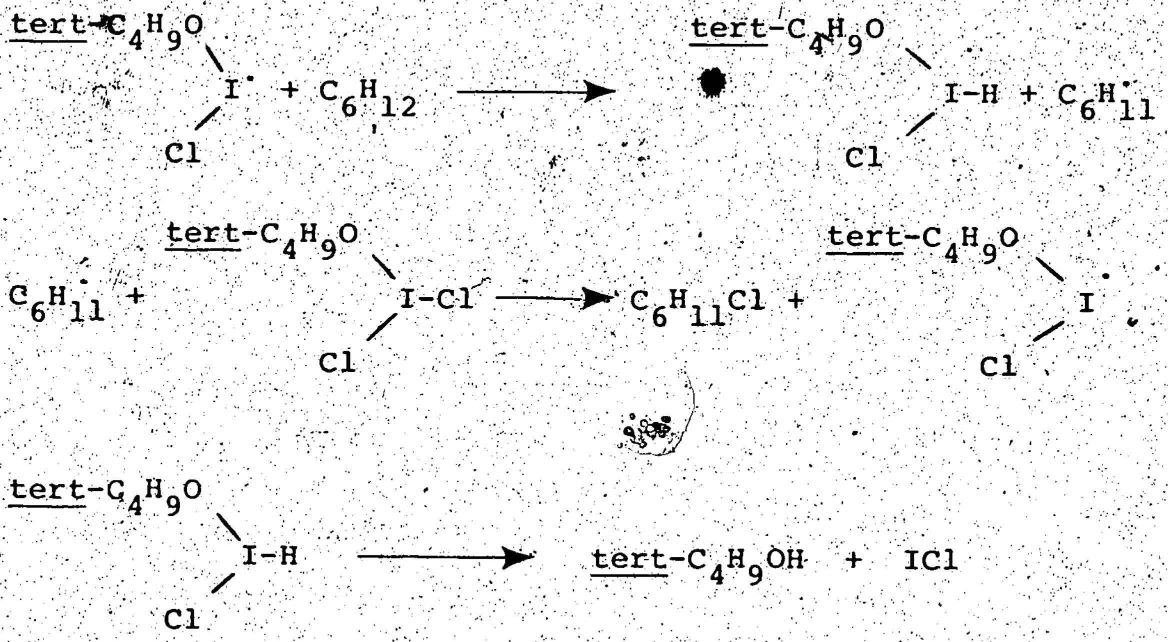
[a] Mol x 10^4

[b] At 40°

[c] n=1; at 0°

[d] n=3; at 0°

elucidated, a mechanism similar to that proposed for iodine trichloride (114) and iodobenzene dichloride (81,82) is probable.



$$\text{tert-}C_4H_9O(Cl)I^\cdot + C_6H_{12} \rightarrow \text{tert-}C_4H_9O(Cl)I\text{-}H + C_6H_{11}^\cdot$$

$$C_6H_{11}^\cdot + \text{tert-}C_4H_9O(Cl)I\text{-}Cl \rightarrow C_6H_{11}Cl + \text{tert-}C_4H_9O(Cl)I^\cdot$$

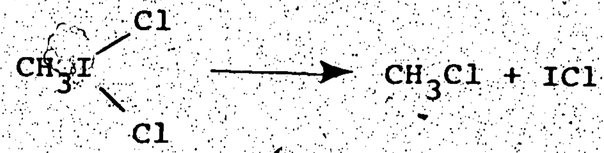
$$\text{tert-}C_4H_9O(Cl)I\text{-}H \rightarrow \text{tert-}C_4H_9OH + ICl$$

$$C_6H_{11}^\cdot + ICl \rightarrow C_6H_{11}I + Cl^\cdot$$

$$C_6H_{12} + Cl^\cdot \rightarrow C_6H_{11}^\cdot + HCl$$

The subsequent ionic reaction could involve either reaction of iodine monochloride with iodocyclohexane or alternatively addition of "tert-butyl hypoiodite" to the iodocyclohexane followed by decomposition to chlorocyclohexane and the dihalides. This last reaction is similar to the reaction of methyl iodide with chlorine (118).

$$CH_3I + Cl_2 \rightarrow CH_3ICl_2$$



$$CH_3I(Cl)_2 \longrightarrow CH_3Cl + ICl$$

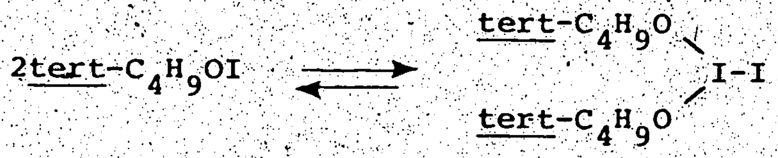
II Reaction of tert-Butyl Hypochlorite with Metal Iodides

"*tert*-Butyl hypoiodite" was prepared by the reaction of *tert*-butyl hypochlorite with silver or mercuric iodides in benzene or carbon tetrachloride as solvent. Both methods resulted in purple solutions in which the molecular iodine was found by visible spectroscopy to be 10-15% of the total active halogen, determined by titration with sodium thiosulfate. In these reactions, the *tert*-butyl protons in the nmr spectra shifted from their position in *tert*-butyl hypochlorite (τ 8.69) to τ 8.75-8.85 (carbon tetrachloride solutions). This shift is in the opposite direction to that observed in the reaction with iodine (τ 8.50-8.55).

The average molecular weight of the species present in the solution from the reaction of the hypochlorite with silver iodide was determined to be 320 by the depression of the freezing point of benzene. Hydrolysis of the solution led to a ratio of the iodine released in the hydrolysis reaction to the iodine formed by the oxidation of iodide ions of 1:4. Evaporation of the aqueous phase led to iodic acid.

