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A MECHANISM FOR THE REACTION OF LEAD TETRAACETATE AND HYDROGEN FLUORIDE WITH OLEFINS

by

© PETER BERNHARD VAN BOSTELEN

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

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OF

DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA

SPRING 1972

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

"A MECHANISM FOR THE REACTION OF LEAD TETRAACETATE AND HYDROGEN FLUORIDE WITH OLEFINS"

submitted by PETER BERNHARD VAN BOSTELEN in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

Supervisor

External Examiner

Date May 1, 1972

TO MY PARENTS

ABSTRACT

The reaction of the reagent lead tetraacetate (LTA) and anhydrous hydrogen fluoride (HF) with the olefins 1,1-diphenylethylene, norbornene, dibenzobicyclo[2.2.2]-octatriene, and 1-^{13}C-1-octene has been studied. On the basis of the products formed from these olefins, a mechanism for the reaction has been proposed.

For the bicyclic olefin, norbornene, an initial *cis-exo*-lead-ligand addition product is postulated. This intermediate is assumed to react by two distinct processes. The first is the heterolysis of the lead-carbon bond with concomitant elimination of a proton to yield nortricyclyl products. The second process is the heterolysis of the lead-carbon bond accompanied by Wagner-Meerwein rearrangement leading to 2-*exo*-7-*syn*-disubstituted products. This process can be accompanied by a 6,1-hydride shift which leads to 2-*exo*-7-*anti*-disubstituted products. Products arising from a competing 6,2-hydride shift are not observed in this reaction.

The mechanism for the LTA-HF reaction with dibenzobicyclo[2.2.2]octariene can also be proposed to proceed by the formation of an initial *cis*-lead-ligand addition product. The products obtained from this reaction were exclusively rearranged 4-*exo*-8-*syn*-disubstituted products. This observation requires that an initial lead-ligand

addition product leads to rearranged products in a geitonodesmic fashion. This process in turn requires a heterolysis of the lead-carbon bond. The stereospecificity of the observed products is taken as evidence against a possible lead-carbon bond homolysis followed by a rapid oxidation of the free-radical so formed.

The products from the reaction of the LTA-HF reagent with the terminal olefins 1,1-diphenylethylene and 1-^{13}C-1-octene are also postulated to proceed by an initial lead-ligand adduct. These adducts are formed in a Markovnikov fashion. The lead-carbon bond cleaves heterolytically with concomitant aryl migration in the 1,1-diphenylethylene system or with either alkyl or hydrogen migration in the 1-^{13}C-1-octene system. Also observed, especially in the 1-^{13}C-1-octene system, is the formation of a significant amount of products which can be rationalized as arising from a direct displacement of the lead species by a nucleophile.

A C K N O W L E D G E M E N T S

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Peter Van Bostelen

Peter B. Van Bostelen

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INTRODUCTION

The use of lead tetraacetate and anhydrous hydrogen fluoride as a reagent to selectively fluorinate an olefin was first described by Dimroth and Bockemüller.[1] They observed that when 1,1-diphenylethylene was treated with a 4:1 mixture of anhydrous hydrogen fluoride and lead tetraacetate, a difluorinated hydrocarbon was isolated in a 28% yield. They assigned the structure of this material as 1,2-difluoro-1,1-diphenylethane. The structure has subsequently properly been reassigned as 1,1-difluoro-1,2-diphenylethane.[2] Deoxybenzoin was also isolated from the reaction in a 15% yield. The authors did not speculate on the mechanism of the reaction nor did they rationalize the formation of the deoxybenzoin. They suggested that the fluorinating agent was lead tetrafluoride formed *in situ* from the reaction of lead tetraacetate with anhydrous hydrogen fluoride.

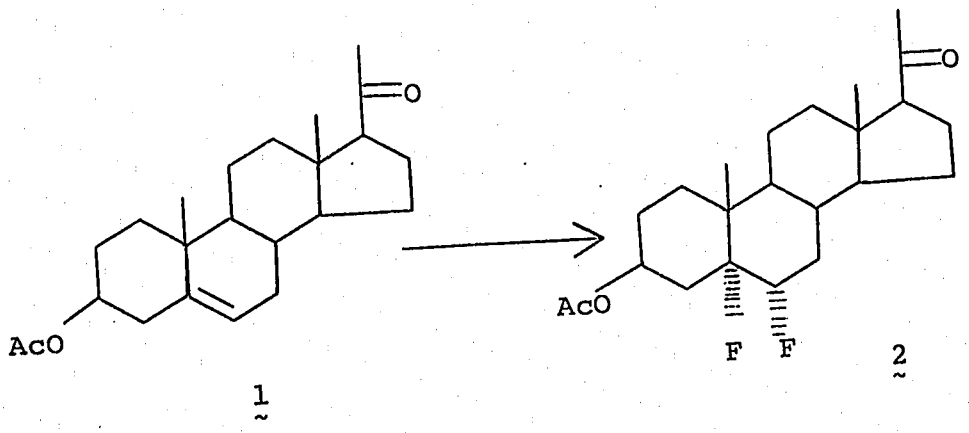
Henne and Waalkes could not repeat the work of Dimroth and Bockemüller.[3] However, they did fluorinate highly halogenated olefins with what they claimed to be nascent lead tetrafluoride prepared *in situ* from lead dioxide and anhydrous hydrogen fluoride. In a typical example of this reaction, 2 moles of tetrachloroethylene, 28 moles of hydrogen fluoride, and 2.2 moles of lead dioxide were mixed together at -78° in an autoclave. The vessel was sealed

and the temperature was allowed to rise. The reaction which ensued was vigorous and was accompanied by the evolution of much heat and the generation of high pressure. This reaction resulted in a 28% yield of 1,2-difluoro-1,1,2,2-tetrachloroethane ("Freon 112"). These workers suggested that the lead tetrafluoride decomposes to lead difluoride and a molecule of fluorine which then fluorinates the olefin. Other workers have used this method to fluorinate double bonds of highly halogenated olefins.[4] In some systems, hydrogen is replaced by fluorine. For example when 2,3-dichloro-2-butene is treated with lead dioxide-hydrogen fluoride, 2,3-dichloro-1,1,1,2,3,4,4,4-octafluorobutane is formed in 26% yield.[4a] Similarly when 1,1-difluoroethane is treated as described above, 1,1,1-trifluoroethane is formed.[4d] These conversions are typical reactions of high valence metallic fluorides, including lead tetrafluoride.[5]

More recently this method has been modified to use lead dioxide and sulfur tetrafluoride (instead of lead dioxide and hydrogen fluoride) as the fluorinating agent.[6] The reagent thus formed fluorinates halogenated olefins. The yields of products formed in this reaction were found to range from 5 - 95%, usually somewhat better than those found in the lead dioxide-hydrogen fluoride system. In a typical experiment, 0.015 mole of lead dioxide was placed

in a pressure vessel. The vessel was evacuated and cooled with liquid nitrogen and then charged with 0.01 mole tetrachloroethylene and 0.05 mole of sulfur tetrafluoride. The vessel was warmed to room temperature and then heated to 100°. This procedure resulted in a 77% yield of "Freon 112". The same product could be obtained in a 28% yield using the lead dioxide-hydrogen fluoride method. The authors suggest that presumably lead tetrafluoride is the fluorinating agent. The advantage of using sulfur tetrafluoride rather than hydrogen fluoride lay in the fact that water would not be one of the products, thus eliminating the need for a large excess of the fluorinating agent to drive the formation of the metal fluoride to completion. However, the authors noted that when preformed lead tetrafluoride was used under conditions found to give the best yields in the lead dioxide-sulfur tetrafluoride system, the yields of products were very low.

The method described by Dimroth and Bockemüller has been successfully used to fluorinate an unsaturated steroid. Bowers and co-workers [7] treated pregnenolone acetate, 1, with an excess of lead tetraacetate and anhydrous hydrogen fluoride for 15 minutes at -75°C and obtained a 27% yield of the difluoro derivative 2 and 63% recovered 1. Longer reaction times or higher temperatures did not improve the yield but only led to a low yield of a product which appears

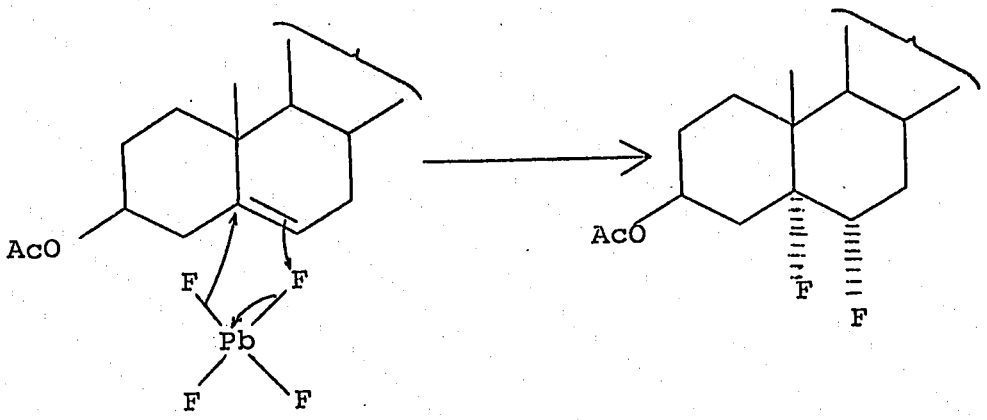


1 2

to be the result of a molecular rearrangement. The stereochemistry at the C-6 position of compound 2 was assigned the α-configuration on the basis of chemical degradation. Since ionic addition to olefins of this type always gives the *trans*-5α-6β-diaxial compound [7,8], the authors conclude that compound 2 arises from a *cis* molecular addition of lead tetrafluoride to the double bond from the least hindered side (Scheme I). This mechanistic pathway is analogous to the reaction of osmium tetroxide to yield the 5α,6α-diol [9] and that which had been proposed for the reaction of iodobenzene dichloride to give the 5α,6α-dichloro compound.[10] It is on the basis of these analogies that the *cis* difluoro compound, 2, was assigned the 5α,6α-configuration.

Bornstein and co-workers have repeated the older work on the fluorination of 1,1-diphenylethylene.[11]

SCHEME I



These workers obtained essentially the same results as the earlier workers. However, when the reaction was run at -40° for 10 minutes, not only were 1,1-difluoro-1,2-diphenylethane (3) and deoxybenzoin formed, but also a new compound. This was shown to be 1,4-difluoro-1,1,4,4-tetraphenylbutane (4) and was isolated in a 25% yield. In order to rationalize these findings, these workers proposed the free radical sequence shown in Scheme II. Bornstein suggested that

SCHEME II

i $Ph_2C{=}CH_2 \longrightarrow Ph_2CFCH_2\cdot$ (5)

ii $2Ph_2CFCH_2\cdot \longrightarrow Ph_2CFCH_2CH_2CFPh_2$ (4)

iii $Ph_2CFCH_2\cdot$ (6) $\longrightarrow PhCFCH_2Ph$

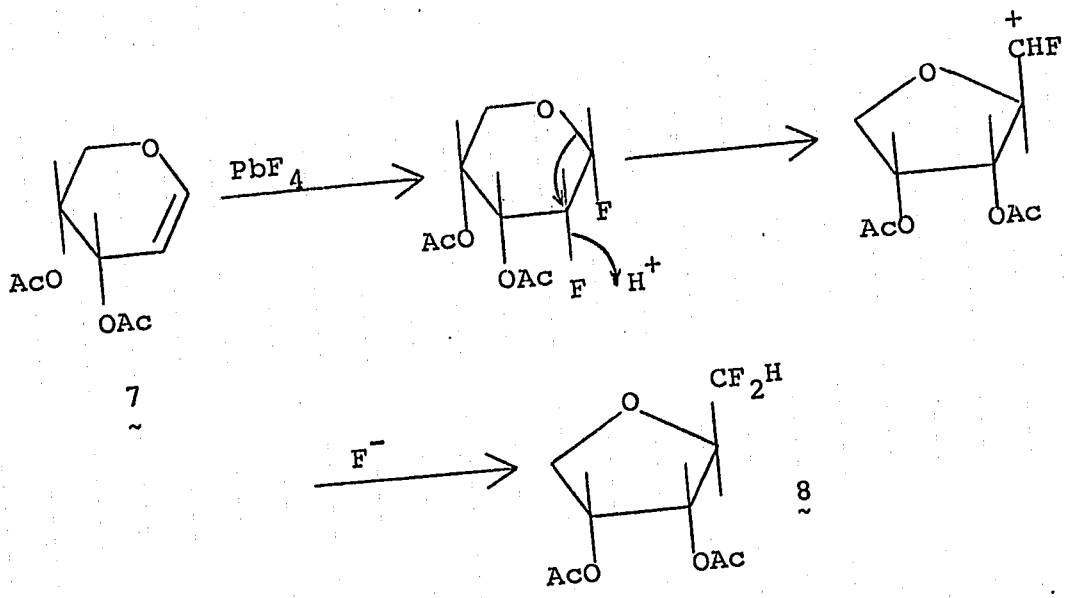
iv $PhCFCH_2Ph \longrightarrow PhCF_2CH_2Ph$

3

the sole fluorinating species is lead tetrafluoride. No attempt was made to rationalize the formation of substantial amounts of deoxybenzoin.

The fluorination of an unsaturated sugar, di-O-acetyl-D-arabinal (7), with lead tetraacetate and anhydrous hydrogen fluoride in methylene chloride at -70° led to a rearrangement product (8).[12] To rationalize the formation of 8, these workers proposed the mechanism shown in Scheme III.

SCHEME III



7

8

Neither the yield of 8 nor the formation of any side products was reported..

Recently Bornstein and Skarlos [13] have shown that pre-formed lead tetrafluoride did not react with 1,1-diphenylethylene. The addition of hydrogen fluoride did not have any effect on the reaction. However, when 1 to 4 moles of glacial acetic acid was added, the reaction went smoothly giving the difluoro compound 3 in the same yield as that realized with the lead tetraacetate-hydrogen fluoride reaction. From the mixture of lead tetrafluoride and glacial acetic acid, these workers isolated and characterized lead diacetate difluoride. When this compound was allowed to react with 1,1-diphenylethylene in chloroform solution, the difluoro compound 3 was formed in yields approximating those obtained with the fluorinating agent generated *in situ*. These workers did not report whether deoxybenzoin or the dimer 4 were formed in either of the above reactions.

The mechanistic conclusions reached by the previous workers bears some comment. The cyclic mechanism proposed by Bowers was of particular interest. A molecular mechanism of this type had been invoked by Barton and Millar [10] to explain the appearance of the *cis*-5α,6α-dichloro isomer isolated when cholesteryl benzoate was chlorinated with iodobenzene dichloride. When cholesteryl benzoate

was chlorinated with molecular chlorine or with iodobenzene dichloride and large amounts of added water, the *trans*-5α,6β-dichloride was obtained. It appeared that *trans* addition to this steroid was the product of ionic halogenation.

Subsequently this reaction of iodobenzene dichloride with norbornene [14] was shown to proceed by two competing mechanisms. When the reaction was carried out in the absence of oxygen, the sole chlorinated products were *trans*-2,3-dichloronorbornane (74%) and *exo-cis*-2,3-dichloronorbornane (26%). Both these products were shown to arise *via* a free-radical chain addition mechanism. These products could be suppressed by the presence of oxygen as well as other radical inhibitors. The inhibition of radical chain addition was so efficient with atmospheric amounts of molecular oxygen, that the slower formation of ionic products became dominant.

In the light of the above results, it should be reasonable to conclude that the formation of the *cis*-5α,6α-dichloro isomer obtained from the cholesteryl benzoate chlorination reaction, may well have been the normal product from homolytic addition rather than from the proposed molecular *cis* addition process. By analogy, the formation of compound 2 from the reaction of pregnenolone acetate with the lead tetraacetate-hydrogen fluoride reagent could presumably also have arisen *via* a free-radical

chain addition process. If this were true, it could be possible, using the LTA-HF reagent, to fluorinate saturated hydrocarbons since it had been shown that chlorination reactions of iodobenzene dichloride with saturated hydrocarbons proceeded *via* a free-radical chain mechanism.[15]

The cyclic mechanism proposed by Bowers could not explain the formation of 1,1-difluoro-1,2-diphenylethane obtained from the reaction of 1,1-diphenylethylene with the lead tetraacetate-hydrogen fluoride reagent, unless an addition - displacement pathway such as that shown in Scheme II was involved. To test this possibility, Bornstein [11] subjected 1,2-difluoro-1,1-diphenylethane to the reaction conditions and found this compound to be stable.