These results suggest that both monovalent and trivalent iodine species are present and enable the following reactions to be proposed:

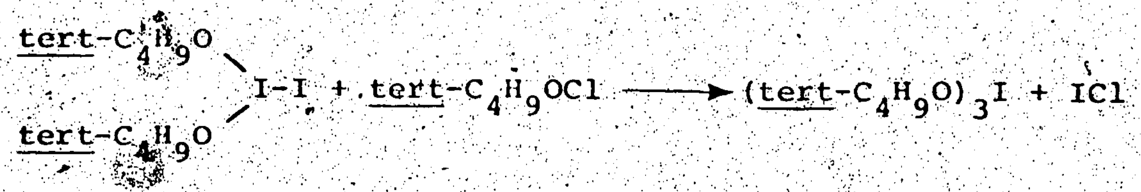
$$\underline{\text{tert}}\text{-C}_4\text{H}_9\text{OCl} + \text{AgI} \longrightarrow \underline{\text{tert}}\text{-C}_4\text{H}_9\text{OI} + \text{AgCl}$$



$$2\underline{\text{tert}}\text{-C}_4\text{H}_9\text{OI} \rightleftharpoons \left.\begin{matrix}\underline{\text{tert}}\text{-C}_4\text{H}_9\text{O}\\ \underline{\text{tert}}\text{-C}_4\text{H}_9\text{O}\end{matrix}\right\rangle \text{I-I}$$

In a reaction with silver iodide, the weight of the silver halides recovered was 107% of the theoretical for silver chloride. Analysis of the recovered halides gave the composition as 92% silver chloride and 8% silver iodide. The yield of mercuric chloride from the reactions with mercuric iodide has previously been shown to be nearly quantitative (85).

The mechanism for the formation of the molecular iodine is not apparent in this sequence. The following reactions can be tentatively proposed to overcome this difficulty.



$$\left.\begin{matrix}\underline{\text{tert}}\text{-C}_4\text{H}_9\text{O}\\ \underline{\text{tert}}\text{-C}_4\text{H}_9\text{O}\end{matrix}\right\rangle \text{I-I} + \underline{\text{tert}}\text{-C}_4\text{H}_9\text{OCl} \longrightarrow (\underline{\text{tert}}\text{-C}_4\text{H}_9\text{O})_3\text{I} + \text{ICl}$$

$$\text{ICl} + \text{AgI} \longrightarrow \text{AgCl} + \text{I}_2$$

Silver iodide was shown to react with iodine monochloride in carbon tetrachloride to give a quantitative yield of iodine.

The reaction with cyclohexane was again chosen for study. It has the advantage that iodocyclohexane is formed in a good yield (85) and that further reaction of the product is not significant (85). The reactions were carried out in sealed, degassed Pyrex ampoules at 40° by irradiation with two 200-W tungsten lamps. The results are given in Table 25. Included in the Table are the data from the photoinitiated reaction with cyclohexane of the reagent formed by the reaction of potassium *tert*-butoxide with iodine.

The presence of chlorinated products was surprising. There was no indication of any excess *tert*-butyl hypochlorite in these solutions. The characteristic absorption in the ir spectrum at 692 cm^{-1} (O-Cl stretching vibration) (98) was entirely absent and the *tert*-butyl protons always appeared as a singlet in the nmr somewhat upfield from the position in *tert*-butyl hypochlorite itself. There was however a weak absorption in the ir at 282 ± 2 cm^{-1} of variable intensity which could be assigned to an I-Cl stretching vibration. It is noteworthy that this absorption was absent in the spectrum of the "*tert*-butyl hypoiodite" derived from the reaction of

TABLE 25

The Photoinitiated Reaction of "*tert*-C_4H_9OI" with Cyclohexane at 40°

Product	Method for Preparation of "*tert*-C_4H_9OI"		
	tert-C_4H_9OCl + AgI[a]	2*tert*-C_4H_9OCl + HgI_2[a]	*tert*-C_4H_9OK + I_2[b]
tert-C_4H_9OH	0.999 ± 0.008	0.969 ± 0.003	1.144 ± 0.014
$C_6H_{11}Cl$	0.0316 ± 0.0002	0.0296 ± 0.0005	-----
$C_6H_{11}I$	0.872 ± 0.011	0.858 ± 0.002	0.738 ± 0.013
trans-$C_6H_{10}Cl_2$	trace	trace	-----
trans-$C_6H_{10}ClI$	0.0161 ± 0.0006	0.0189 ± 0.0015	-----
I_2	0.0143 ± 0.000	trace	0.213 ± 0.003

---

[a] mol/mol *tert*-butyl hypochlorite

[b] mol/mol active halogen equivalent as determined by titration with standard sodium thiosulfate.

potassium tert-butoxide with iodine. Thus it appears that the "tert-butyl hypoiodite" derived from the metal iodides contains small variable amounts of tert-$C_4H_9O-\overset{|}{I}-Cl$ type species.

CONCLUSION

In the earlier communication from this laboratory (85), "tert-butyl hypoiodite" prepared by the reaction of tert-butyl hypochlorite with metal iodides was found in some limited cases to give preparatively useful yields of alkyl iodides. In this work, iodocyclohexane in as high as 87% yield was prepared using this method. The experiments carried out on the reagent (molecular weight, hydrolysis) indicate that it is probably a mixture of iodine (I) and iodine (III) species.

tert-Butyl hypochlorite and iodine were found to react in a complex fashion, with the appearance and the physical properties of the solutions being dependent on the exact composition of the reaction mixture. Iodine (I) compounds both in the monomeric and dimeric forms were proposed on the basis of the data obtained. The photoinitiated reaction with hydrocarbons led to a complex product mixture. A mechanism which had both a free radical and an ionic component was proposed to explain the observed results.

EXPERIMENTAL

I Materials

Iodine and iodine monochloride (British Drug Houses Ltd., laboratory reagents) were used as supplied. Iodine trichloride was prepared from iodine and chlorine by a literature method (97).

Carbon tetrachloride (Fisher Scientific Co., "Spectranalysed" Reagent) was distilled from phosphorus pentoxide. Freon 112 (1,2-difluoro-1,1,2,2-tetrachloroethane) was distilled prior to use and had a bp 89.5-90.0°/700 mm. No impurities were detected by glpc.

Cyclohexane was Phillips pure or research grades and was used as supplied.

Bromocyclohexane, trans-1,2-dichlorocyclohexane (Aldrich Chemical Co.) and iodocyclohexane (Eastman Organic Chemicals) were distilled prior to use.

trans-1-Chloro-2-iodocyclohexane was prepared by the procedure of Birckenback and Goubeau (119) by the reaction of iodine and a slight excess of cuprous chloride with a large excess of cyclohexene in anhydrous ether. The product was obtained as a slightly pink liquid in 80% yield, bp 58°/0.8 mm (Lit. (114) 117°/14 mm). The nmr spectral data were identical to the data for trans-1-chloro-2-iodocyclohexane published by Premuzic and Reeves (120).

tert-Butyl hypochlorite was prepared by the method of Teeter and Bell (121). It was distilled and had bp 77°/700 mm (Lit. (121) 77-78°/760 mm). The purity of the *tert*-butyl hypochlorite was checked by iodometric titration with standard sodium thiosulfate prior to use (99-100% pure).

II Methods and Procedures

In general, the methods and procedures used were the same as those outlined in Part One of this thesis.

In addition to the two instruments described previously, a Varian Aerograph Model 202 was used for glpc analysis.

The ir spectra in the region 250-720 cm^{-1} were recorded on a Beckman Model 11 recording spectrophotometer using cesium bromide cells. Ultraviolet-visible spectra were recorded on a Perkin Elmer Model 202 recording spectrophotometer.

III Reaction of *tert*-Butyl Hypochlorite with Iodine

Preparation of the Reagent

Solutions of *tert*-butyl hypochlorite and iodine of varying composition in carbon tetrachloride as solvent were prepared in a dry box. The following experiment illustrates the general procedure.

tert-Butyl hypochlorite (2.223 g, 2.048×10^{-2} mol) was weighed into a 10 ml volumetric flask and the flask was made up to the mark with carbon tetrachloride. Aliquots of this solution were added by means of a pipet to the required amount of iodine in 5 ml volumetric flasks. For example, 1 ml of the stock tert-butyl hypochlorite solution was added to iodine (0.5054 g, 1.991 x 10^{-3} mol) and the resulting solution was shaken vigorously for 30 minutes. It still retained the characteristic purple color of iodine. The quantity of carbon tetrachloride required to fill the flask to the mark was added.

The color of the solutions prepared in this manner was dependent on the composition (Table 19). The singlets for the tert-butyl protons were found at τ 8.53 ± 0.03 and were almost independent of the composition (Table 19).

The ir spectra of the solutions (240-720 cm^{-1}) in cesium bromide cells were determined using a Beckman Model 11 spectrophotometer. Water vapor was used for calibration. The observed ir bands are listed in Table 20.

Hydrolysis of the Solutions

A solution of 3 tert-$C_4H_9OCl:I_2$ was prepared in a 10 ml volumetric flask in the usual manner. An aliquot (5 ml) of this solution was added to distilled water (20 ml) in a separatory funnel. On shaking the yellow carbon tetrachloride layer immediately turned purple. This layer was transferred to a 25 ml volumetric flask and the aqueous layer extracted twice more with carbon tetrachloride (5 ml). The carbon tetrachloride layers were combined in the volumetric flask and the required volume of the solvent added. The concentration of the iodine was determined both by visible spectroscopy and by titration with standard sodium thiosulfate.

The aqueous layer was also diluted to 25 ml in a volumetric flask and the concentration of iodine determined by visible spectroscopy. Potassium iodide (2.0 g) and 1N HCl (10 ml) were added to the aqueous solution and the iodine liberated was titrated with sodium thiosulfate. In this manner the ratio of the iodine formed on hydrolysis to the iodine derived from the iodic acid could be estimated (1.0:9.3 ± 0.8).

In another experiment, the water was removed by vacuum distillation and after drying the solid formed, the weight (80% of theoretical for iodic acid) and equivalent weight by iodometric titration (58.6 ± 0.5; theoretical for HIO_3, 58.6) were determined. The ir spectrum (KBr disc) was found to be identical to the spectrum obtained from authentic iodic acid.

Hydrolysis of the 2:1 solution led to a ratio of the iodine formed in the hydrolysis reaction to the iodine formed by the oxidation of iodide ion of 1:5.4.

Average Molecular Weights Determined in Benzene Solutions

The average molecular weights of the species present were determined from the freezing point depression of a benzene solution (108), using equation (11).

$$M = 1000 \frac{gK_f}{G\Delta T_f} (1-k_f\Delta T_f) \qquad (11)$$

M is the molecular weight of the solute, ΔT_f is the difference between the freezing point of the solvent and a solution prepared by dissolving g grams of solute in G grams of the solvent, K_f is the freezing point depression constant for the solvent (5.12 deg molal^{-1} for benzene) and k_f is a correction constant (0.011 deg^{-1} for benzene), required because K_f otherwise depends slightly on the actual freezing point of the solution.

In a typical experiment, the freezing point of a solution of iodine (0.6085 g, 2.397 x 10^{-3} mol) and tert-butyl hypochlorite (0.5248 g, 4.833 x 10^{-3} mol) in benzene (17.01 g) was determined to be 1.615. The melting point of pure benzene was 2.355 leading to a freezing point depression of 0.74° and a molecular weight of 457. The reliability of the procedure was established by determining the molecular weight of tert-butyl hypochlorite (105.4; theoretical, 108.6) and bromocyclohexane (155.7; theoretical 163.1) under the same conditions.

A known amount of Freon 112 in benzene was added and the active halogen destroyed by the addition of aqueous, acidified potassium iodide. The iodine formed was destroyed with sodium thiosulfate solution. The benzene solution was separated, dried over anhydrous sodium sulfate and analysed by glpc to determine any reaction with the solvent during the molecular weight determination. In the 4:1 and 3:1 solutions, halogenated benzenes, approximately 2-3% based on the initial hypochlorite concentration, were found. No products were observed in the 1:1 and 2:1 solutions.

Reaction with Cyclohexene

Solutions of tert-butyl hypochlorite and iodine in carbon tetrachloride of varying compositions were prepared. Aliquots (1-2 ml) of these solutions were added to cyclohexene (4 ml) at 0°C and stirred for 10 minutes in the dark. The reactions were quenched by pouring them into a solution of potassium iodide (2.0 g) and 1N HCl (10 ml) in water (30 ml). The iodine liberated was determined by titration with standard sodium thiosulfate. The organic layer was separated, dried over anhydrous sodium sulfate and the products analysed by glpc on both a 10% DEGS on Chromosorb P-AW, 6 ft. x 0.25 in. glass column and a 10% SE30 on Chromosorb W-AW, 12 ft. x 0.25 in. glass column. The products were identified by their retention times being identical to those of authentic compounds on both the columns used. The data obtained are given in Table 22.

Reaction with Cyclohexane

Solutions of tert-butyl hypochlorite and iodine were prepared in the usual manner. An aliquot (2 ml) of the carbon tetrachloride solution was added to cyclohexane (2 ml) in a Pyrex ampoule. After degassing, sealing under vacuum, and equilibration in a Pyrex water bath at 40.0 ± 0.2°, the ampoules were irradiated with two 200 W tungsten lamps placed at a distance of 3-4 inches for 8 hours. Other ampoules were wrapped in aluminum foil and left in the water bath for the same time.