The free radical mechanism proposed, also appeared to be unsatisfactory. This mechanism could not explain the formation of deoxybenzoin nor did it rationalize the initial formation of the least stable radical 5 (Scheme II).

It appeared that the lead tetraacetate-hydrogen fluoride reagent should potentially be of synthetic use in the fluorination of olefins. The yields from the reaction are generally satisfactory, the starting materials are readily accessible and the equipment is standard. However, the mechanistic conclusions reached by the previous workers are inconsistent in that a mechanism

proposed for one system cannot be used to predict the products in another system. This inconsistency limits the general usefulness of this reagent. Moreover, the possibility that this reagent could act as a free-radical chain fluorinating agent analogous to the iodobenzene dichloride chlorinating agent required investigation. It was these considerations that prompted the study of the reaction of the lead tetraacetate-hydrogen fluoride reagent with several selected olefins.

RESULTS AND DISCUSSION

The Reaction of 1,1-Diphenylethylene with Lead Tetraacetate-Hydrogen Fluoride

In order to standardize the conditions necessary for the study of the reaction mechanism of the reagent with an olefin, the fluorination of 1,1-diphenylethylene was reinvestigated. The reaction was carried out by a method similar to that described by Bornstein [11] with the exception that methylene chloride (rather than chloroform) was used as solvent for the reaction. To enable one to follow the reaction by gas liquid partition chromatography (glpc) and to determine the quantity of the products formed, "Freon 112" was added as an internal standard. The molar amount of the major product (1,1-difluoro-1,2-diphenylethane - compound 3) was determined using a standard calibration curve (see Appendix for an example).

Reaction mixtures were quenched after varying reaction times and subjected to glpc analysis. A reaction that had been run for one minute showed only three volatile components. A comparison of the glpc retention times of the materials indicated that they were the major product 3, unreacted starting material and a minor product. The starting material was shown to have reacted to 90% and the area ratio of the major product to the minor product was 1.6:1. It was assumed that the area ratio was equival-

ent to the mole ratio so that the molar amount of the minor product could be estimated.

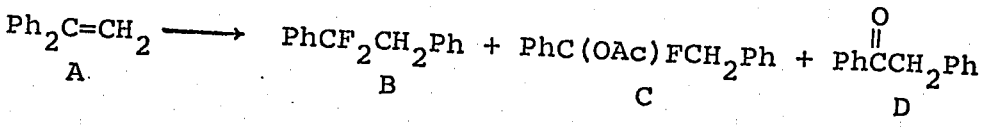
A second reaction which was quenched after five minutes reaction time showed that 93% of the starting material had reacted. The minor product had diminished in area but a new compound with a retention time shorter than that of the minor product had appeared. A comparison of the glpc retention time of this new material with that of an authentic sample of deoxybenzoin, indicated that this material was deoxybenzoin.

The reaction was repeated and quenched at various reaction times. The results of these reactions are tabulated in Table I. Throughout these reactions, the amount of deoxybenzoin increased at the expense of its precursor. The glpc area ratio of 3 to deoxybenzoin plus its precursor was found to be 1.5:1.

The products of the reaction were collected by preparative glpc and the identifications of 3 and deoxybenzoin were confirmed by comparison of their infrared (ir) spectra with those of the authentic materials. The precursor, 9, of deoxybenzoin could be collected admixed with some deoxybenzoin. The ir spectrum of 9 showed strong absorption peaks at 1760 and 1211 cm^{-1} which are characteristic of an acetate. Its mass spectrum gave as the highest significant fragment (>0.5%) a peak at m/e 238 and a satellite peak at m/e 239 whose ratio (100/18)

TABLE I

The Yields of Products from the Reaction of 1,1-Diphenylethylene at Various Reaction Times



Reaction time (minutes)	Molar Yields of Products		
	A	B	C + D
0	0.058	0	0
1	0.006	0.028	0.017
5	0.004	0.028	0.018
45	0	0.029	0.019
125	0	0.029	0.019

is consistent with a $C_{16}H_{14}O_2$ ion. This has been assigned the mass of the parent ion minus hydrogen fluoride or acetic acid. The structure of the precursor to deoxybenzoin has been tentatively proposed to be either 1-acetoxy-1-fluoro-1,2-diphenylethane (9a) or 1,1-diacetoxy-1,2-diphenylethane (9b).

The precursor could have had one of the nine possible structures listed below. Compound iv had been prepared by

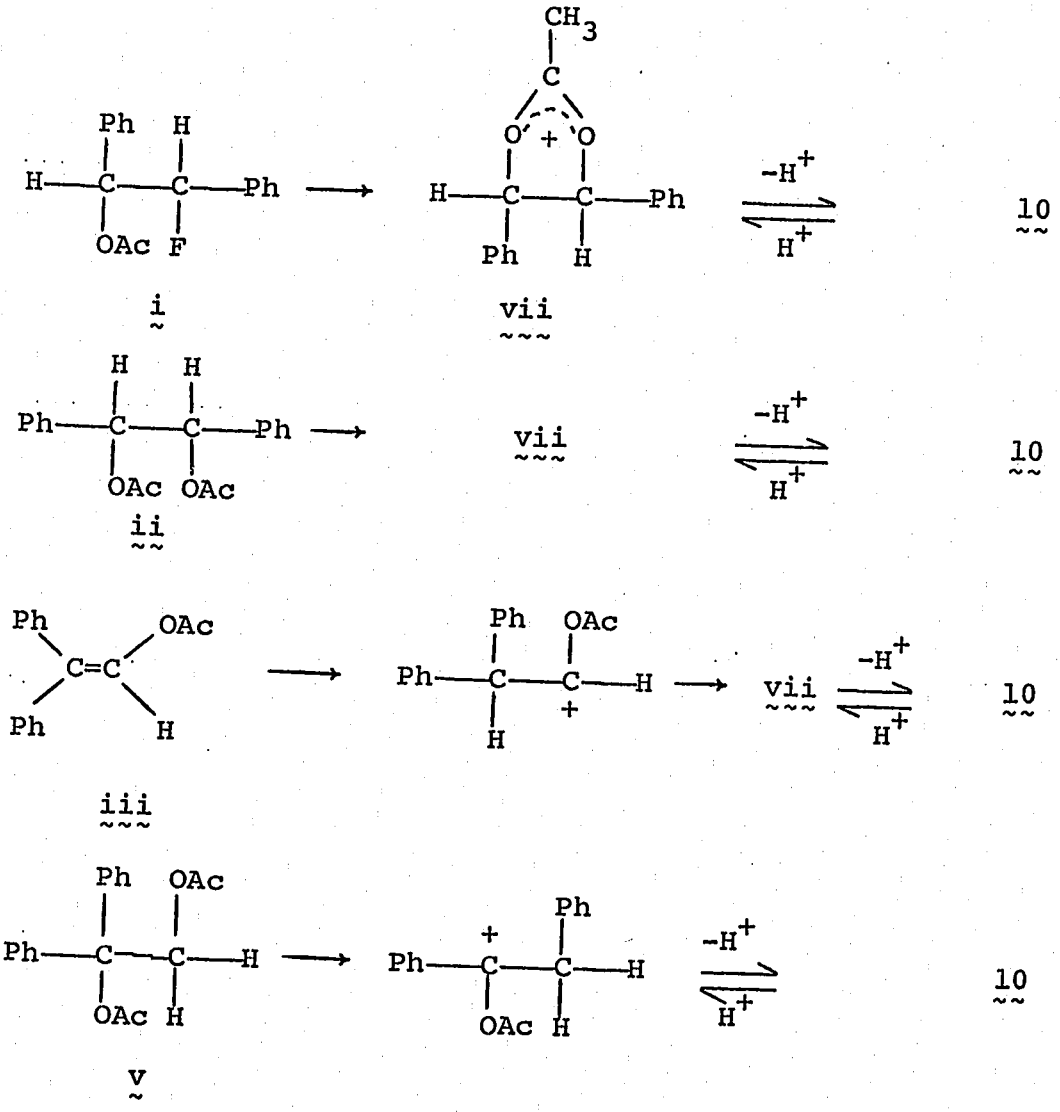
$PhCF(OAc)CH_2Ph$	$PhC(OAc)_2CH_2Ph$	$PhCH(OAc)CHFPh$
9a	9b	i
$PhCH(OAc)CH(OAc)Ph$	$PhC(OAc)=CHPh$	$Ph_2C=CH(OAc)$
ii	10	iii
$Ph_2C(OAc)CH_2F$	$Ph_2C(OAc)CH_2(OAc)$	$Ph_2CFCH_2(OAc)$
iv	v	vi

Bornstein [11] and subjected to the reaction conditions. It was found that this compound gave a 36% yield of 1,2-difluoro-1,1-diphenylethane. No deoxybenzoin was reported to have resulted from this reaction. Therefore this compound could be ruled out as a possible precursor to deoxybenzoin.

The enol acetate, 10, was prepared and subjected to the reaction conditions. No trace of deoxybenzoin or 3 was observed. Hence 10 could be eliminated as a possible precursor to deoxybenzoin. Since, on mechanistic grounds

compounds i, ii, iii, and v can yield deoxybenzoin only *via* the intermediacy of 10 or its protonated analog (see Scheme IV), these compounds can also be eliminated as the

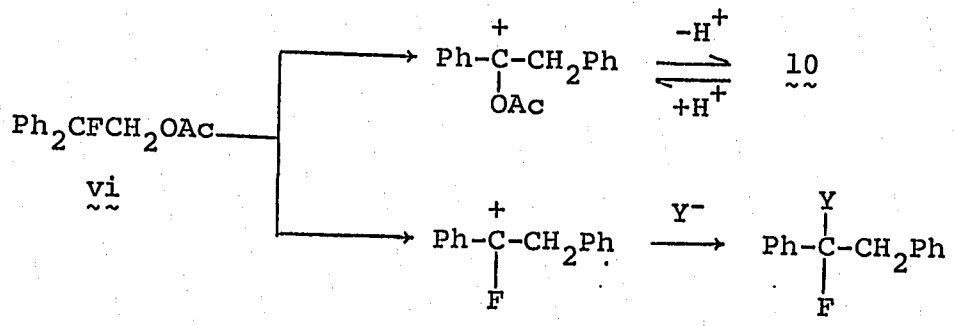
SCHEME IV



structure of the precursor. Structure vi, to yield deoxybenzoin, must proceed through the intermediacy of the

protonated form of 10 or through an intermediate that could as well yield 3 (Scheme V). Since the ratio of 3 to deoxybenzoin and its precursor remained constant throughout the course of the reaction, structure vi could also be eliminated as the deoxybenzoin precursor.

SCHEME V



Y = F 3
Y = OAc 9a

It appears that only one precursor to deoxybenzoin is involved since only one signal for it was observed in the glpc chart. Moreover, the ratio of 3 to deoxybenzoin and its precursor remained the same throughout the reaction time, also indicating that only one precursor is involved. The precursor had nearly the same retention time as deoxybenzoin indicating that it is probably 9a rather than 9b. The ir data are consistent with these observations (see Table X, page 53).

Along with the products mentioned, two very minor products were observed. These products were found to have the same retention time as 3-methyl-1,1,3-triphenylindane (11) and 1,4-difluoro-1,1,4,4-tetraphenylbutane (4). The yields of these products were estimated to be 1% and 1.5% respectively. From an experiment in which the products were isolated, 4 was obtained in a 1.5% yield.

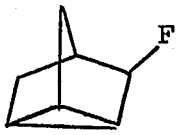
The Reaction of Norbornene with Lead Tetraacetate-Hydrogen Fluoride.

Norbornene (12) was allowed to react with the lead tetraacetate (LTA) - hydrogen fluoride (HF) reagent. A total of twelve products were isolated from the reaction. The total yield of these 12 products correspond to 101% of the starting material. Analysis of the reaction mixture by glpc using "Freon 112" as an internal standard gave the yields (based on nobornene consumed) which are listed in Table II.

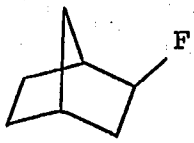
The products of the reaction were collected by preparative glpc. The structures of compounds 13, 17, and 18 were assigned by comparison of their ir spectra with those of authentic samples prepared by known pathways. An authentic sample of compound 14 was prepared by the addition of HF to 12. The compound prepared in this way had a nuclear magnetic resonance (nmr) spectrum identical to that published for compound 14.[16] Compounds 23 and 24 were isolated as a 1:3 mixture (nmr integration) from the reaction of LTA with 12 in acetic acid. The ir and nmr spectra of this mixture

TABLE II

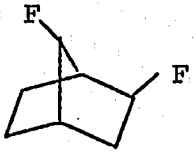
The Products and Their Yields Obtained from the Reaction of Norbornene with LTA-HF



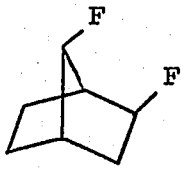
13 (10%)



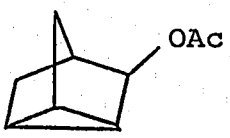
14 (1%)



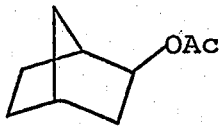
15 (13%)



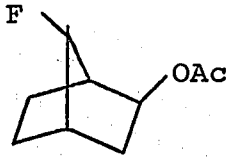
16 (39%)



17 (1.5%)



18 (0.5%)



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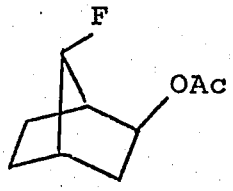

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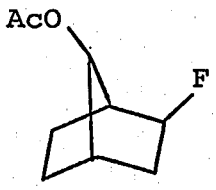
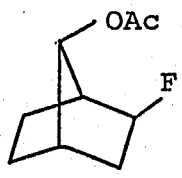
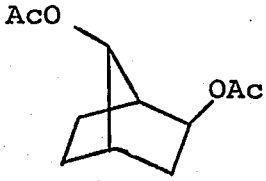


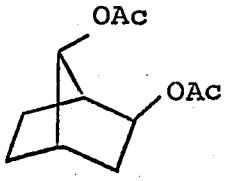
21 (1%)



22 (5%)



23



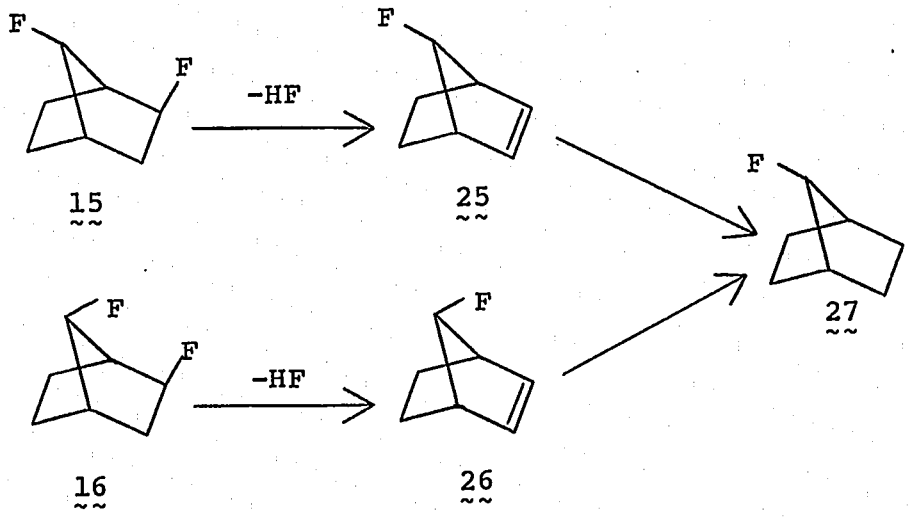
24

(9%)

were identical to those of the material, having the same retention time, isolated from the reaction of LTA-HF with 12. (For physical constants, ir, and nmr spectra of compounds 23 and 24, see Baird and Buza.[17])

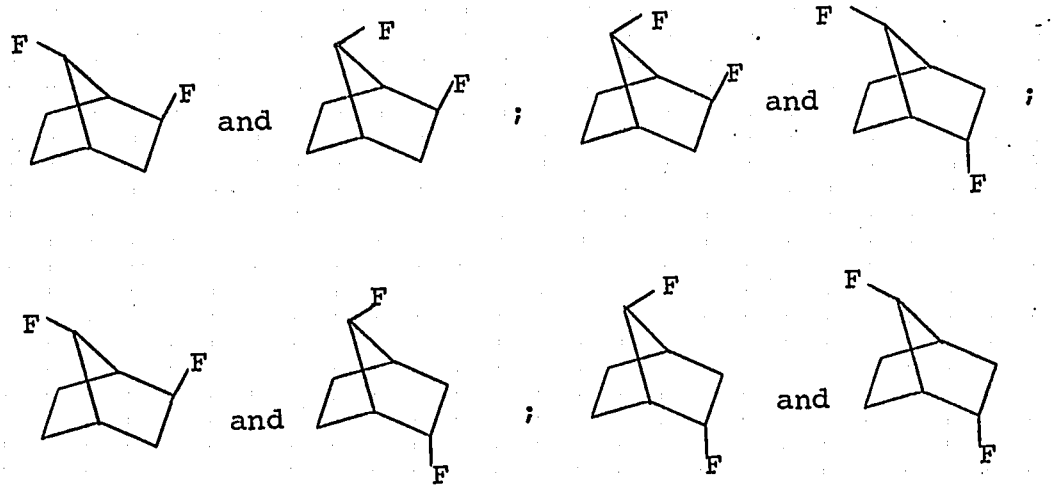
Compounds 15 and 16 were shown to be difluoronorbornanes on the basis of their microanalyses and their nmr spectra. It was evident from the integrated nmr spectra that both difluorides had two non-equivalent fluorine atoms each attached to a carbon carrying a hydrogen. The base promoted dehydrofluorination (Scheme VI) yielded two different monosubstituted norbornenes 25 and 26.