Before opening, the ampoules were frozen under liquid nitrogen. Any escaping gas was bubbled through water (122) so that any hydrogen halides present would be absorbed. The iodine present was determined by titration with standard sodium thiosulfate.

$$I_2 + 2\,S_2O_3^{=} \longrightarrow 2I^- + S_4O_6^{=}$$

To determine the concentration of any hydrogen halide present, potassium iodide (2.0 g) and excess potassium iodate (0.30 g) were added and the iodine released titrated with the thiosulfate (123).

$$6H^+ + 5I^- + IO_3^- \longrightarrow 3H_2O + 3I_2$$

A known concentration of bromocyclohexane in carbon tetrachloride was added as the external standard. The organic layer was separated and dried over anhydrous sodium sulfate. The products were analysed by glpc on a 10% DEGS on Chromosorb P-AW, 6 ft. x 0.25 in. glass column. They were identified by a comparison of their retention times on the DEGS column with authentic compounds. These assignments were confirmed by collecting the products by preparative glpc and comparing their ir spectra with those from authentic samples.

The data obtained from the reactions with cyclohexane are given in Table 23.

Reaction with Iodocyclohexane

Aliquots of the tert-$C_4H_9OCl-I_2$ solutions and iodocyclohexane in carbon tetrachloride were added by means of a pipet to the Pyrex ampoules at -78°. The composition was such that the mol ratio of iodocyclohexane to initial tert-butyl hypochlorite was approximately 2:1. The ampoules were evacuated and sealed under vacuum. After thawing they were wrapped in aluminum foil and placed in a water bath at 40.0 ± 0.2° for 5 hours.

After reaction all ampoules contained purple solutions with crystals of iodine in suspension. The iodine was determined by titration with sodium thiosulfate. No additional iodine was liberated on the addition of potassium iodate. An aliquot of a solution of bromocyclohexane in carbon tetrachloride was added as the external standard. The organic layer was separated, dried over anhydrous sodium sulfate and the products analysed by glpc on both a 10% DEGS on Chromosorb P-AW, 6 ft. x 0.25 in. glass column and a 10% SE 30 on Chromosorb W-AW, 12 ft. x 0.25 in. glass column. The data obtained from these reactions are given in Table 24. The products were identified by their retention times being identical to those of authentic compounds on both the columns used.

IV Reactions of Iodine Monochloride

Reaction with Cyclohexane

A solution of iodine monochloride (1.0837 g, 6.674 x 10^{-3} mol) in cyclohexane (25 ml) was prepared. Aliquots (3 ml) of this solution were added by means of a pipet to Pyrex ampoules. After degassing, sealing under vacuum and equilibration in a water bath at 10.0°, the ampoules were irradiated with a 140-W Hanovia uv lamp for 5 hours. Other ampoules were wrapped in aluminum foil and placed in the water bath at the same temperature for the same time.

After irradiation, the ampoules contained purple solutions with crystals of iodine in suspension. The molecular iodine and any hydrogen halides produced were determined by the method described previously (122).

The product yields were determined relative to bromocyclohexane by glpc on a 10% Butanediol Succinate on Chromosorb W-AW, 6 ft. x 0.25 in. glass column and were identified by comparing their retention times to those of authentic compounds. The data obtained are given in Table 23.

Reaction with Iodocyclohexane

Solutions of iodine monochloride (0.5538 g, 3.411 x 10^{-3} mol) in carbon tetrachloride (5 ml) and iodocyclohexane (1.366 g, 6.503 x 10^{-3} mol) in carbon tetrachloride (5 ml) were prepared. Aliquots (2 ml) of each solution were added by means of a pipet to Pyrex ampoules at -78°. The ampoules were evacuated and sealed under vacuum. After thawing, they were wrapped in aluminum foil and placed in a water bath at 10° for 5 hours. The iodine and hydrogen halides formed were determined in the usual manner (122) and the products determined relative to bromocyclohexane by glpc on a 10% DEGS on Chromosorb P-AW, 6 ft. x 0.25 in. glass column. The data obtained are given in Table 24.

V Reactions with Iodine Trichloride

Reaction with Cyclohexane

Iodine trichloride (0.450 g, 1.93 x 10^{-3} mol) was weighed into a Pyrex ampoule and cyclohexane (10 ml) was added. After degassing, sealing under vacuum and equilibration in a water bath at 10°, the ampoules were irradiated with a Hanovia 140-W uv lamp for 18 hours. Other ampoules were wrapped in aluminum foil and placed in a water bath at the same temperature for the same time. After reaction, the iodine and hydrogen halides formed were determined in the usual manner (122) and the products determined relative to bromocyclohexane by glpc on a 10% Butanediol Succinate on Chromosorb W-AW, 6 ft. x 0.25 in. metal column. The data obtained are given in Table 23. The products were identified by comparing the retention times on the glpc column and the ir spectra obtained from the samples collected by preparative glpc with the data from authentic compounds.

Reaction with Iodocyclohexane

A solution containing iodocyclohexane (5.18×10^{-3} mol) in carbon tetrachloride (4 ml) was added to a Pyrex ampoule containing iodine trichloride (0.624 g, 2.67×10^{-3} mol) at -78°. The ampoules were evacuated and sealed under vacuum. After thawing, they were wrapped in aluminum foil and placed in a bath at 0° for 3 hours. The iodine and hydrogen halides were determined and the products analysed by glpc on a 10% DEGS on Chromosorb W-AW, 5 ft. x 0.25 in. metal column in the manner described previously. The results of these experiments are given in Table 24.

VI Reaction of tert-Butyl Hypochlorite with Metal Iodides

Preparation of the Reagent

tert-Butyl hypochlorite (9.924×10^{-3} mol) in carbon tetrachloride (6 ml) was added dropwise with stirring over 60 minutes to a suspension of silver iodide (1.067×10^{-2} mol) in carbon tetrachloride (10 ml) at 0°C under an atmosphere of nitrogen. The resulting purple solution was filtered through a sintered glass funnel to remove the silver halides.

An aliquot (1 ml) of this solution was added to a solution of potassium iodide (2.0 g) and acetic acid (3 ml) in water (30 ml). The iodine liberated was titrated with 0.03002 M sodium thiosulfate leading to an active halogen equivalent of 6.039×10^{-4} mol of iodine (97.4% of theoretical). The molecular iodine in another aliquot (1 ml) was determined by visible spectroscopy to be 8.86×10^{-5} mol (14.6%) [λ max. 508 mμ-assuming the extinction coefficient is the same as for iodine in carbon tetrachloride (λ max. 516 mμ, ε 903)].

In one experiment, the weight of the silver halide recovered was 107% of the theoretical for silver chloride. The composition of the recovered halides was determined by the method of Bekk (124). The silver halide (0.3 g), potassium dichromate (2 g) and sulfuric acid (30 ml), in an Erlenmeyer flask, were heated on a boiling water bath for 18 hours.

$$6AgCl + K_2Cr_2O_7 + 7H_2SO_4 \longrightarrow 3Ag_2SO_4 + K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3Cl_2$$

$$2AgI + 2K_2Cr_2O_7 + 9H_2SO_4 \longrightarrow Ag_2SO_4 + 2K_2SO_4 + 2Cr_2(SO_4)_3 + 8H_2O + 2HIO_3$$

Towards the end of the reaction, air was bubbled through the solution to remove the last traces of chlorine. After cooling to room temperature, the acid solution was diluted to 300 ml with water and a slight excess of sodium bisulfite solution was added.

$$3HSO_3^- + IO_3^- \longrightarrow I^- + 3HSO_4^-$$

The silver iodide formed was collected by filtration through a weighed sintered glass funnel, washed with water and dried in an oven at 120°. Excess potassium iodide solution was added to the filtrate and the silver iodide formed collected and dried in the same manner. The weight of the silver iodide in the two funnels enabled the amount of silver initially present as silver iodide (8%) and that present as silver chloride (92%) to be calculated. Control experiments with silver iodide and silver chloride gave >99% recovery of the silver salt.

An average molecular weight of 320 for the species present in a benzene solution using the method described previously was found. Hydrolysis led to a ratio of the iodine released in the initial reaction to the iodine formed on the oxidation of iodide ions of 1:4. In another experiment, evaporation of the solution to dryness gave a solid, which on the ba[illegible]s of its ir spectrum was iodic acid.

The ir spectrum for the region 250-700 cm^{-1} was determined using cesium bromide cells. A strong absorption due to the O-I stretching vibration at 603 cm^{-1} and other absorptions at 457, 382, 347 and 283 cm^{-1} were apparent. The weak absorption at 283 cm^{-1} was assigned to an I-Cl stretching vibration.

The hypoiodite was also prepared by reacting *tert*-butyl hypochloride (9.947 x 10^{-3} mol) with mercuric iodide (5.306 x 10^{-3} mol). This solution was found to contain 17% molecular iodine by visible spectroscopy. The ir spectrum was almost identical with the spectrum described above. The *tert*-butyl protons appeared as a singlet in the nmr at τ 8.85.

Photoinitiated Reaction with Cyclohexane

"*tert*-Butyl hypoiodite" (1.208 x 10^{-3} mol) in carbon tetrachloride (2 ml) was added to cyclohexane (2 ml) in a Pyrex ampoule. The solution was degassed and sealed under vacuum. After equilibration in a Pyrex water bath at 40.0 ± 0.2°C, the ampoules were irradiated with two 200-W tungsten lamps placed at a distance of 3-4 inches from the sample. After irradiation for 8 hours, the ampoules were frozen under liquid nitrogen, broken open and bromocyclohexane (4.837×10^{-4} mol) in carbon tetrachloride (2 ml) was added.

The products were determined by glpc analysis on both a 10% SE 30 on [illegible] W-AW, 12 ft. x 0.25 in. glass column and a 10% DEGS on Chromosorb P-AW, 6 ft. x 0.25 in. glass column. The products were identified by comparing their retention times to those of authentic compounds on both columns. The yields are summarized in Table 25.

VII Reaction of Potassium tert-Butoxide with Iodine

Preparation of Potassium tert-Butoxide

Potassium (3.60 g, 9.21×10^{-2} mol) was added to a 3-necked flask containing dry tert-butyl alcohol (80 ml) (freshly distilled from sodium metal). A slow stream of dry nitrogen was allowed to pass into the flask. The alcohol was heated under reflux until all the potassium had dissolved (15 hours) and the excess tert-butyl alcohol was removed by vacuum distillation (5mm) leaving a colorless solid which has previously been shown to be a 1:1 complex of potassium tert-butoxide and tert-butyl alcohol (125). Pure potassium tert-butoxide was prepared by sublimation (170°/0.01 mm) of this crude product (Lit. (126) 220°/1 mm).

Preparation of the Reagent

Freshly sublimed potassium tert-butoxide (0.238 g, 2.12×10^{-3} mol) was weighed into a small flask (10 ml) equipped with a ground glass stopper. Iodine (0.500 g, 1.97×10^{-3} mol) and carbon tetrachloride (4 ml) were added and the resulting suspension was shaken in a dry box for 2 hours (room temperature). The potassium iodide formed and any unreacted potassium tert-butoxide were removed by filtration through a sintered glass funnel.

The iodine equivalent and the concentration of the unreacted molecular iodine (35%) were determined in the manner described previously for the metal iodides. The ir absorption bands (240-720 cm^{-1}) were at 346, 382, 459 and 603 cm^{-1}.

Photoinitiated Reactions with Cyclohexane

The "tert-butyl hypoiodite" prepared in this manner was reacted with cyclohexane under irradiation using procedures identical to those described previously.

The product yields are summarized in Table 25.

REFERENCES

1. C. Walling, "Free Radicals in Solution", John Wiley and Sons, Inc., New York, N.Y., 1957, pp.369-376.
2. W. A. Thaler, Methods Free-Radical Chem., 2, 121 (1969).
3. M. L. Poutsma, Free Radicals, 2, 159 (1973).
4. P. S. Skell, Chem. Soc., Spec. Publ., No. 19, 131 (1964).
5. P. S. Skell and K. J. Shea, Isr. J. Chem., 10, 493 (1972).
6. P. S. Skell and K. J. Shea, Free Radicals, 2, 809 (1973).
7. L. Kaplan, "Bridged Free Radicals", Marcel Dekker, Inc., New York, N.Y., 1972.
8. W. A. Thaler, J. Amer. Chem. Soc., 85, 2607 (1963).
9. P. S. Fredricks and J. M. Tedder, J. Chem. Soc., 144 (1960).
10. H. Singh and J. M. Tedder, J. Chem. Soc., 473[illegible] (1964).
11. H. Singh and J. M. Tedder, J. Chem. Soc., B, 608 (1966).
12. J. M. Tedder, Quart. Rev., Chem. Soc., 14, 336 (1960).
13. P. R. Taussig, G. B. Miller and P. W. Storms, J. Org. Chem., 30, 3122 (1965).
14. P. S. Skell, D. L. Tulleen and P. D. Readio, J. Amer. Chem. Soc., 85, 2849 (1963).