SCHEME VI



The nmr spectra of 25 and 26 both showed two vinyl hydrogens and a hydrogen attached to a carbon carrying a

fluorine, thereby establishing that compounds 15 and 16 are not vicinal difluorides. The hydrogenation of both 25 and 26 yielded the same monofluoronorbornane, 27. This firmly establishes that both 15 and 16 are 2,7-difluoronorbornanes and that compound 27 must be 7-fluoronorbornane. The stereochemistry of the substituents in compounds 15, 16, 25, and 26 could be established from their nmr spectra, and their structural assignments as well as that of 27 could likewise be confirmed spectrally. The chemical evidence demands that 15 and 16 must be one of four sets of isomeric pairs of epimeric difluorides listed below.



The nmr spectra of 15 and 16 (see Figures I and II) are compared with those of their halogenated analogs tabulated in Table III.

TABLE III

Nmr Spectral Data for 2,7-Dihalonorbornanes

Compound	τ, C_2-H	Mult.	$J_{(cps)}$	τ, C_7-H	Mult.	$W_{½(cps)}$	$J_{(cps)}$	Ref.
2-*exo*-F-7-*anti*-F (15)	5.50	d^m	58	5.01	d	5	58	
2-*exo*-Br-7-*anti*-Br	6.07	t		5.57	s	4		18
2-*exo*-F-7-*anti*-Br	5.14	d^t	52	5.81	s	4		19
2-*exo*-F-7-*syn*-F (16)	5.37	d^m	57	5.32	d	4	56	
2-*exo*-Cl-7-*syn*-Cl	6.22	m		6.18	s	4.5		14
2-*exo*-Br-7-*syn*-Br	6.10	m		6.07	s	4.5		18
2-*exo*-F-7-*syn*-Br	5.3	d^m	60	6.13	s	4		19

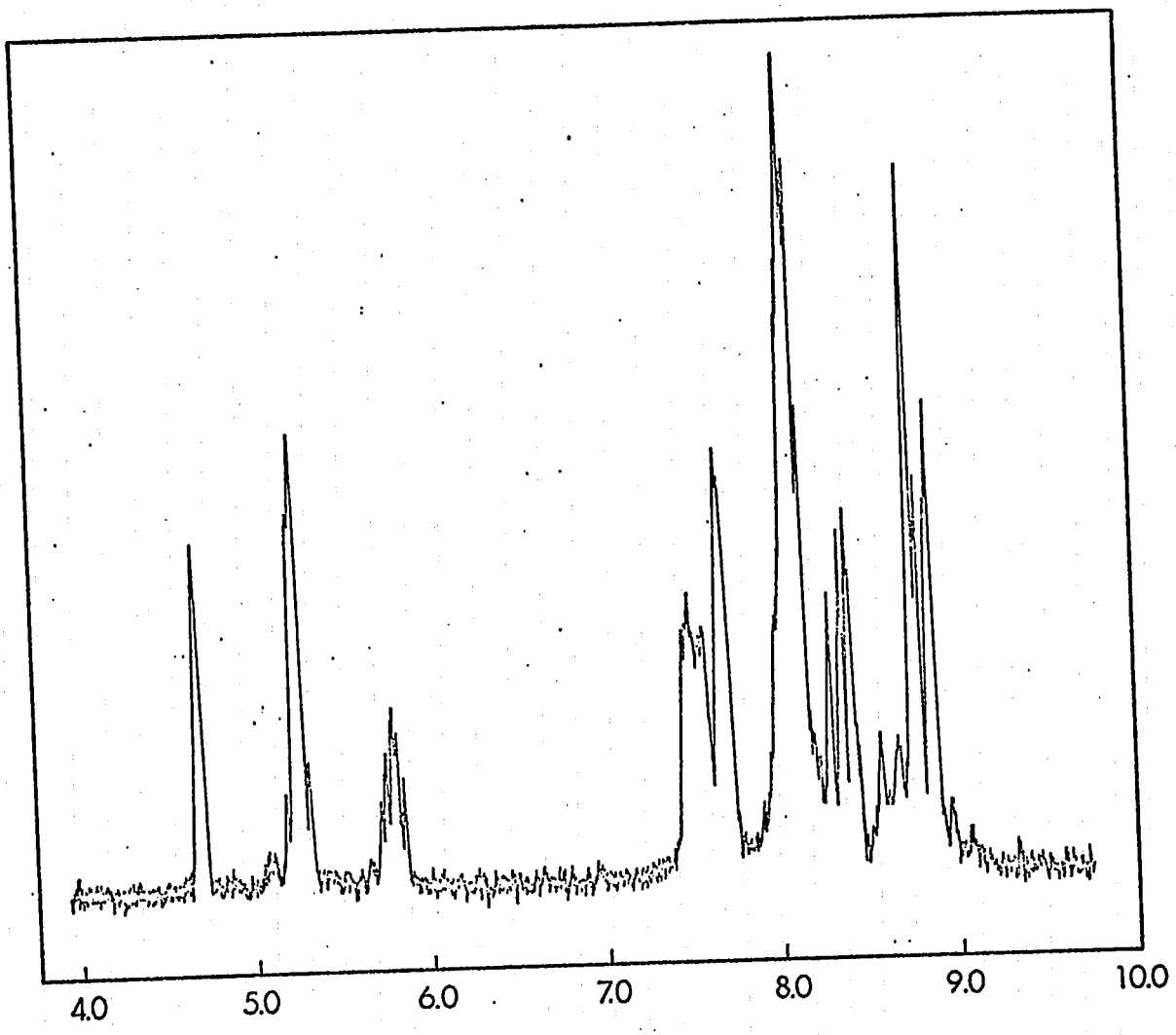


FIGURE I Nmr Spectrum of 2-*exo*-7-*anti*-difluoronorbornane in CCl_4 Solution at 100 Mc/s.

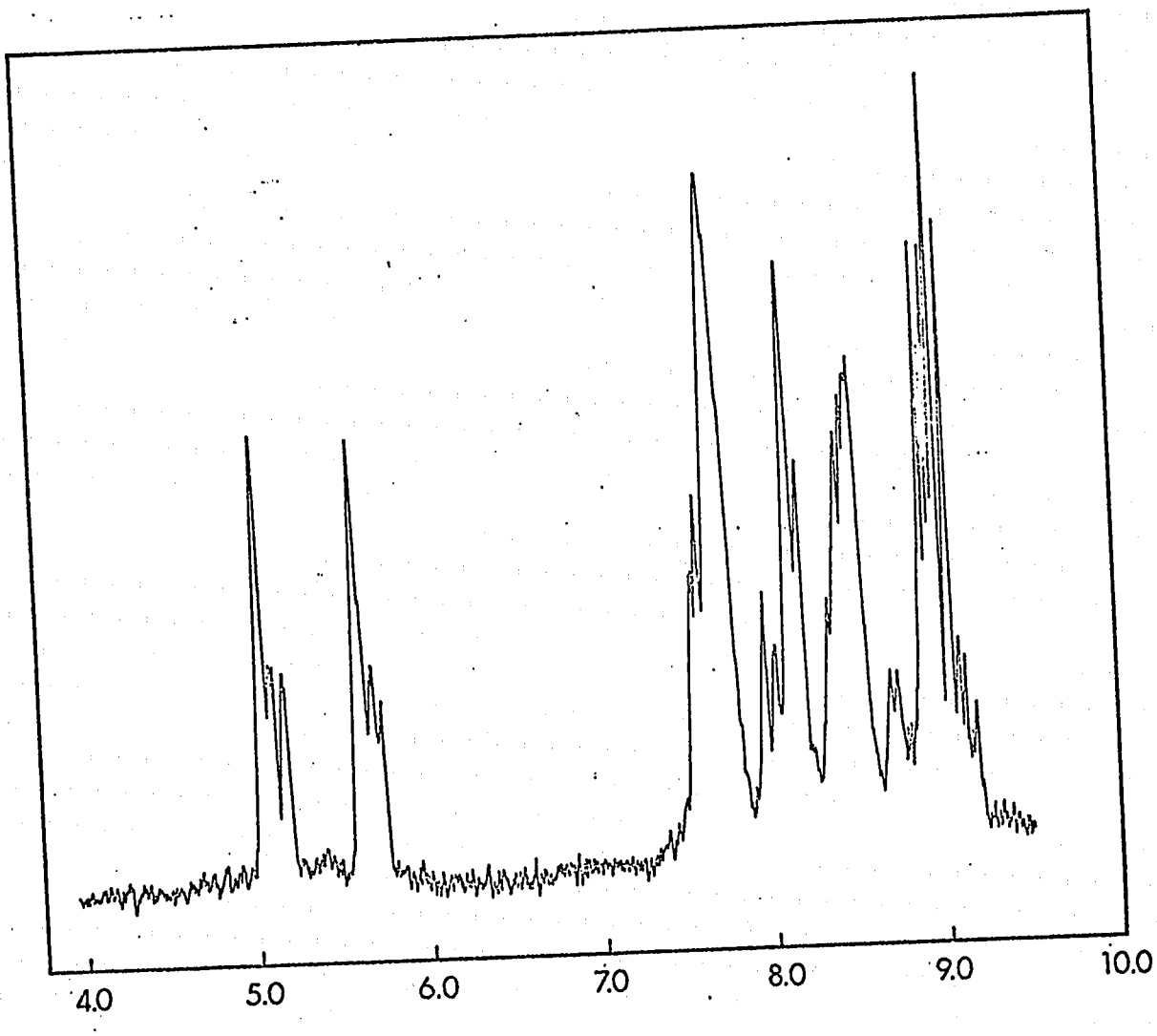


FIGURE II Nmr Spectrum of 2-*exo*-7-*syn*-difluoronorbornane in CCl_4 Solution at 100 Mc/s.

Of the two hydrogens which are geminate to the fluorine in both 15 and 16, the low field absorption can be assigned to the C-7 hydrogen by analogy with the assignments made for their halogenated analogs*.

The *endo*-C-2 hydrogen of 15 shows a large geminal coupling due to the fluorine to give a doublet (J = 58 cps), vicinal couplings due to the *exo*- and *endo*-C-3 hydrogens, a small vicinal coupling due to the C-1 hydrogen and a long range coupling due to the *anti*-C-7 fluorine (W effect) causing each branch of the doublet to appear as a multiplet. Similar couplings for the *endo*-C-2 hydrogens are seen for all the other compounds listed in Table III with the qualifications that only 15 has present the long range coupling to the *anti*-C-7 fluorine and that the large geminal fluorine coupling is present only in the compounds containing a C-2 fluorine.

Now that the stereochemistry at C-2 for both 15 and 16 had been established, an analysis of the nmr spectra of the epimeric dehydrofluorination products 25 and 26 allowed the assignment of the stereochemistry at C-7 for each difluoride. The nmr spectrum of 25 shows the C-7

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* We wish to thank Professor E. W. Warnhoff of the University of Western Ontario for making the spectra of the bromine containing analogs of 15 and 16 available to us prior to their publication.

hydrogen absorption to be centered at τ 5.82 (doublet of broadened singlets, J = 60 cps; $W_{\frac{1}{2}}$ = 4 cps). The nmr spectrum of 26 shows the C-7 hydrogen absorption to be centered at τ 5.53 (doublet of broadened singlets, J = 57 cps; $W_{\frac{1}{2}}$ = 4 cps). The shift of the C-7 hydrogen absorption to higher field in the case of 7-*anti*-fluoronorbornene (25) when compared to its epimer, 7-*syn*-fluoronorbornene (26), is expected since the C-7 hydrogen is shielded by the double bond in the case of a variety of simple *anti*-7-substituted norbornene derivatives.[20]

Further support for the stereochemical assignments of 25 and 26 was obtained from their mass spectral fragmentation patterns tabulated in Table IV. Mass spectral analysis of 26 showed a molecular ion at m/e 112. The first major fragmentation peak was at m/e 97 which corresponds to $(M-15)^+$. The same fragmentation was observed in the fragmentation of the parent hydrocarbon, norbornene.[21] In the case of 25 the molecular ion could not be seen. The mass spectrum of this compound gave as the highest fragment a peak at m/e 93 which was also the base peak. This indicates the formation of a stable ion by the loss of the fluorine atom. Presumably the loss of fluorine in 25 is assisted by the *anti*-olefinic bond analogous to the stabilization which takes place upon solvolysis of *anti*-7-norbornenyl derivatives.[22]

TABLE IV

Mass Spectral Fragmentation of the 7-Fluoronorbornenes[a]

Compound	Fragmentation Pattern (Relative Abundance)[b,c]
25	26(4), 27(11), 28(32), 29(4), 32(12), 38(3), 40(5), 41(10), 44(18), 50(4), 51(9), 52(4), 53(8), 54(3) 62(3), 63(4), 65(15), 66(15), 76(5), 77(32), 78(9), 79(19), 80(6), 81(6), 82(3), 83(7), 85(25), 91(45), 92(16), 93(100), 94(11), 95(3)
26	27(3), 28(100), 32(24), 39(5), 51(3), 77(4), 79(13), 83(4), 84(19), 91(3), 97(11), 112(7)

a Spectra obtained on A.E.I. MS9 spectrometer

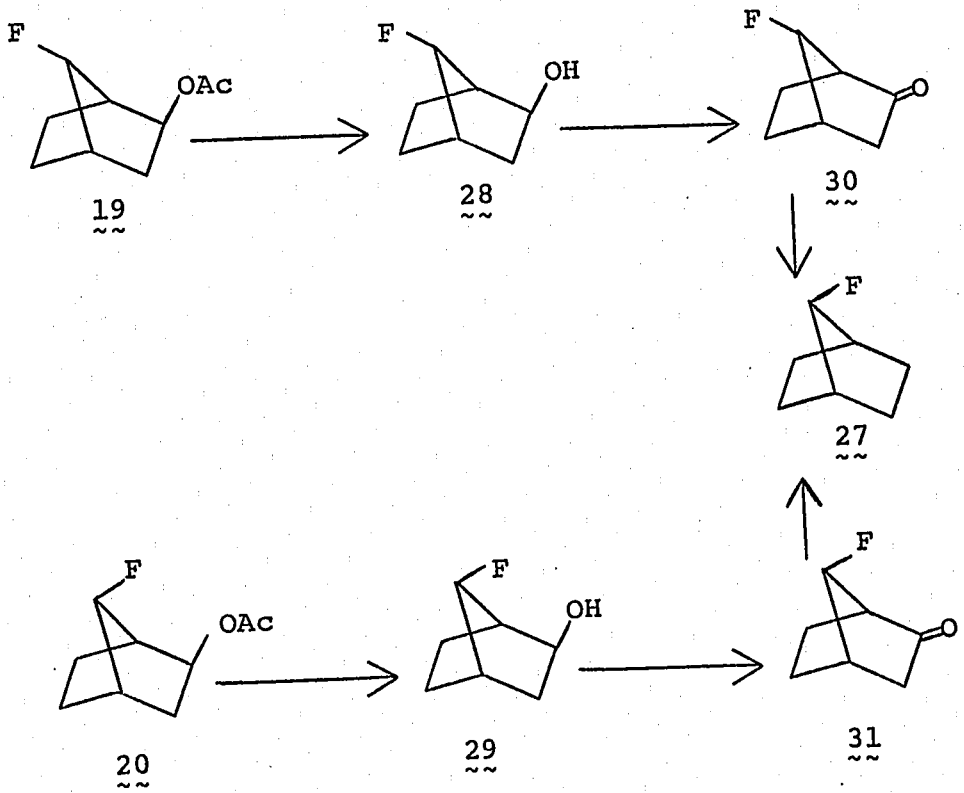
b Ionization voltage 70 ev

c Base peak is equal to 100

The fluoro acetates 19, 20, 21, and 22 could be separated and isolated with difficulty. Fluoro acetate 22 could be collected admixed with a minor amount of 21. A nmr spectrum of 22 is consistent with the structure 7-*syn*-acetoxy-2-*exo*-fluoronorbornane. By analogy with the other products found in the reaction mixture, 21 is probably 7-*anti*-acetoxy-2-*exo*-fluoronorbornane. However, these assignments must remain speculative.