15. P. S. Skell, D. L. Tulleen and P. D. Readio, J. Amer. Chem. Soc., 85, 2850 (1963).

16. H. C. Brown, M. S. Kharasch and T. H. Chao, J. Amer. Chem. Soc., 62, 3435 (1940).

17. P. S. Skell, R. G. Allen and N. D. Gilmour, J. Amer. Chem. Soc., 83, 504 (1961).

18. J. G. Traynham and W. G. Hines, J. Amer. Chem. Soc., 90, 5208 (1968).

19. D. D. Tanner, D. Darwish, M. W. Mosher and N. J. Bunce, J. Amer. Chem. Soc., 91, 7398 (1969).

20. D. D. Tanner, M. W. Mosher, N. C. Das and E. V. Blackburn, J. Amer. Chem. Soc., 93, 5846 (1971).

21. C. Walling, A. L. Rieger and D. D. Tanner, J. Amer. Chem. Soc., [illegible], 3129 (1963).

22. R. E. Pearson and J. C. Martin, J. Amer. Chem. Soc., 85, 3142 (1963).

23. G. A. Russell and K. M. Desmond, J. Amer. Chem. Soc., 85, 3139 (1963).

24. J. G. Traynham, E. E. Green, Y-S. Lee, F. Schweinsberg and C-E. Low, J. Amer. Chem. Soc., 94, 6552 (1972).

25. D. S. Ashton, J. M. Tedder, M. D. Walker and J. C. Walton, J. Chem. Soc., Perkin Trans. 2, 1346 (1973).

26. D. D. Tanner, Y. Kosugi, R. J. Arhart and N. Wada, J. Amer. Chem. Soc., submitted for publication.

27. Ref. (2), pp.184-195.

28. D. D. Tanner, M. W. Mosher and N. J. Bunce, Can. J. Chem., 47, 4709 (1969).

29. K. B. Wiberg and L. H. Slaugh, J. Amer. Chem. Soc., 80, 3033 (1958).

30. H. R. Anderson, H. A. Scheraga and E. R. Van Artsdalen, J. Chem. Phys., 21, 1258 (1953).

31. P. S. Skell and K. J. Shea, J. Amer. Chem. Soc., 94, 6550 (1972).

32. D. S. Ashton, J. M. Tedder and J. C. Walton, Chem. Commun., 1487 (1971).

33. W. O. Haag and E. I. Heiba, Tetrahedron Lett., 3679 (1965).

34. P. D. Bartlett and J. O. McBride, Pure Appl. Chem., 15, 89 (1967).

35. K. R. Kopecky and T. Gillan, Can. J. Chem., 47, 2371 (1969).

36. D. D. Tanner and N. J. Bunce, J. Amer. Chem. Soc., 91, 3028 (1969).

37. M. L. Poutsma and P. A. Ibarbia, J. Org. Chem., 34, 2848 (1969).

38. K. Heusler and J. Kalvoda, Angew. Chem., Int. Ed. Engl., 3, 525 (1964).

39. Unpublished results of T. C. S. Ruo from this laboratory.

40. D. D. Tanner, H. Yabuuchi and E. V. Blackburn, J. Amer. Chem. Soc., 93, 4802 (1971).

1. K. J. Shea and P. S. Skell, J. Amer. Chem. Soc., 95, 283 (1973).

2. W. O. Haag and E. I. Heiba, Tetrahedron Lett., 3683 (1965).

3. C. Ronneau, J.-P. Soumillion, P. Dejaifve and A. Bruylants, Tetrahedron Lett., 317 (1972).

4. S. J. Cristol, M. A. Imhoff and D. C. Lewis, J. Org. Chem., 35, 1722 (1970).

5. D. D. Tanner, J. E. Rowe, T. Pace and Y. Kosugi, J. Amer. Chem. Soc., 95, 4705 (1973).

6. M. J. Hutchinson and M. W. Mosher, J. Chem. Educ., 48, 629 (1971).

7. Ref. (1), p.469.

8. J. C. Martin and P. D. Bartlett, J. Amer. Chem. Soc., 79, 2533 (1957).

9. Private communication from P. S. Skell.

0. E. A. Youngman, Ph.D. Thesis, University of Washington, Seattle, Washington, 1952; quoted in Ref. (22).

1. Unpublished results of T. Pace from this laboratory.

2. H. W. Johnson Jr. and D. E. Bublitz, J. Amer. Chem. Soc., 79, 753 (1957); 80, 3150 (1958).

3. Ref. (1), p.381.

4. A. G. Davies, B. P. Roberts and J. M. Smith, Chem. Commun., 557 (1970).

5. A. G. Davies, B. P. Roberts and J. M. Smith, J.

Chem. Soc., Perkin Trans. 2, 2221 (1972).

56. E. Hedaya, R. L. Hinman, V. Schomaker, S. Theodoropulos and L. M. Kyle, J. Amer. Chem. Soc., 89, 4875 (1967).

57. G. R. Chalfont, M. J. Perkins and A. Horsfield, J. Chem. Soc., B, 401 (1970).

58. E. N. Zil'berman, Russian Chem. Rev., 31, 615 (1962).

59. J. Grundnes and P. Klaboe, "The Chemistry of the Cyano Group", Z. Rappoport, Ed., Interscience Publishers, New York, N.Y., 1970.

60. G. J. Janz and S. S. Danyluk, J. Amer. Chem. Soc., 81, 3846, 3850 (1959).

61. O. D. Trapp and G. S. Hammond, J. Amer. Chem. Soc., 81, 4876 (1959).

62. Unpublished results of T. Ochiai from this laboratory.

63. G. A. Russell, A. Ito and R. Konaka, J. Amer. Chem. Soc., 85, 2988 (1963).

64. D. S. Ashton, J. M. Tedder, J. C. Walton, A. Nechvatal and I. K. Stoddart, J. Chem. Soc., Perkin Trans. 1, 846 (1973).

65. D. S. Ashton and J. M. Tedder, J. Chem. Soc., B, 1723 (1971).

66. C. C. Price, C. D. Beard and K. Akune, J. Amer. Chem. Soc., 92, 5916 (1970).

67. G. A. Russell and A. Ito, J. Amer. Chem. Soc., 85, 2983 (1963).

68. D. S. Ashton and J. M. Tedder, J. Chem. Soc., B, 1031 (1970).

69. J. F. O'Donnell, J. T. Ayrs and C. K. Mann, Anal. Chem., <u>37</u>, 1161 (1965).

70. "Handbook of Chemistry and Physics", 50th Ed., The Chemical Rubber Co., Cleveland, Ohio, 1969-1970, p.C-212.

71. L. Crombie and S. H. Harper, J. Chem. Soc., 2685 (1950).

72. H. L. Goering and L. L. Sims, J. Amer. Chem. Soc., <u>77</u>, 3465 (1955).

73. A. F. Bickel and W. A. Waters, Rec. Trav. Chim. Pays-Bas, <u>69</u>, 1490 (1950).

74. O. O. Orazi, R. A. Corral and J. D. Bonafede, An. Asoc. Quim. Argent., <u>45</u>, 139 (1957); Chem. Abs., <u>52</u>, 15507e (1958).

75. W. Kwestroo, F. A. Meijer and E. Havinga, Rec. Trav. Chim. Pays-Bas, <u>73</u>, 717 (1954).

[illegible]6. Unpublished result of E. V. Blackburn from this laboratory.

77. H. M. van Dort and Th. J. Sekuur, Tetrahedron Lett., 1301 (1963).

78. H. M. van Dort and E. Havinga, Proc. Koninkl. Ned. Akad. Wetenschap., Ser. B, <u>66</u>, 45 (1963).

79. O. Hassel and K. Lunde, Acta Chem. Scand., <u>6</u>, 1126 (1952).

80. V. A. Atkinson and K. Lunde, Acta Chem. Scand., 14, 2139 (1960).

81. D. D. Tanner and P. B. Van Bostelen, J. Org. Chem., 32, 1517 (1967).

82. D. F. Banks, E. S. Huyser and J. Kleinberg, J. Org. Chem., 29, 3692 (1964).

83. D. D. Tanner and G. C. Gidley, J. Org. Chem., 33, 38 (1968).

84. D. D. Tanner and G. C. Gidley, Can. J. Chem., 46, 3537 (1968).

85. D. D. Tanner and G. C. Gidley, J. Amer. Chem. Soc., 90, 808 (1968).

86. D. F. Banks, Chem. Rev., 66, 243 (1966).

87. R. Breslow, J. A. Dale, P. Kalicky, S. Y. Liu and W. N. Washburn, J. Amer. Chem. Soc., 94, 3276 (1972).

88. C. Walling and J. Kjellgren, J. Org. Chem., 34, 1487 (1969).

89. C. Walling and B. B. Jacknow, J. Amer. Chem. Soc., 82, 6108 (1960).

90. M. Akhtar and D. H. R. Barton, J. Amer. Chem. Soc., 86, 1528 (1964).

91. M. Akhtar, Advan. Photochem., 2, 263 (1964).

92. D. H. R. Barton, A. L. J. Beckwith and A. Goosen, J. Chem. Soc., 181 (1965).

93. D. H. R. Barton, H. P. Faro, E. P. Serebryakov

and N. F. Woolsey, J. Chem. Soc., 2438 (1965).

94. Unpublished results of G. C. Gidley from this laboratory.

95. Unpublished results of N. C. Das from this laboratory.

96. C. Walling and A. Padwa, J. Amer. Chem. Soc., 85, 1593 (1963).

97. H. S. Booth and W. C. Morris, Inorg. Syn., 1, 167 (1939).

98. R. Fort, J. Favre, and L. Denivelle, Bull. Soc. Chim. Fr., 534 (1955).

99. L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry", Holden-Day, Inc., San Francisco, California, 1964.

100. R. Foster, "Organic Charge-Transfer Complexes", Academic Press, Inc., London, 1969.

101. J. W. H. Oldham and A. R. Ubbelohde, J. Chem. Soc., [illegible]68 (1941).

102. S-Y. Yeh and R. M. Noyes, J. Org. Chem., 27, 2978 (1962).

103. J. L. Gay Lussac, Ann. Chim. Phys., 91, 5 (1814), quoted in J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. 2, Longmans, Green and Co., London, 1922, p.118.

104. J. H. Faull, J. Amer. Chem. Soc., 56, 522 (1934).

105. W. B. Person, R. E. Humphrey, W. A. Deskin and

A. I. Popov, J. Amer. Chem. Soc., 80, 2049 (1958).

106. J. Yarwood and W. B. Person, J. Amer. Chem. Soc., 90, 3930 (1968).

107. F. Daniels, J. W. Williams, P. Bender, R. A. Alberty and C. D. Cornwell, "Experimental Physical Chemistry", McGraw-Hill Book Company, Inc., New York, N.Y., 1962, p. 78.

108. J. S. Martin and A. D. Jordan, "Physical Chemistry Laboratory Manual - Chemistry 370-372", Department of Chemistry, University of Alberta, Edmonton, Alberta, 1971, Experiment 7.