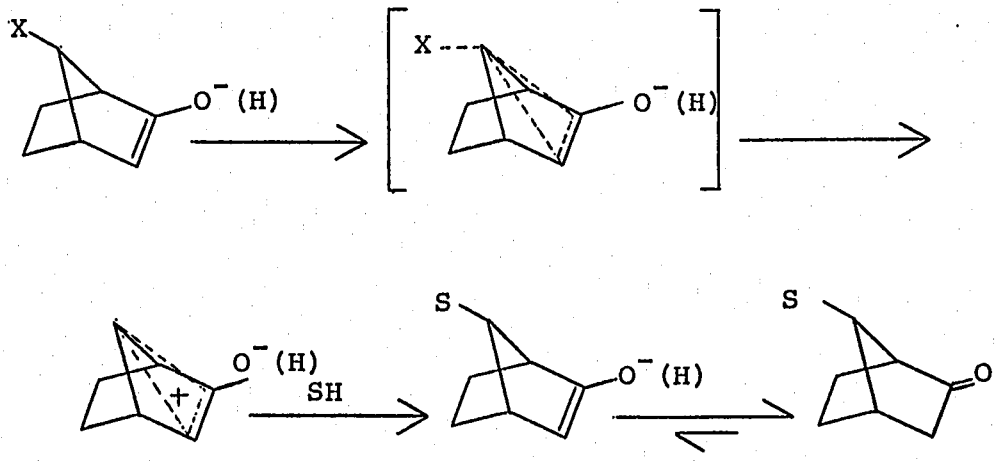
Compounds 19 and 20 were both converted to 7-fluoronorbornane (27) by the reactions shown in Scheme VII, thus establishing the structures of both to be 2-acetoxy-7-fluoronorbornanes. The sterochemistry for the two fluoro acetates was established chemically and by nmr.

SCHEME VII



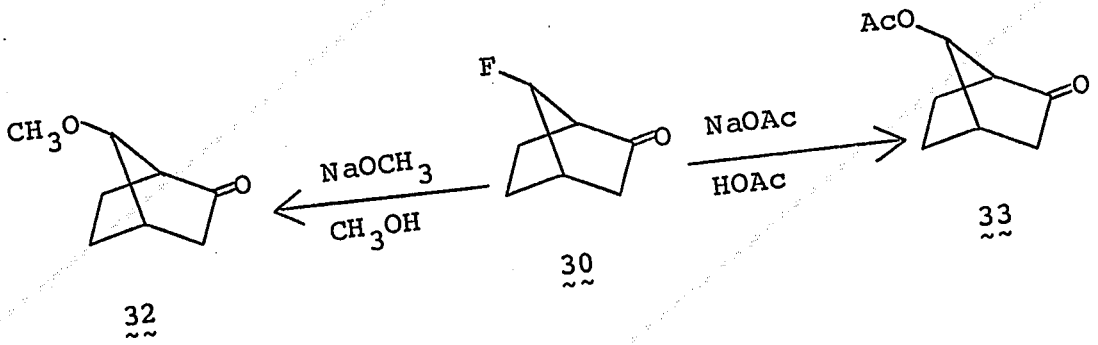
Whitham has shown that 7-*anti*-chloronorbornan-2-one is solvolysed by sodium methoxide - methanol to give exclusively 7-*anti*-methoxynorbornan-2-one while the epimeric 7-*syn*-chloronorbornan-2-one does not react under these conditions.[23] Similarly, Gassman [24] has observed a rate enhancement of 10^7 for the solvolysis of 7-*anti*-hydroxynorbornan-2-one *p*-toluenesulfonate. The sole product obtained from the ketone sulfonate solvolysis was 7-*anti*-acetoxynorbornan-2-one. In both of these reactions, presumably the enolate (enol) of the ketone is involved in assisting the departure of the leaving group from the backside as shown in Scheme VIII. This participation results in the maintenance of stereochemistry prior to nucleophilic attack by the solvent.

SCHEME VIII



When the fluoro ketone, 30, derived from 19, was subjected to solvolysis in sodium methoxide-methanol at 75° for 11 hours, a 95% yield of a single methoxy ketone (32) was obtained as shown in Scheme IX.

SCHEME IX



32 30 33

Compound 32 had the same nmr and ir spectra as those of an authentic sample of 7-*anti*-methoxynorbornan-2-one*. Compound 31 did not react when similarly treated.

When compound 30 was subjected to acetolysis in dry acetic acid at 150° for 800 hours, a single acetate was formed in 75% yield. The ir spectrum of this acetate was identical to that of 7-*anti*-acetoxynorbornan-2-one (33)*. When compound 31 was subjected to the same conditions, four

* We are indebted to Professor G. H. Whitham of Dyson Perrin Laboratory, Oxford for kindly providing us with the spectra of authentic compound 32 and to Professor P. G. Gassman of Ohio State University for kindly providing us with the ir spectrum of authentic compound 33.

roducts were formed in *ca.* 10% yield. These solvolysis reactions establish the stereochemistry of the C-7 fluorine as *anti* in compounds 19, 28, and 30, and *syn* in compounds 20, 29, and 31.

To establish the stereochemistry at the C-2 position the nmr (^{1}H and ^{19}F) spectra of the fluoro alcohols 28 and 29 were taken with and without added tris(dipivalomethanato)europium ($Eu(DPM)_3$), a paramagnetic shift reagent. The results of this experiment are tabulated in Table V.

Various workers have shown that organic compounds having function groups containing non-bonded electron pairs are able to complex with rare earth chelates. This complexing results in induced pseudocontact shifts in the nmr spectrum of the organic compound.[25] The magnitude of the observed pseudocontact shift depends upon the distance from the metal ion to the proton in the metal chelate-organic substrate complex. The closer the proton is to the coordinating groups the greater will be its pseudocontact shift. The pseudocontact shift arises only through the magnetic dipolar field effects of unpaired electrons and does not affect the bonding electron density. Thus the coupling constants are not affected as they are field invariant.

In the nmr spectra of compounds 28 and 29, the C-7 proton resonance can readily be assigned since it is the farthest downfield and is the only one showing a geminal

TABLE V

Chemical Shifts Observed for the Norbornyl Fluoro Alcohols with and without Added $Eu(DPM)_3$[a]

Compound	τ C_7-H (J_d, cps)	τ C_2-H	δ C_7-F[b] (J_d, cps)
28	5.12 (57)	6.35	210.1 (57)
28 + $Eu(DPM)_3$[c]	3.94 (57)	0.75	210.4 (57)
29	5.17 (54)	6.25	200.7 (54)
29 + $Eu(DPM)_3$[c]	4.70 (54)	1.72	199.9 (54)

(a) Spectra taken on a Varian A 56/60 Spectrometer

(b) ppm from $CFCl_3$

(c) 5% $Eu(DPM)_3$ added

fluorine coupling. When 5% $Eu(DPM)_3$ is added to CCl_4 solutions of 28 and 29, the C-7 proton resonances for each compound are shifted downfield by the magnitudes shown in Table V. The large shifts observed for the C-7 proton resonances in both these compounds establish the close proximity of the complexed alcohol function to the indicated proton and thereby establish the structure of both 28 and 29 to be 2-*exo*-norborneols.

The fluorine resonances in 28 and 29 are also affected by the shift reagent. The fluorine resonance of compound 29 is shifted downfield while the fluorine resonance of compound 28 is shifted upfield as shown in Table V. This confirms that the alcohol function is *exo* in both 28 and 29. The observed upfield shift for the *anti*-7-fluorine resonance in compound 28 is a phenomenon which is not understood at this time.

The chemical evidence obtained from the solvolysis reactions on compounds 30 and 31 combined with the nmr spectral evidence obtained from compounds 28 and 29, unequivocally establishes the structure of compound 28 to be 7-*anti*-fluoro-2-*exo*-norborneol and 19 its acylated derivative, and the structure of compound 29 to be 7-*syn*-fluoro-2-*exo*-norborneol and 20 its acylated derivative.

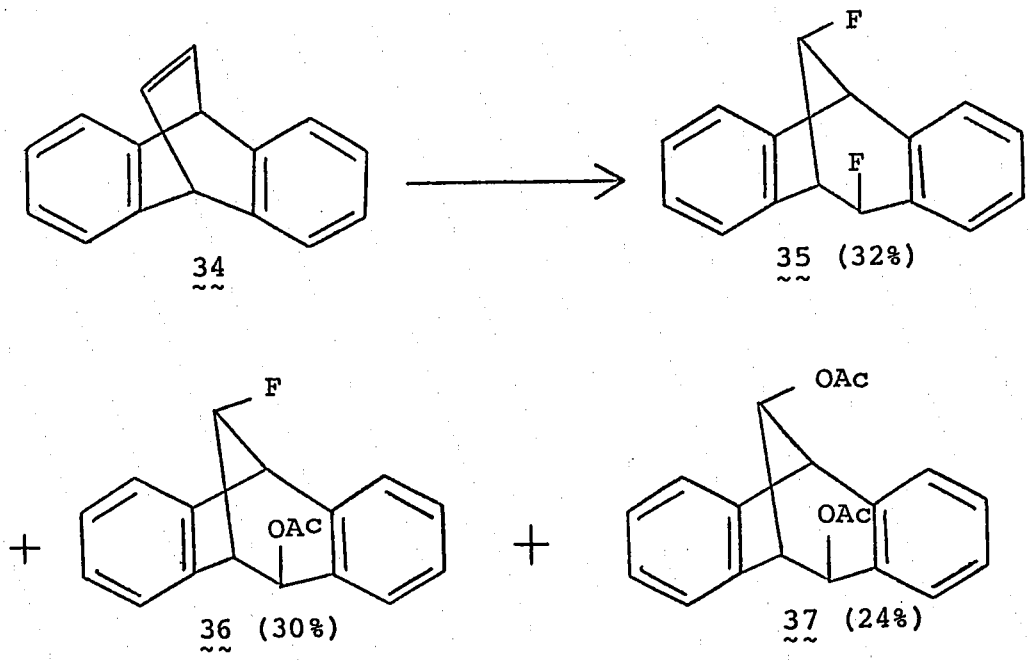
Since it is conceivable that the nortricyclyl derivatives 13 and 17 could give rise to some of the products shown in Table II, these compounds were synthesized and

subjected to the reaction conditions. Both were found to be stable.

The Reaction of Dibenzobicyclo[2.2.2]octatriene with LTA-HF

The reaction of LTA-HF with dibenzobicyclo[2.2.2]octatriene (34) gave an 86% isolated yield of the three products shown in Scheme X. The compounds were isolated by preparative thin layer chromatography.

SCHEME X



34

35 (32%)

36 (30%)

37 (24%)

Compound 37 was identified by comparing its melting

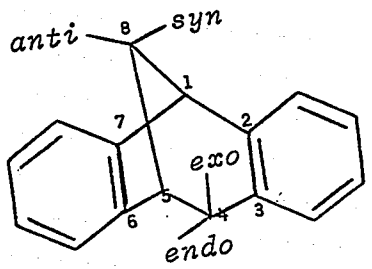
point and nmr spectrum with those reported in the literature.[26]

Compound 36 was shown to be 2-*exo*-acetoxy-8-*syn*-fluoro-dibenzobicyclo[3.2.1]octadiene on the basis of its microanalysis and its nmr spectrum. Upon inspection of the nmr spectrum of compound 36, it immediately became apparent that one was dealing with the rearranged bicyclo[3.2.1] ring system rather than with the unrearranged bicyclo [2.2.2] ring system.[27] Once it was established that one was dealing with the rearranged [3.2.1] ring system, the steric arrangement at the C-8 and C-4 positions could be established by an examination of the proton coupling constants. The observed coupling constants for a large number of 4- and 8-disubstituted dibenzobicyclo[3.2.1] octadienes are tabulated in Table VI.

The nmr spectrum of 36 shows a doublet at τ 4.32 (J = 1.5 cps) assigned to the *endo*-2 proton, a doublet of triplets at τ 4.69 (J_d = 53 cps; J_t = 5 cps) assigned to the *anti*-8 proton, a doublet at τ 6.03 (J = 5 cps) assigned to the C-5 proton, and a doublet of doublets at τ 6.42 (J = 5 cps; J = 1.5 cps) assigned to the C-1 proton. These assignments could be made by comparing the coupling constants with those tabulated in Table VI. The *endo*-2 proton should appear as a doublet since it is coupled with the C-1 proton, the magnitude of the coupling constant being 1.3 to 2.3 cps. The *anti*-8 proton should

TABLE VI[a]

Average Values for Coupling Constants for 4- and 8- Substituted Dibenzobicyclo[3.2.1]octadienes



Steric Arrangement	No. of Examples	Coupling Constants (cps)
exo-4-Substituted (*endo*-4 proton)	12	$J_{45} = 1.8 \pm 0.5$
endo-4-Substituted (*exo*-4 proton)	7	$J_{45} = 5.1 \pm 0.5$
syn-8-Substituted (*anti*-8 proton)	14	$J_{18} = J_{58} = 4.2 \pm 1.0$
anti-8-Substituted (*syn*-8 proton)	9	$J_{18} = J_{58} < 1$

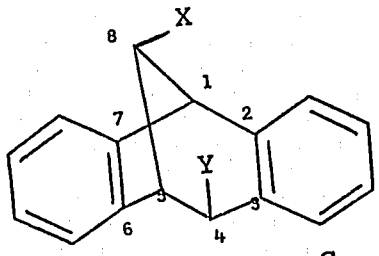
(a) Adapted from reference 26

appear as a doublet of triplets, the large coupling due to geminal H-F coupling and the small coupling due to coupling with the bridgehead protons, the magnitude of the small coupling constant being 4.6 to 5.6 cps. The C-5 proton is coupled only with the *anti*-8 proton and therefore should appear as a doublet. The C-1 proton is coupled with the *anti*-8 proton as well as with the *endo*-4 proton and therefore should appear as a doublet of doublets. The nmr spectrum of 36 compares well with those of other 2-*exo*-acetoxy-8-*syn*-halodibenzobicyclo[3.2.1]octadienes tabulated in Table VII.