109. K. H. Boswijk and E. H. Wiebenga, Acta Crystallogr., 7, 417 (1954).

110. R. Forneris, J. Hiraishi, F. A. Miller and M. Uehara, Spectrochim. Acta, 26A, 581 (1970).

111. A. E. Gillam and R. A. Morton, Proc. Roy. Soc. Ser. A, 124, 604 (1929).

112. W. B. Person, R. E. Erickson and R. E. Buckles, J. Amer. Chem. Soc., 82, 29 (1960).

113. H. Stammreich, R. Forneris and Y. Tavares, Spectrochim. Acta, 17, 1173 (1961).

114. W. W. Hess, E. S. Huyser and J. Kleinberg, J. Org. Chem., 29, 1106 (1964).

115. R. M. Keefer and L. J. Andrews, J. Amer. Chem. Soc., 75, 543 (1953).

116. R. M. Keefer and L. J. Andrews, J. Amer. Chem. Soc., 76, 253 (1954).

117. G. A. Russell and H. C. Brown, J. Amer. Chem. Soc., 77, 4025 (1955).

118. J. Thiele and W. Peter, Justus Liebigs Ann. Chem., 369, 119 (1909).

119. L. Birckenbach and J. Goubeau, Ber., 67, 1420 (1934).

120. E. Premuzic and L. W. Reeves, Can. J. Chem., 40, 1870 (1962).

121. H. M. Teeter and E. W. Bell, Org. Syn., 32, 20 (1952).

122. B. G. Brownlee, M.Sc. Thesis, University of Alberta, Edmonton, Alberta, 1968, p.50.

123. G. H. Cady, Inorg. Syn., 5, 156 (1957).

124. J. Bekk, Chemiker Ztg., 39, 405 (1915); Chem. Abs., 9, 2042 (1915).

125. B. B. Graves and B. F. Vincent, Chem. Ind. (London), 2137 (1962).

126. H. Feuer, J. W. Shepherd and C. Savides, J. Amer. Chem. Soc., 78, 4364 (1956).

APPENDIX A

Relative Kinetics

The relative rate constants (k_1/k_2) are obtained from the competitive hydrogen abstraction from two substrates, R_1H and R_2H.

$$R_1H + X^{\cdot} \xrightarrow{k_1} R_1^{\cdot} + HX$$

$$R_2H + X^{\cdot} \xrightarrow{k_2} R_2^{\cdot} + HX$$

$$\frac{-d(R_1H)}{dt} = k_1 [R_1H) [X^{\cdot}] \Longrightarrow [X^{\cdot}] = -\frac{1}{k_1} \frac{d\ \ln[R_1H]}{dt}$$

$$\frac{-d[R_2H]}{dt} = k_2 [R_2H] [X^{\cdot}] \Longrightarrow [X^{\cdot}] = -\frac{1}{k_2} \frac{d\ \ln[R_2H]}{dt}$$

Thus
$$-\frac{1}{k_1} \frac{d\ \ln[R_1H]}{dt} = -\frac{1}{k_2} \frac{d\ \ln[R_2H]}{dt}$$

Multiplying both sides by dt and integrating with respect to time:

$$-\frac{1}{k_1} \int_{t=0}^{t=t} \left[\frac{d\ \ln[R_1H]}{dt}\right] dt = -\frac{1}{k_2} \int_{0}^{t=t} \left[\frac{d\ \text{[illegible]}[R_2H]}{dt}\right] dt$$

Then
$$-\frac{1}{k_1} \int_{[R_1H]_o}^{[R_1H]_f} d\ \ln\ [R_1H] = -\frac{1}{k_2} \int_{[R_2H]_o}^{[R_2H]_f} d\ \ln\ [R_2H].$$

Integration of this expression gives:

$$(\ln[R_1H]_f - \ln[R_1H]_o) = -\frac{k_1}{k_2}(\ln[R_2H]_f - \ln[R_2H]_o)$$

$$\frac{k_1}{k_2} = \frac{\ln[R_1H]_o - \ln[R_1H]_f}{\ln[R_2H]_o - \ln[R_2H]_f}$$

or using logarithms to the base ten

$$\frac{k_1}{k_2} = \frac{\log([R_1H]_o/[R_1H]_f)}{\log([R_2H]_o/[R_2H]_f)} \qquad (12)$$

The required terms $[R_1H]_o/[R_1H]_f$ and $[R_2H]_o/[R_2H]_f$ can be conveniently found by means of gas liquid partition chromotography (glpc).

Assuming that the glpc detector gave a linear response based upon the mols of material passing over it, then the area of the peaks is directly proportional to the number of mols of the components. Thus to evaluate the terms of equation (12), it is sufficient to determine by glpc the ratios of the peak areas of the reactants to an inert internal standard (ST) both before and after the reaction.

$$\frac{[R_1H]_o}{[R_1H]_f} = \frac{(\text{area } R_1H/\text{area ST})_o}{(\text{area } R_1H/\text{area ST})_f}$$

$$\frac{[R_2H]_o}{[R_2H]_f} = \frac{(\text{area } R_2H/\text{area ST})_o}{(\text{area } R_2H/\text{area ST})_f}$$

Substitution of these values into equation (12) gives the relative rate (k_1/k_2).

APPENDIX B

The construction and use of a calibration graph for the determination of molar amounts of products in a reaction mixture can be best illustrated by considering an actual example. The example chosen is the calibration of chlorocyclohexane and Freon 112.

Stock solutions of Freon 112 (1.3442 g, 6.596×10^{-3} mol) in Freon 113 (5 ml) and chlorocyclohexane (0.3264 g, 2.752×10^{-3} mol) in Freon 113 (5 ml) were prepared. Aliquots of these two solutions in varying proportions were added to small flasks and tightly stoppered. The solutions so formed were analysed by glpc on a 10% DEGS on Chromosorb W-AW, 20 ft. x 0.25 in. glass column under the same conditions (i.e., same carrier gas flow rate, column temperature and program rate, detector and injector temperature, and filament current) as those employed for the analysis of a reaction mixture. The results are tabulated in Table 26.

TABLE 26

Glpc Calibration of Chlorocyclohexane and Freon 112

Mol ratio	0.209	0.417	0.835
Area ratio	0.192 ± 0.000	0.389 ± 0.001	0.774 ± 0.002

The plot of the above data is shown in Figure 1.

From a reaction mixture of the NBS bromination of chlorocyclohexane (e.g., entry 3 in Table 11), it was found that the area ratio of the chlorocyclohexane remaining/Freon 112 was 0.114 ± 0.002. From the calibration graph, the mol ratio corresponding to this area ratio was 0.123. Since 2.80 x 10^{-3} mol of Freon 112 was present in the reaction mixture, the molar amount of chlorocyclohexane remaining is (0.123 x 2.80 x 10^{-3}) = 3.44 x 10^{-4} mol. The initial amount of chlorocyclohexane was 4.21 x 10^{-4} mol, so that the percentage remaining at the end of the reaction was 81.7%.

Similar calibration graphs were constructed for the other systems studied by glpc except for <u>cis</u>-1-bromo-3-chlorocyclohexane and <u>trans</u>-1-bromo-4-chlorocyclohexane which were assumed to have the same response as the average response from <u>trans</u>-1-bromo-2-chlorocyclohexane, <u>trans</u>-1-bromo-3-chlorocyclohexane and <u>cis</u>-1-bromo-4-chlorocyclohexane.

FIGURE 1. Glpc Calibration Graph (Mol Ratio vs Area Ratio) for Chlorocyclohexane and Freon 112.