Compound 35 was shown to be 4-*exo*-8-*syn*-difluoro-dibenzobicyclo[3.2.1]octadiene on the basis of its micro-analysis and its nmr spectrum. On inspection of the nmr spectrum, it again became apparent that one was dealing with the rearranged bicyclo[3,2.1] ring system. The nmr spectrum of compound 35 shows a doublet of triplets at τ 4.51 (J_d = 54 cps; J_t = 5 cps) assigned to the *anti*-8 proton, a doublet of broadened singlets at τ 4.58 (J_d = 50 cps; $W_{\frac{1}{2}}$ = 3 cps) assigned to the *endo*-4 proton, a doublet at τ 5.87 (J = 5 cps) assigned to the C-1 proton, and a doublet of multiplets at τ 6.10 (J ~ 11 cps) assigned to the C-5 proton. These assignments were made on the basis of a comparison of the observed coupling constants with those summarized in Table VI. The *anti*-8 proton should appear as a doublet of triplets. The large

TABLE VII

Proton Assignments for the *exo*-4-*syn*-8-Disubstituted Dibenzobicyclo[3.2.1]octadiene System [a,b]



Compound	Chemical Shifts (τ)[c]					J (cps)[d,e,f]
	endo 4-H	*anti* 8-H	5-H	1-H	Acetate	
X = Y = F (35)	4.58	4.51	6.10	5.87		J_{18} = 5 J_{45} small J_{4F5H} = 11
X = Y = Cl	5.12	5.36	6.31	6.10		J_{45} = 1 J_{18} = 4.4
X = Y = OAc (37)	4.26	4.68	6.15	6.01	7.94 8.12	J_{45} = 1.5 J_{18} = 5.0
X = F Y = OAc (36)	4.32	4.69	6.42	6.03	7.91	J_{45} = 1.5 J_{18} = 5
X = Cl Y = OAc	4.33	5.30	6.37	6.03	7.90	J_{45} = 1.5 J_{18} = 4.3
X = Br Y = OAc	4.36	5.23	6.33	5.97	7.86	J_{45} = 1.6 J_{18} = 4.3
X = I Y = OAc	4.47	5.31	6.39	6.06	7.90	J_{45} = 1.0 J_{18} = 3.5

(continued...)

TABLE VII (continued)

(a) With the exception of the data for compounds 35, 36, and 37, the data in this table were taken from reference 26.

(b) For purposes of simplifying this Table, all the compounds are designated as 4-substituted compounds, realizing that the numbering order changes for the acetate containing compounds.

(c) The chemical shifts for the aromatic protons are omitted.

(d) Geminal H-F coupling constants are reported in the text.

(e) The coupling constants reported for compounds 35, 36, and 37 were obtained from first order analysis.

(f) $J_{18} = J_{58}$.

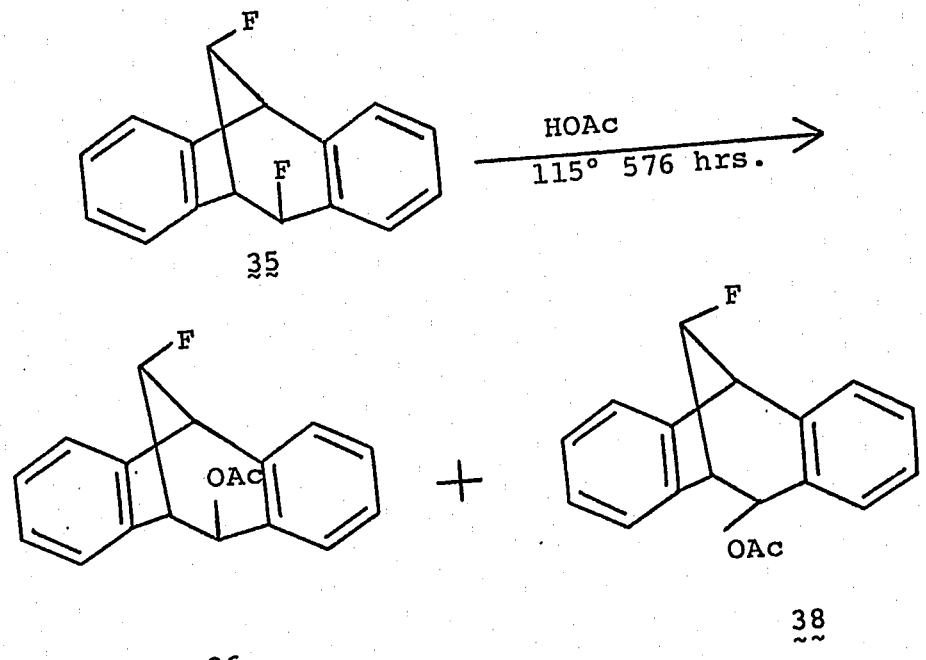
coupling is again due to geminal H-F coupling. The small coupling of 1.3 to 2.3 cps due to the C-5 hydrogen is not resolved causing each branch of the doublet to appear as a broadened singlet. The C-1 proton should appear simply as a doublet due to coupling with the C-8 hydrogen. This is observed even though each branch of the doublet shows some fine structure apparently due to coupling with the *syn*-8 fluorine. The C-5 proton appears as a doublet of multiplets since it is coupled to the *anti*-8 proton (J = 5 cps), the *syn*-8 fluorine (small), the *endo*-4 hydrogen (1.3 to 2.3 cps) and the *exo*-4 fluorine. Williamson [28] has shown that vicinal proton-fluorine spin-spin coupling is extremely dependent on the dihedral angle, the dependence being like vicinal proton-proton spin-spin coupling - a maximum at 0°, a minimum at 90°, and a maximum at 180° the values being *ca.* 31, 0, and 41 cps respectively. Since the coupling between an *exo*-4 proton and a C-5 proton in the dibenzobicyclo[3.2.1]octadiene system is 4.6 to 5.6 cps, a significant coupling between an *exo*-4 fluorine and a C-5 proton should be expected. This coupling was observed to be *ca.* 11 cps in compound 35.

The structure of 35 was further established by spin decoupling experiments. When the signal at τ 5.87 (1-H) was irradiated, the signal at τ 4.58 (*anti*-8-H) collapsed into a doublet of doublets. When the signal at τ 6.10 (5-H) was irradiated, both the signals at τ 4.58 and 4.51

(*endo*-4-H) were affected. These results are consistent with structure 35.

Solvolysis of 35 in dry acetic acid at 115° for 576 hours resulted in the displacement of the C-4 fluorine and the formation of two compounds, 36 and 2-*endo*-acetoxy-8-*syn*-fluorodibenzobicyclo[3.2.1]octadiene (38) (see Scheme XI) in a 1:2 ratio (nmr integration). The C-8 fluorine was left intact (doublet of triplets, J_d = 54 cps; J_t = 5 cps at τ 4.65 integrating for one proton). The signal due to the *endo*-2 proton in 36 was readily discernible (Table VII). The *exo*-2 proton of 38 appeared as a doublet at τ 3.73 (J = 5 cps). The nmr data are in good agreement

SCHEME XI



35

36

38

with those of the chloro and bromo analogs of compounds 36 and 38.[26] For the epimeric 8-*syn*-halo-2-*exo*- and *endo*-acetates, it was found that the *anti*-8 proton had the same chemical shift in both isomers. The *exo*-2 proton resonance (*endo* - substituted) appeared at lower field than the *endo*-2 proton resonance (*exo*- substituted). The same nmr behaviour is observed for the fluoro analogs of these compounds.

Along with the formation of compounds 36 and 38 from the solvolysis reaction, a minor amount (*ca.* 10%) of another compound was observed. The nmr data indicates that this is probably a substituted dibenzobicyclo[2.2.2]octadiene (acetate resonance at τ 8.12 - see reference 27).

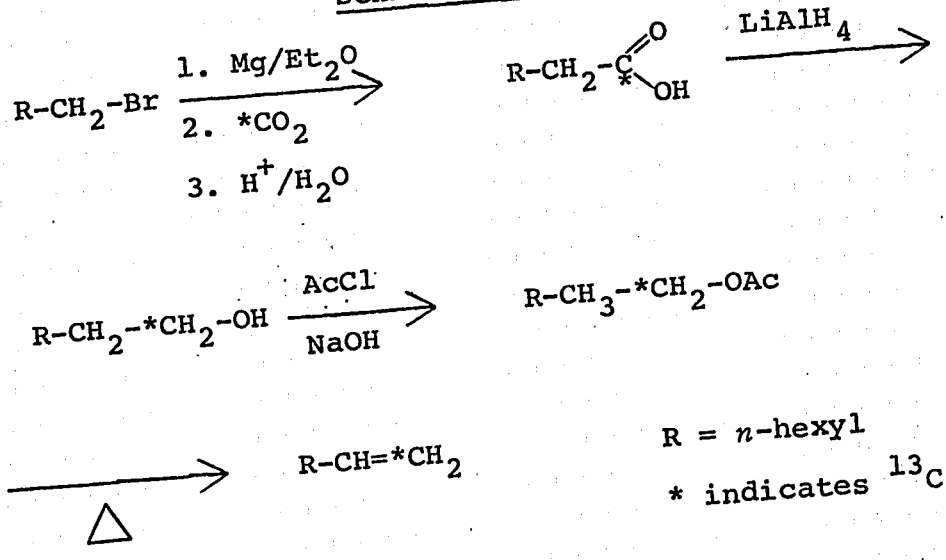
The results of the solvolysis reaction confirm that one is dealing with the rearranged dibenzobicyclo[3.2.1]-octadiene system. Had 35 been an unrearranged dibenzobicyclo[2.2.2]octadiene system it probably would not have solvolysed unless even more forcing conditions had been used. For example, it had been found that *cis*- and *trans*-7,8-dichlorodibenzobicyclo[2.2.2]octadiene were very resistant to solvolysis in acetic acid. These compounds will readily solvolyze when silver acetate is added and the mixture heated under reflux for prolonged periods.[29] On the other hand, the dichloro analog of 35 readily undergoes solvolysis in buffered acetic acid at 74.74° to give 2-*exo*- and *endo*-acetoxy-8-*syn*-chlorodibenzobicyclo[3.2.1]-

octadiene (specific rate constant varied from 16×10^{-6} sec^{-1} to 3.3×10^{-6} sec^{-1} due to the isomerization of the 4-*exo*-chloride to the less reactive 4-*endo*-chloride).[30] Under reversible conditions, solvolysis of the dibenzobicyclo[3.2.1]octadiene system leads to rearrangement to the thermodynamically more stable dibenzobicyclo[2.2.2]-octadiene system.[31] This observation could possibly explain the formation of the minor product arising from the solvolysis of 35, since the formation of HF could lead to reversible conditions in the solvolysis reaction.

The Reaction of 1-Octene and 1-^{13}C-1-Octene with LTA-HF

The synthesis of 1-^{13}C-1-octene, 39, was carried out as outlined in Scheme XII. The position of the label was confirmed by ^{13}C nmr spectroscopy (see Experimental Section). Upon reaction with LTA-HF, 39 gave a 90% yield

SCHEME XII



of seven products all in greater than 2% yield and a number of minor (<2%) products (see Figure III). Analysis of the reaction mixture by glpc using "Freon 112" as an internal standard gave the yields (based on 39 consumed) which are listed in Table VIII.

The products of the reaction mixture were isolated by preparative glpc. The molecular structure of 1-^{13}C-2,2-difluorooctane (40) was determined by comparison of its physical constants and ir spectrum with those of an unenriched authentic sample prepared by a known method.[32] The position of the label in compound 40 was determined by ^{13}C nmr spectral studies.

The proton decoupled ^{13}C nmr spectrum of the difluoride 40 shows a triplet centered at 23.25 ppm* (J = 28 cps). This indicates that the ^{13}C resonance is split by two equivalent fluorine atoms. The proton coupled ^{13}C nmr spectrum shows a quadruplet of triplets (J_q = 128 cps; J_t = 28 cps). The multiplicity and the magnitude[33] of the coupling constant indicate that there are three protons directly attached to the enriched carbon. The magnitude of the C-F coupling constant[34] indicates that the two fluorine atoms are vicinal to the labelled carbon. The ^{13}C nmr data unequivocally establish that the labelled carbon is in the C-1 position in 1-^{13}C-2,2-difluorooctane.

*Carbon-13 resonances are quoted as ppm from tetramethylsilane.

TABLE VIII

The Products and Their Yields Obtained from the Reaction of 1-^{13}C-1-Octene with LTA-HF

$RCF_2\overset{*}{C}H_3$	$R\overset{*}{C}H_2CHF_2$	$RCHF\overset{*}{C}H_2F$	$RCF(OAc)\overset{*}{C}H_3$
40 (13%)	41 (34%)	42 (6%)	43 (3%)

$R\overset{*}{C}H_2CHF(OAc)$	$RCHF\overset{*}{C}H_2(OAc)$	$RCH(OAc)CH_2(OAc)$ [a]
44 (15%)	45 (12%)	46 (7%)

R = *n*-hexyl

* indicates ^{13}C.

(a) The position of the label was not determined in this compound.

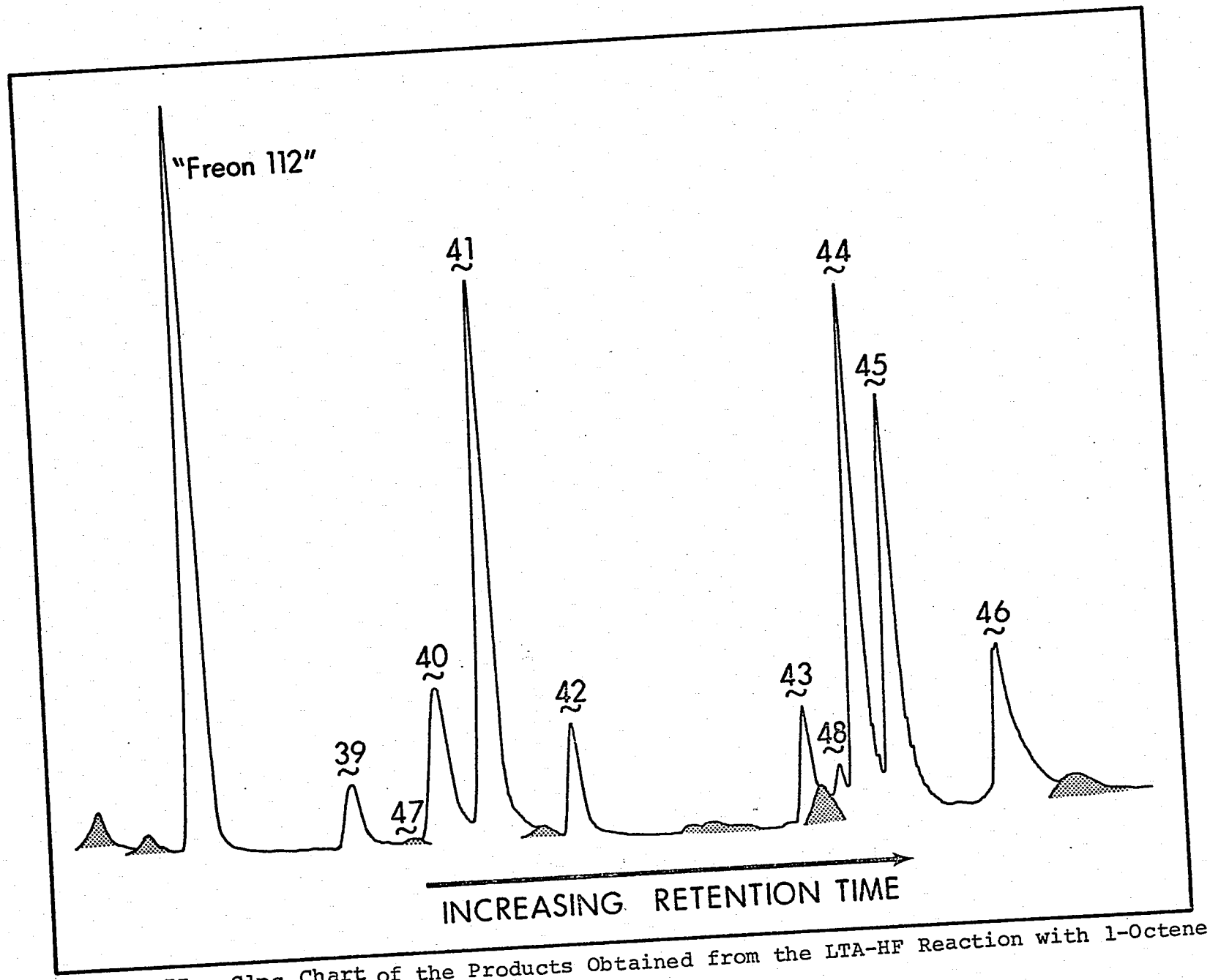


FIGURE III. Glpc Chart of the Products Obtained from the LTA-HF Reaction with 1-Octene

The molecular structure of 1-^{13}C-1-acetoxy-2-fluorooctane (45) was determined by the comparison of its ir spectrum and glpc retention time with those of the unenriched materials. The structure of the unenriched compound 45 was determined on the basis of its micro-analysis, ir spectrum, ^{1}H and ^{19}F nmr spectra, and its physical constants were compared with those reported in the literature.[35] The position of the label in the fluoro acetate 45 was determined by ^{13}C nmr spectral studies. The proton decoupled ^{13}C nmr spectrum of 45 shows a doublet centered at 65.83 ppm (J = 23 cps). The proton coupled ^{13}C nmr spectrum shows a triplet of doublets (J_t = 147 cps; J_d = 23 cps). The large coupling constant can be assigned to the ^{13}C resonance split by the two hydrogen atoms directly attached to the enriched carbon while the small coupling constant can be assigned to the ^{13}C resonance split by the fluorine atom attached to carbon vicinal to the enriched carbon. The nmr data is consistent with that of 1-^{13}C-1-acetoxy-2-fluorooctane.

An authentic sample of unenriched 1,2-diacetoxy-octane (46) was prepared by hydrogen peroxide oxidation of 1-octene in formic acid followed by acylation of the resultant diol. The ir spectrum of the compound prepared in this manner was found to be identical to that of 46 isolated from the reaction mixture.

The molecular structure of 2-^{13}C-1,1-difluorooctane (41) was determined by the comparison of its ir spectrum and glpc retention time with those of the unenriched material. The unenriched material was shown to be a difluorinated octane on the basis of its microanalysis and its ^{1}H and ^{19}F nmr spectra. The proton nmr spectrum shows a triplet of triplets centered at τ 4.29 (J = 57 cps; J = 5 cps) which integrates for one hydrogen. The large coupling constant is due to the proton resonance being split by two geminal fluorine atoms while the small coupling constant is due to the proton resonance being split by two vicinal methylene hydrogens. These observations are expected for the C-1 proton of the unenriched difluoride 41. The methylene protons in the C-2 position appear as a multiplet centered at τ 8.1. In a spin decoupling experiment, irradiation of this multiplet caused the signal at τ 4.29 to collapse into a triplet (J = 57 cps).

The ^{19}F nmr spectrum of the unenriched compound 41 shows a doublet of triplets centered at 116.37 ppm* (J_d = 57 cps; J_t = 17 cps). Since there is only one signal, it follows that both fluorine atoms must be on the same carbon. The large coupling constant is due to the fluorine resonance being split by one geminal proton.

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* Fluorine resonances quoted as ppm from $CFCl_3$.

This doublet is further split into triplets by the vicinal methylene protons. The nmr data establish the unenriched compound 41 to be 1,1-difluorooctane.

The position of the labelled carbon was determined by ^{13}C nmr spectral studies. The proton decoupled ^{13}C nmr spectrum of compound 41 shows a triplet centered at 24.41 ppm (J = 19 cps). The proton coupled ^{13}C nmr spectrum shows a triplet of triplets (J = 128 cps; J = 19 cps). This data shows that there are two protons directly attached to the labelled carbon and that there are two fluorine atoms attached to the carbon vicinal to the labelled carbon. That the two fluorine atoms are vicinal to the labelled carbon can be confirmed by inspection of the proton nmr spectrum of enriched compound 41. This shows that part of the multiplet centered at τ 8.1 is split into a doublet (J ~ 125 cps). Since compound 39 is only *ca.* 60% enriched with carbon-13, the nmr spectrum of 41 is essentially the spectrum of a 60:40 mixture of enriched and unenriched 41. If 41 had been 100% enriched, the signal at τ 8.1 would have appeared as a doublet of multiplets with J = 125 cps. However, since this compound is only 60% enriched, 60% of the multiplet is split into a doublet while 40% of the signal remains untouched. Thus the signal at τ 8.1 (due to the C-2 methylene hydrogens) is a nominal 1:1:1 triplet. The large coupling constant indicates that the labelled carbon is in the C-2 position.

The combined nmr data unequivocally establish compound 41 to be 2-^{13}C-1,1-difluorooctane.

The molecular structure of 1-^{13}C-1,2-difluorooctane (42) was determined by the comparison of its ir spectrum and glpc retention time with those of the unenriched material. The unenriched material was shown to be a difluorinated octane on the basis of its microanalysis and its ^{1}H and ^{19}F nmr spectra. The proton nmr spectrum of unenriched compound 42 shows a very broad multiplet centered at τ 5.5. This signal is tentatively assigned to the C-2 proton. The C-2 proton will be coupled with a geminal fluorine atom, a vicinal fluorine atom, and four vicinal hydrogen atoms. Since C-2 is an asymmetric center, the C-2 hydrogen could couple diastereotopically with each of the adjacent methylene protons.[36] The result would be a broad featureless signal. Overlapping this signal is a doublet of doublets of doublets centered at τ 5.62. This signal is tentatively assigned to the C-1 protons. In 1,2-difluorooctane, these protons will be coupled with a geminal fluorine atom (J = 49 cps), a vicinal fluorine atom (J = 22 cps), and a vicinal proton (J = 4.5 cps). The combined signals centered at τ 5.5 and τ 5.62 integrate for three protons confirming that one fluorine atom must be on a terminal carbon while the other is on a methylene carbon. The nmr data is consistent with an unenriched compound having the structure 42. This is

reinforced by the ^{19}F nmr spectrum.

The ^{19}F nmr spectrum of unenriched 42 shows two signals, a broad featureless multiplet centered at 189.5 ppm and a twelve line signal centered at 230.7 ppm confirming that the two fluorine atoms are on different carbons. The same arguments used to explain the multiplet in the proton nmr spectrum of unenriched compound 42 can be used to explain the multiplet in the ^{19}F nmr spectrum of unenriched compound 42. Therefore the multiplet is assigned to the C-2 fluorine resonance while the 12 line signal can be assigned to the C-1 fluorine resonance. This resonance is split into a triplet by two geminal protons (J = 49 cps) each branch of which is further split into a doublet by the vicinal proton (J = 22 cps) each branch of which is still further split into a doublet by the vicinal fluorine atom (J = 15 cps).

The position of the carbon-13 label in compound 42 can be determined by ^{13}C nmr spectral studies. The proton decoupled nmr spectrum shows a doublet of doublets centered at 84.45 ppm (J = 174 cps; J = 24 cps). The proton coupled spectrum shows 10 lines in the intensity ratio of 1:1:2:3:1:1:3:2:1:1. The carbon-13 resonance in 1-^{13}C-1,2-difluorooctane would be split into a doublet by a geminal fluorine atom (J = 174 cps) each branch of which would be further split into a triplet by the two geminal protons (J = 150 cps) each branch of which is still further

split into a doublet by the vicinal fluorine atom (J = 24 cps) leading to the observed spectrum. The combined nmr data unequivocally establish compound 42 to be 1-^{13}C-1,2-difluorooctane. The ^{13}C nmr data obtained from compounds 39, 40, 41, 42, and 45 are compiled in Table IX.

The compound, 1-^{13}C-2-acetoxy-2-fluorooctane (43) could not be isolated. The molecular structure of 43 was established primarily on the basis of the proton nmr spectrum of its unenriched analog obtained from the reaction of 1-octene with LTA-HF. One would expect the C-1 methyl resonance of unenriched 43 to be drawn downfield by the electron withdrawing groups at C-2, and to be split into a doublet by the C-2 fluorine atom. In the nmr spectrum of 43, this signal appears at τ 8.35 (J = 19 cps).

The assignment of 2-acetoxy-2-fluorooctane was further based on its ir spectrum. The ir spectrum of unenriched 43 shows a carbonyl frequency at 1770 cm^{-1} and carbon-oxygen stretching frequency at 1225 cm^{-1}. This is a shift to higher wave number for the carbonyl frequency and a shift to lower wave number for the carbon-oxygen stretching frequency when compared to the ir spectrum of 2-acetoxyoctane (see Table X). This same behaviour was seen for other geminal fluoro acetates.

Furthermore, the unenriched fluoro acetate 43 tended to decompose upon standing or when too much of it was injected onto the glpc column. The decomposition

TABLE IX

The Chemical Shifts and Coupling Constants Obtained from the ^{13}C nmr Spectra of Carbon-13 Enriched Compounds

Compound	δ ppm[a]	$J_{gem\ CF}$ cps	$J_{gem\ CH}$ cps	$J_{vic\ CF}$ cps
39	114.46		154	
40	23.25		128	28
41	24.41		128	19
42	84.45	174	150	24
45	65.83		147	23

(a) Chemical shift of the labelled carbon downfield from TMS

TABLE X

Comparison of Carbonyl and Carbon-Oxygen Stretching Frequencies for Some Substituted and Unsubstituted Acetates[a]

Compound	Carbonyl[b] Stretch, cm^{-1}	Δ[c]	Carbon-Oxygen[b] Stretch, cm^{-1}	Δ[c]
1-acetoxy-1,2-diphenyl ethane	1740	20	1240	29
1-fluoro-1-acetoxy-1,2-diphenylethane 9a	1760		1211	
2-acetoxyoctane	1735	35	1243	18
2-acetoxy-2-fluoro-octane 43	1770		1225	
1-acetoxyoctane	1740	30	1235	17
1-acetoxy-1-fluoro-octane 44	1770		1218	
1-acetoxy-2-fluoro-octane 45	1745		1230	
1-acetoxy-2,2-difluoro-octane 48	1755		1243	
1,2-diacetoxyoctane 46	1740		1225 1240	

(a) Spectra were taken as 1.5% CCl_4 solutions on 0.5 mm NaCl cells on a Perkin-Elmer 337 Grating Spectrometer;

(continued....)

Footnotes to Table X (continued)

(b) Frequencies were calibrated against the 1601.4 cm^{-1} peak of polystyrene.

(c) The difference in wave numbers between the geminal substituted and unsubstituted acetates.

product could be isolated and was shown to be 2-octanone by comparison of its ir and nmr spectra with those of an authentic sample.

The enriched fluoro acetate 43 decomposed during the course of its isolation. The decomposition product was reduced with lithium aluminum hydride and shown to be enriched 2-octanol by a comparison of its ir spectrum with that of an authentic sample of the unenriched alcohol. The ^{1}H nmr of the carbon-13 enriched 2-octanol shows a doublet of doublets centered at τ 8.83 (J = 125 cps; J = 6 cps). The large coupling constant is due to the C-1 methyl hydrogens split by carbon-13. The small coupling constant is due to the C-1 methyl hydrogens being split by the proton on the C-2 position. These nmr data establish that the labelled carbon is in the C-1 position of 2-octanol. The combined spectral data establish compound 43 to be 1-^{13}C-2-acetoxy-2-fluoro-octane.

The molecular structure of 2-^{13}C-1-acetoxy-1-fluoro-octane (44) was determined by the comparison of its ir spectrum and glpc retention time with those of the unenriched material. The unenriched material was shown to be a fluoro-acetoxyoctane on the basis of its microanalysis and its ^{1}H and ^{19}F nmr spectra. The proton nmr spectrum of the unenriched material shows a doublet of triplets centered at τ 3.77 (J_d = 56 cps; J_t = 5 cps) which integrates for one proton. The large coupling constant is due to the proton

resonance being split into a doublet by a geminal fluorine atom while the small coupling constant is due to the proton resonance being split by two methylene hydrogens. These observations are expected for the C-1 proton of the unenriched compound 44.

The ^{19}F nmr spectrum of unenriched compound 44 shows a doublet of triplets centered at 128.62 ppm (J_d = 56 cps; J_t = 17 cps). The large coupling constant is due to the fluorine resonance being split by one geminal proton while the small coupling constant is due to the fluorine resonance being split into a triplet by two vicinal methylene protons. The nmr data establish the unenriched compound 44 to be 1-acetoxy-1-fluorooctane.

The enriched fluoro acetate 44 decomposed during the course of its isolation. The decomposition product was reduced with lithium aluminum hydride and shown to be 1-octanol by a comparison of its ir spectrum with that of an authentic sample. The nmr of the carbon-13 enriched 1-octanol shows a doublet of multiplets centered at τ 8.4 (J = 125 cps). The chemical shift establishes this doublet to be due to the C-2 methylene protons in enriched 1-octanol. The large coupling constant is only seen for geminal ^{13}C-H coupling thereby showing that the label in the enriched 1-octanol is in the C-2 position. The combined nmr data establish compound 44 to be 2-^{13}C-1-acetoxy-1-fluorooctane.

The ir spectrum of compound 44 shows a carbonyl fre-

quency at 1770 cm^{-1} and the carbon-oxygen stretching frequency at 1218 cm^{-1}. This is a shift to higher wave number for the carbonyl frequency and a shift to lower wave number for the carbon-oxygen stretch frequency when compared to the ir spectrum of 1-acetoxyoctane (see Table X). It has been found that a halogen attached to a carbon atom β to the carbonyl function of a ketone shifts the carbonyl frequency to higher wave number.[37] Much the same arrangement of atoms occurs in a geminal fluoro acetate and a shift to higher wave number for the carbonyl frequency should be expected. The magnitude of this shift was found to be from 20 to 30 cm^{-1}. This shift is attributed to the effect of the geminal fluorine atom since a vicinal fluorine atom or acetoxy group has little effect on either the carbonyl frequency or the carbon-oxygen stretching frequency as shown by the last three entries in Table X although there is an appreciable shift observed for compound 48 having two fluorines on the β-carbon. These observations lend support to the argument that 1-acetoxy-1-fluoro-1,2-diphenylethane is the precursor to the deoxybenzoin formed in the LTA-HF reaction with 1,1-diphenylethylene.

From a reaction of unenriched 1-octene with LTA-HF, the minor product 2-fluoro-1-octene (47) (see Figure III) could be collected admixed with 2,2-difluorooctane (40). The yield of 47 is estimated to be less than 0.5%. The ir spectrum of this mixture had an absorption peak at 1660 cm^{-1} which is indicative of an unsymmetric olefin.[38] An nmr

spectrum of this mixture showed that olefinic hydrogens are present. It was found that 2-octene had the same glpc retention time as 1-octene under the conditions employed thereby indicating that the olefin 47 is probably not an isomerized octene. On the basis of these observations, it is concluded that compound 47 is 2-fluoro-1-octene but this assignment must remain tentative.

Also from a reaction of unenriched 1-octene with LTA-HF, the minor product 1-acetoxy-2,2-difluorooctane (48) (see Figure III) could be isolated. The yield of 48 is estimated to be about 0.5%. The proton nmr spectrum of compound 48 showed a two proton triplet at τ 5.84 (J = 12 cps) and a three proton singlet at τ 7.93. These signals can be assigned to the C-1 hydrogens and the acetate methyl hydrogens respectively. The ir spectrum of this compound (see Table X) shows the carbonyl and carbon-oxygen stretching frequencies expected for an acetate. The fluorine nmr spectrum shows a single resonance (multiplet centered at 105.35 ppm) indicating that only one type of fluorine is present. The combined spectral data are consistent with that of a compound having the structure 1-acetoxy-2,2-difluorooctane.

MECHANISTIC CONCLUSIONS

General Mechanism

Bornstein[13] had found that PbF_4 did not react with olefins unless glacial acetic acid was present. Prior to this work, it has been assumed that PbF_4 was the sole fluorinating agent in the LTA-HF reaction. Bornstein et al suggested that the active fluorinating agent in the LTA-HF reaction was $PbF_2(OAc)_2$. They had shown that this reagent is formed in the methathesis of PbF_4 with acetic acid and that this reagent does fluorinate olefins. However, there is still some doubt that this is the sole fluorinating agent or that this reagent leads to oxygen containing products since the formation of deoxybenzoin was not reported. The formulation $PbF_n(OAc)_{4-n}$ is the preferred formulation for the reagent since it is likely that due to the rapid metathesis of this compound, all of the lead species from n = 0 to n = 4 are present in the reaction mixture. The generalized formula will be used in the remainder of this work.

A generalized mechanism can be proposed to rationalize the formation of the products obtained from the various olefins studied (see Scheme XIII).

The first step of the reaction is the formation of a transient lead-ligand addition product, 50.

SCHEME XIII

$$R'HC{=}CHR'' + PbF_n(OAc)_{4-n} \longrightarrow [R'YCH{-}\underset{\underset{PbX}{|}}{C}HR'']$$

49 50

$$[50] \longrightarrow R'YCH{-}\underset{\underset{Z}{|}}{C}HR'' \quad (1)$$

51

$$[50] \longrightarrow {}^{+}YCH{-}CHR'R'' \xrightarrow{Z^{\ominus}} YCH(Z){-}CHR'R'' \quad (2)$$

52 53

$$[50] \longrightarrow {}^{+}R'YC{-}CH_2R'' \xrightarrow{Z^{\ominus}} R'YC(Z){-}CH_2R'' \quad (3)$$

54 55

$$[50] \longrightarrow R'YC{=}CHR'' \quad (4)$$

56

Y = F or OAc

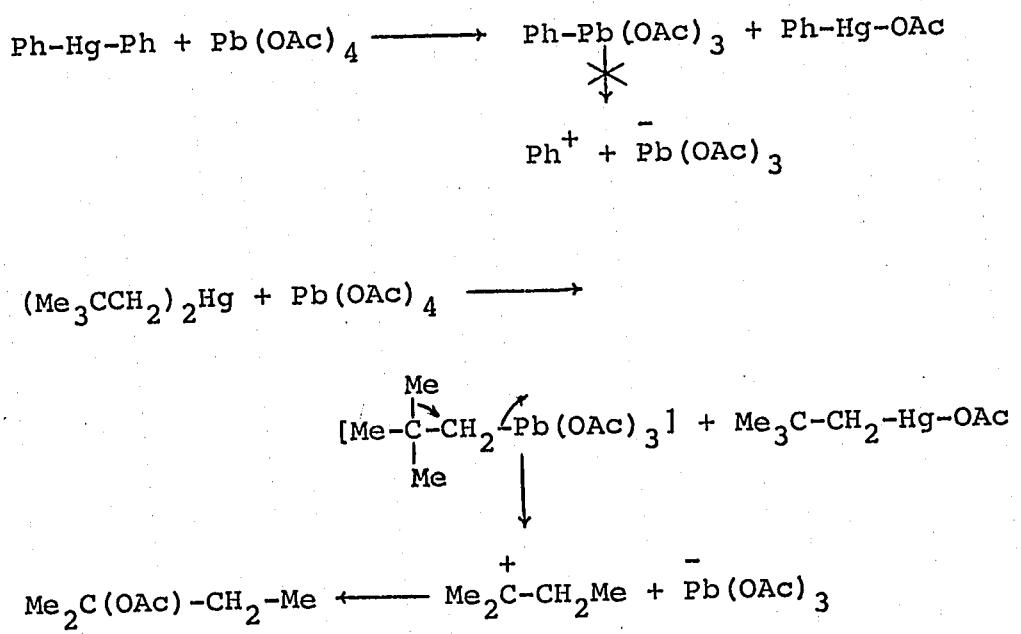
Z = a nucleophile

X = $F_m(OAc)_{3-m}$ where m = 0-3.

Metal-ligand addition products of the type represented by 50 are well documented as intermediate species in the reactions of thallic acetate [39], thallic nitrate [40], and mercuric acetate [41] with olefins and have been suggested, but not isolated, as intermediates in the reaction of lead tetraacetate [42] with olefins. In the case of lead-ligand adducts, it appears that the electron affinity of the quadricovalent lead is such that heterolysis cannot be prevented unless an exceptionally unfavourable carbonium ion results. Such a case is illustrated by phenyllead triacetate.[43] This compound can readily be isolated from the metathesis of LTA with diphenylmercury. However, when this same reaction is carried out with dineopentylmercury, the lead intermediate could not be isolated. Instead, 2-acetoxy-2-methylbutane and lead diacetate were isolated. The organic product strongly suggests that a carbonium ion mechanism is involved and may be depicted as shown in Scheme XIV.

The transient lead-ligand intermediate 50 can undergo a number of reactions. These are represented by equations 1-4 in Scheme XIII. All of these pathways will be discussed individually when applicable with respect to each of the olefins studied.

SCHEME XIV



Equation 1 represents a direct displacement of the lead species by a nucleophile. This pathway can be used to rationalize the formation of the dimeric product isolated from the LTA-HF reaction with 1,1-diphenylethylene and the formation of 1,2-difluorooctane and 1-acetoxy-2-fluorooctane isolated from the reaction of LTA-HF with 1-octene.

Equation 2 shows heterolysis of the lead-carbon bond with concomitant migration of an alkyl or aryl group or a carbon bond to leave the cationic species 52. This intermediate is then attacked by a nucleophile to give

structure 53. This pathway can be used to rationalize the formation of the 1,1-disubstituted products isolated from the 1,1-diphenylethylene and 1-octene systems and the formation of the 2,7-disubstituted products isolated from the norbornene system as well as the formation of the rearranged disubstituted products isolated from the LTA-HF reaction with the dibenzobicyclo[2.2.2]octatriene system.

Equation 3 shows heterolysis of the lead-carbon bond with coincident migration of a hydrogen to leave the cationic species 54 which is then stabilized by attack of a nucleophile to yield structure 55. This pathway may be the one responsible for the formation of the 2,2-disubstituted products isolated from the reaction of LTA-HF with 1-octene, however, this process cannot be distinguished from an elimination-readdition process in this system.

Equation 4 shows heterolysis of the lead-carbon bond with coincident loss of a proton to yield a new olefin having the structure 56. Olefin 56 could then react further with $PbF_n(OAc)_{4-n}$ to yield a new lead-ligand addition product analogous to the intermediate 50. This new intermediate could then undergo the same reactions represented by equations 1-4. This pathway can be used to rationalize the formation of 1-acetoxy-2,2-difluoro-octane isolated from the LTA-HF reaction with 1-octene. The new olefin 56 formed by this pathway could also add HF or acetic acid to yield the 2,2-disubstituted products

isolated from the reaction of LTA-HF with 1-octene. These possibilities will be discussed in connection with the 1-octene system.

The lead-carbon bond could also homolyze to give a free-radical species such as that proposed by Bornstein.[11] A reaction pathway of this type had also been proposed in the LTA oxidation of olefins.[42b, 44] The preponderance of products arising from carbon skeleton rearrangement in the LTA-HF reaction with the olefins studied, requires that a cationic species is involved as an intermediate leading to product formation. However, this observation in itself does not completely rule out a homolytic pathway. If homolysis takes place, the free-radical formed could be oxidized by Pb^{IV} giving a cationic species as shown in Scheme XV. Interconversions of this type have been reported to be facile.[42b,45] A mechanistic pathway of

SCHEME XV

$$Pb^{IV} + R^{\cdot} \longrightarrow R^{+} + Pb^{III}$$

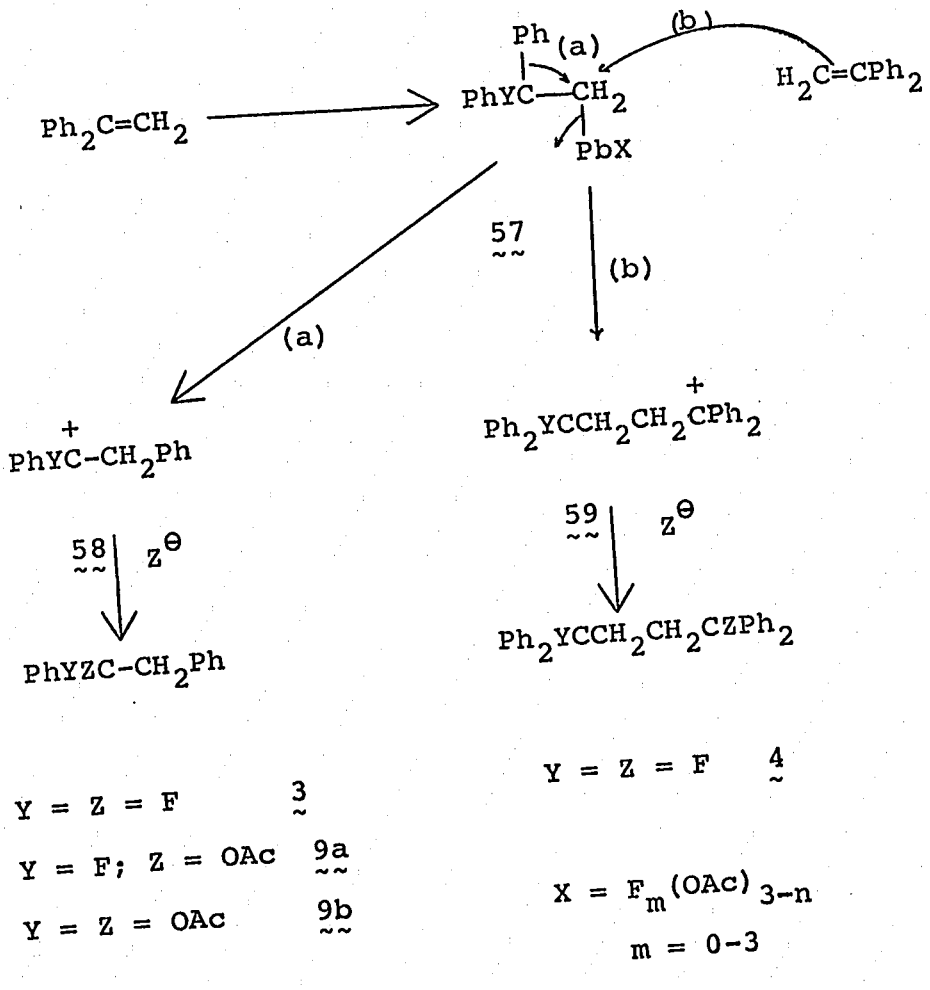
$$2\ Pb^{III} \longrightarrow Pb^{II} + Pb^{IV}$$

this type can be ruled out in the dibenzobicyclo[2.2.2]-octatriene system and will be further discussed in connection with this system.

A Mechanism for the Reaction of LTA-HF with 1,1-Diphenylethylene

The mechanism which best explains the product formation in the 1,1-diphenylethylene system is shown in Scheme XVI. The first step of the reaction is the formation of

SCHEME XVI



the transient lead-ligand intermediate 57. This intermedi-

ate is depicted as arising from Markovnikov addition of lead and a ligand across the double bond where the lead species is the electrophile. This is analogous to the reaction of mercuric acetate with styrene in methanol solvent in which (2-methoxy-2-phenylethyl)mercury acetate (60) was the sole isolated addition product.[46] The synthesis of highly substituted alcohols from the addition of mercuric acetate to olefins followed by sodium borohydride reduction is based on the regiospecificity of this reaction.[47] Similarly, when styrene is treated with thallium triacetate in methanol at 0°[48], (2-methoxy-2-phenylethyl)-thallium diacetate (61) was formed in quantitative yield again showing Markovnikov addition. Intermediate 57 readily explains the formation of all observed products.

$PhCH(OMe)CH_2$-Hg-OAc $PhCH(OMe)CH_2$-$Tl(OAc)_2$

60 61

Products which could arise from anti-Markovnikov addition, for example, 1,2-difluoro-1,1-diphenylethane were not observed.

The intermediate 57 may react further by the two pathways shown in Scheme XVI. Pathway a shows heterolysis of the lead-carbon bond with concomitant phenyl migration to yield the carbonium ion 58. Ion 58 if attacked by a nucleophile may yield the compounds 3, 9a and 9b. Alternatively, pathway b shows nucleophilic dis-

placement of the lead species by another olefin to give the ion 59 which can then be attacked by a nucleophile to yield the dimer 4. This pathway could as well have given rise to 1-acetoxy-4-fluoro-1,1,4,4-tetraphenylbutane or 1,4-diacetoxy-1,1,4,4-tetraphenylbutane. However, since it would be expected that these compounds would have formed in *ca.* the same or lower yield than 4 (1.5%), no attempt was made to identify these products.

At low temperature, the dimer 1,4-difluoro-1,1,4,4-tetraphenylbutane is predominantly formed. A tentative rationalization can be that the carbon-lead bond is a tentative rationalization can be that the carbon-lead bond does not undergo heterolysis at lower temperatures and the reaction only proceeds by nucleophilic displacement, in this case the olefin acts as the nucleophile.

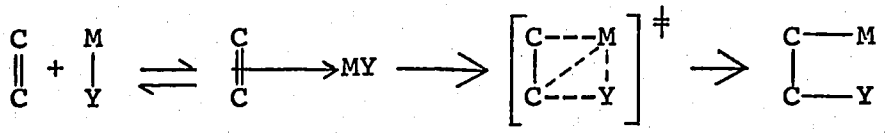
The formation of a small amount of 3-methyl-1,1,3-triphenylindane undoubtedly arises from the acid catalysed dimerization of 1,1-diphenylethylene. The indane is synthesized in this manner.[49]

A Mechanism for the Reaction of LTA-HF with Norbornene

The oxidation of the bicyclic olefin, norbornene, 12, has been used as a mechanistic probe to elucidate the mechanism and stereochemistry of oxymercuration [41a], thallic acetate [39a], and lead tetraacetate [42a] oxidation reactions. It is possible from the identification of the oxidation products to differentiate between the possible mechanistic pathways leading to products, i.e., 1) a

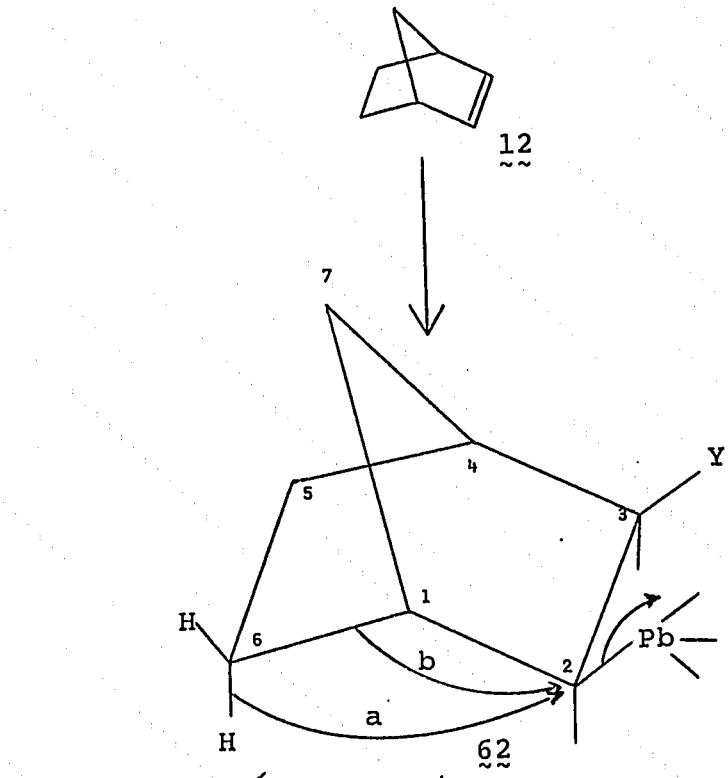
concerted *cis*-molecular addition, 2) a free radical oxidation or, 3) a reaction pathway proceeding *via* cationic intermediates.

The products isolated from the reaction of 12 with LTA-HF can best be rationalized by the mechanism shown in Scheme XVII. The first step of the reaction is the formation of a *cis-exo* addition product (62) of a lead species and a ligand across the double bond. Stable *cis-exo* metal-ligand addition products analogous to 62 have been isolated from oxythallation [39a] and oxymercuration [41a] reactions with 12. To account for this behavior, Traylor[41c] suggests that in the case of strained rigid olefins (e.g. bicyclo[2.1.1]hexyl, bicyclo[2.2.1]heptyl and bicyclo-[2.2.2]octyl) metal salts add to the double bond by a concerted pathway. These *cis* additions are explicable in terms of two factors. (1) The metal salt has a tendency to simultaneously bind the olefin and another nucleophile. This is depicted below.



(2) The geometrical restrictions of the olefin may retard the rate of *trans* addition without greatly affecting the rate of *cis* addition. It is unlikely that an open carbonium ion pathway is used since the addition products always have the *cis - exo* geometry.

SCHEME XVII



Y = F 13

Y = OAc 17

Y = Z = F 16

Y = Z = OAc 24

Y = F; Z = OAc 20

Y = OAc; Z = F 22

Y = Z = F 15

Y = Z = OAc 23

Y = F; Z = OAc 19

Y = OAc; Z = F 21

Since all of the disubstituted products isolated from the LTA-HF reaction with 12 are rearranged 2,7-disubstituted norbornanes, and since no free-radical rearrangements in this system have been reported at ordinary temperatures [50], the mechanistic pathway leading to products must be a cationic one. If homolysis of the lead-carbon bond takes place, it must be rapidly followed by an oxidation step of the type shown in Scheme XV. The cationic species thus formed can then undergo rearrangement. On the other hand, heterolysis of the lead-carbon bond can lead directly to the products *via* the pathways shown in Scheme XVIII. A clear distinction between these two possible pathways cannot be made in this system. However, evidence against this process can be obtained from the LTA-HF reaction with dibenzobicyclo[2.2.2]-octatriene.

Pathway a leads to the formation of nortricyclyl-fluoride (13) and nortricyclylacetate (17). The formation of nortricyclyl products has precedence since ionic additions to norbornene generally lead to significant amounts of substituted nortricyclenes.[51]

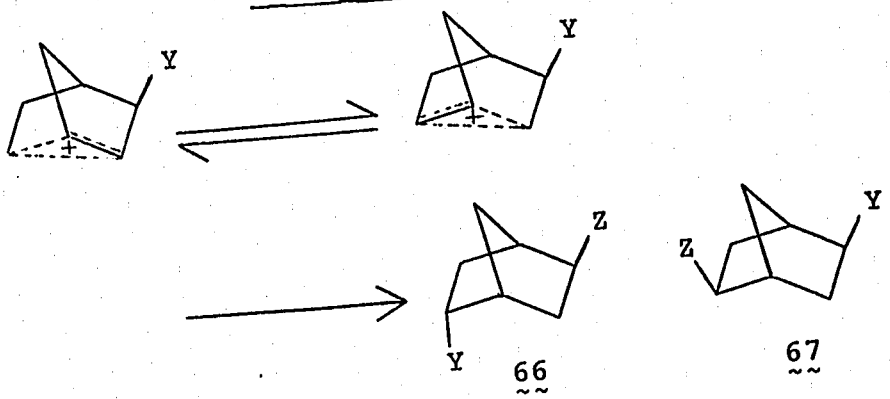
Since cyclopropyl systems have been shown to react with LTA [52] and thallic acetate [53] and have very recently been shown to react with LTA-HF [54], it became important to determine whether the nortricyclyl products were stable under the reaction conditions. Independent experiments

determined that both of these compounds were stable.

Pathway b, by assisted heterolysis of the lead-carbon bond leads to the norbornyl cation 63, which can be attacked by a nucleophile at the carbon carrying the greatest share of the positive charge (that is, at the carbon furthest removed from the electronegative substituent). This results in the formation of the 7-*syn*-2-*exo*-disubstituted norbornanes 16, 20, 22, and 24. Alternatively, cation 63 can undergo a competitive 6,1-hydride shift to give cation 64, which upon nucleophilic attack at the more positively charged center (that is again at the carbon furthest removed from the electronegative substituent) will yield the 7-*anti*-2-*exo*-disubstituted norbornanes 15, 19, 21, and 23. The 6,1-hydride shift has been established as leading to products in a number of ionic additions of norbornene.[18,19]

Cation 63 could also conceivably undergo a 6,2-hydride shift leading to the products shown in Scheme XVIII. Compounds having the structures 66 and 67 have recently been

SCHEME XVIII



isolated from the bromination reaction of 12.[19] However, the 6,2-hydride shift would not be as facile as the 6,1-hydride shift in this system, since the electronegative character of Y destabilizes any positive charge at the C-2 center inhibiting the 6,2-hydride shift as well as inhibiting nucleophilic attack at this center. The failure to find any products analogous to the structures 66 and 67 as well as the failure to find any 2,3-disubstituted norbornanes (which would arise from nucleophilic attack at C-2 in cations 63 and 64) supports this postulate.

The reaction of LTA with 12 in acetic acid yields only three products, namely 17, 23, and 24. Similarly, when the thallic acetate adduct to 12 [39a] is dissolved in acetic acid the same three products were formed. It is interesting to note that the two nortricyclyl products and the eight 2,7-disubstituted products obtained from the LTA-HF reaction with 12 could all be derived from 17, 23, and 24 by maintaining the same stereochemistry but by using every possible combination of fluorine and acetate substitution. These analogies lend substantial support to the postulate that the LTA-HF reaction goes *via* the initial formation of the adduct 62.

The formation of a minor amount of 2-*exo*-fluoronorbornane (14) probably arises from the addition of HF to 12 since 14 was synthesized in this manner. Similarly the formation of 2-*exo*-norbornylacetate, 18, is probably

formed by an acid catalyzed addition of acetic acid to the double bond of 12.

A Mechanism for the Reaction of LTA-HF with Dibenzobicyclo-[2.2.2]octatriene

This system was chosen because a study of the product formation offered the possibility to be able to distinguish between a heterolytic lead-carbon bond cleavage and a homolytic lead-carbon bond cleavage followed by a facile oxidation step to give a cationic species.

The dibenzobicyclo[2.2.2]octatriene system has been used as a diagnostic system for carbonium ion rearrangement.[55] Free-radical additions to this system yield 7,8-disubstituted dibenzobicyclo[2.2.2]octadienes while a carbonium ion mechanism yields 4,8-disubstituted dibenzobicyclo[3.2.1]octadienes. Recently a free-radical addition reaction on this system has been reported[56] which was reported to lead to both unrearranged and rearranged products. The stereochemistry of the rearranged free-radical products obtained were either 8-*syn*-4-*endo*-disubstituted or 8-*anti*-4-*exo*-disubstituted compounds. The products obtained from kinetically controlled ionic addition to the double bond of 34 are invariably 8-*syn*-4-*exo*-disubstituted compounds. Free-radical rearrangement products could only be observed at high temperatures (>100°) and at low concentrations of transfer reagent. It does

not seem probable that any free-radical rearrangement could take place in this system under the conditions employed in the LTA-HF reaction (0° and a 1:1:3 mole ratio of substrate and reagents). However, some reservations must be expressed on this point.

The mechanism which best explains the products obtained from the LTA-HF reaction with 34 is shown in Scheme XIX. Again the first step of the reaction is the formation of the *cis*-lead-ligand addition product 68. The rearranges in a geitonodesmic manner [31,57*] to yield the observed products. If the mechanism follows the concerted pathway, only the *syn-exo* products can be formed. If the mechanism follows the stepwise pathway, the *exo* product is produced by kinetic control. It is possible to accommodate the formation of *exo* (pseudoaxial) products by the assumption of stereoelectronic factors favoring the formation of quasiaxial over quasiequatorial bonds.[29,31,58] Torsional strain effects offer an alternative explanation for *exo*-attack being favoured over *endo*-attack.[59]

The exclusive formation of 8-*syn*-4-*exo*-disubstituted products requires a geitonodesmic reaction which in turn

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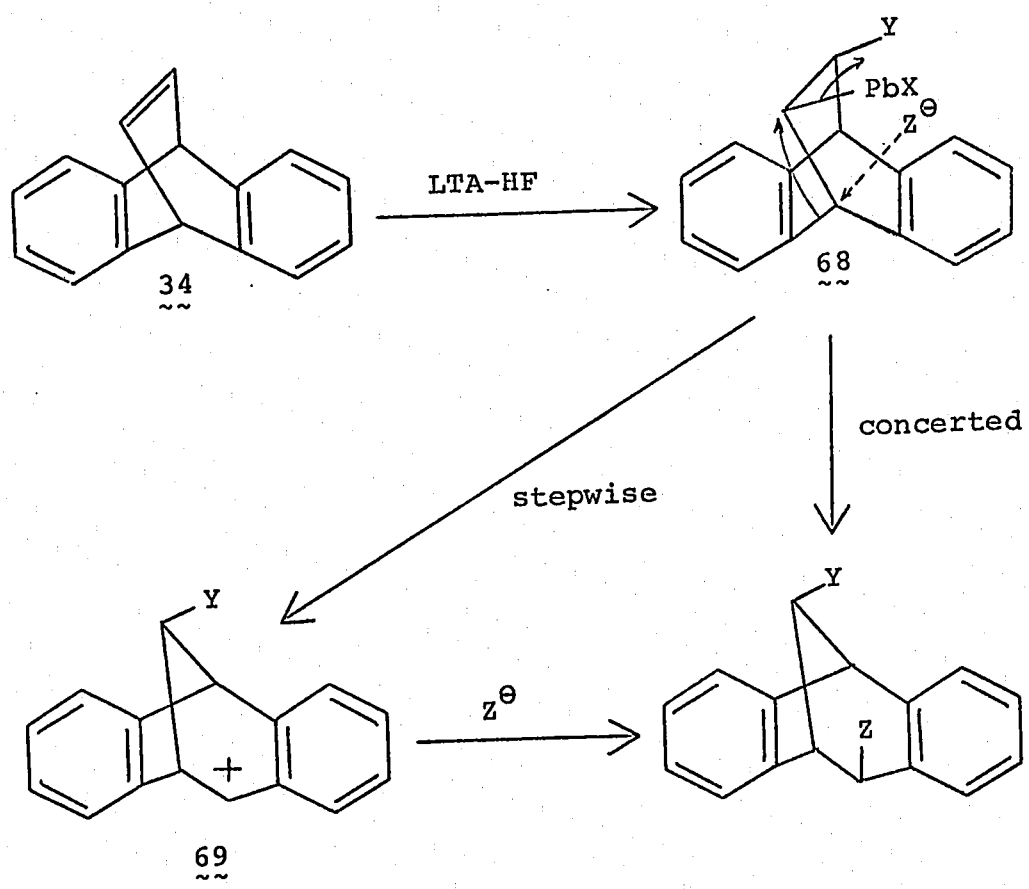
* A geitonodesmic reaction has been defined as one in which a reagent attacks a cation at an atom neighbouring the cationic center with coincident migration of the *anti* bond to the cationic center.

SCHEME XIX



34 68 69

Y = Z = F 35

Y = Z = OAc 37

Y = F; Z = OAc 36

$X = F_m(OAc)_{3-m}$

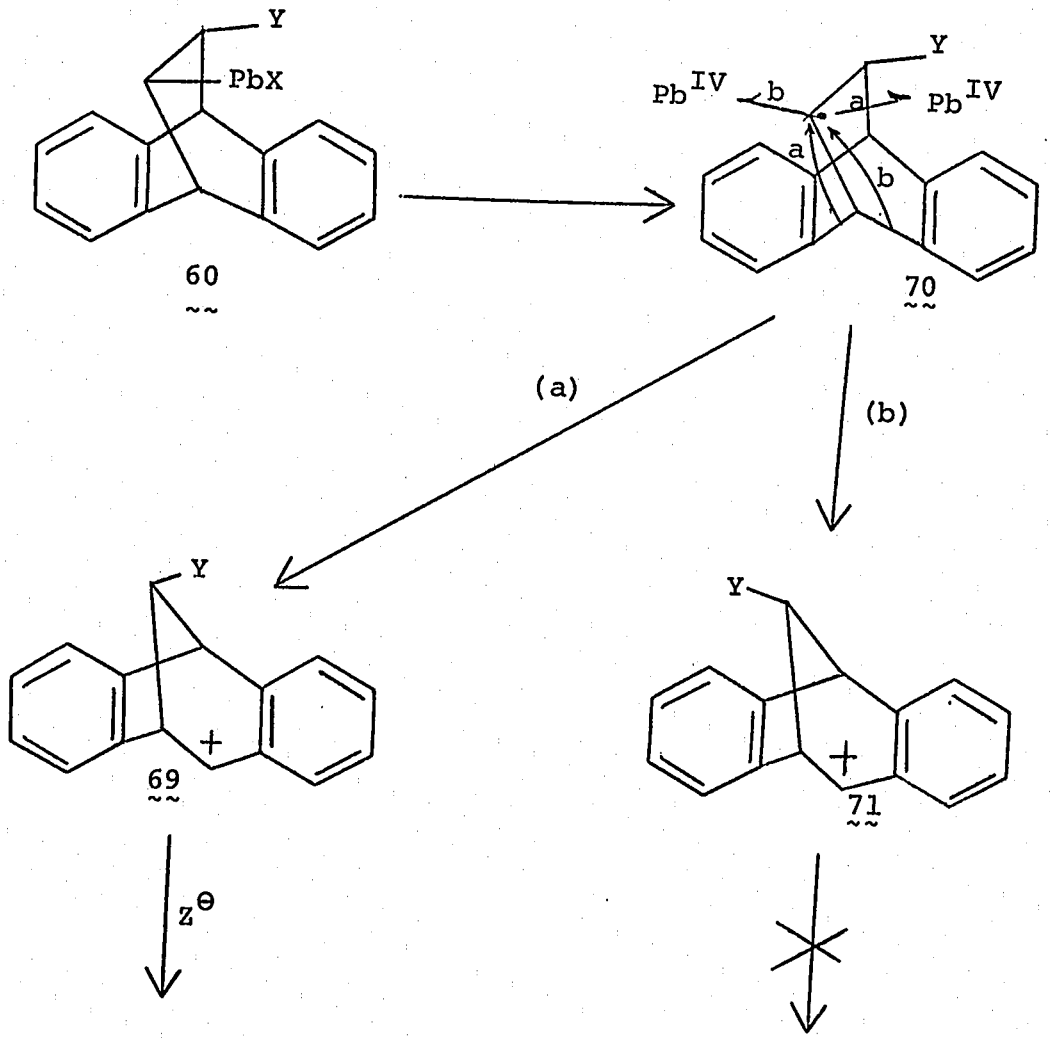
m = 0-3

requires a heterolytic lead-carbon bond cleavage. Had the lead-carbon bond cleaved homolytically and had the resultant free-radical been rapidly and easily oxidized, then the stereospecificity of the products obtained in this system would most likely have been lost. This conclusion is plausible since there does not appear to be any reason to believe that an oxidation step should show any preference for either one side or the other of a free-radical. The implications of a homolysis-oxidation pathway is summarized in Scheme XX. Nucleophilic attack on species 69 would lead to the observed products, but nucleophilic attack on species 71 would lead to 8-*anti*-4-*exo*-disubstituted products. The failure to observe any products arising from species 71 may be taken as evidence against the homolytic-oxidation pathway.

A Mechanism for the Reaction of LTA-HF with 1-Octene

From the reaction of 1,1-diphenylethylene, the formation of the major product, 1,1-difluoro-1,2-diphenylethane, indicated that a benzyl carbonium ion may be stabilized by a geminal fluorine atom. It would be interesting to determine whether this phenomenon could be observed in aliphatic systems. It would also be of interest to determine if products analogous to deoxybenzoin and its precursor could be isolated in other systems. To this end the reaction of LTA-HF with 1-octene was studied.

SCHEME XX



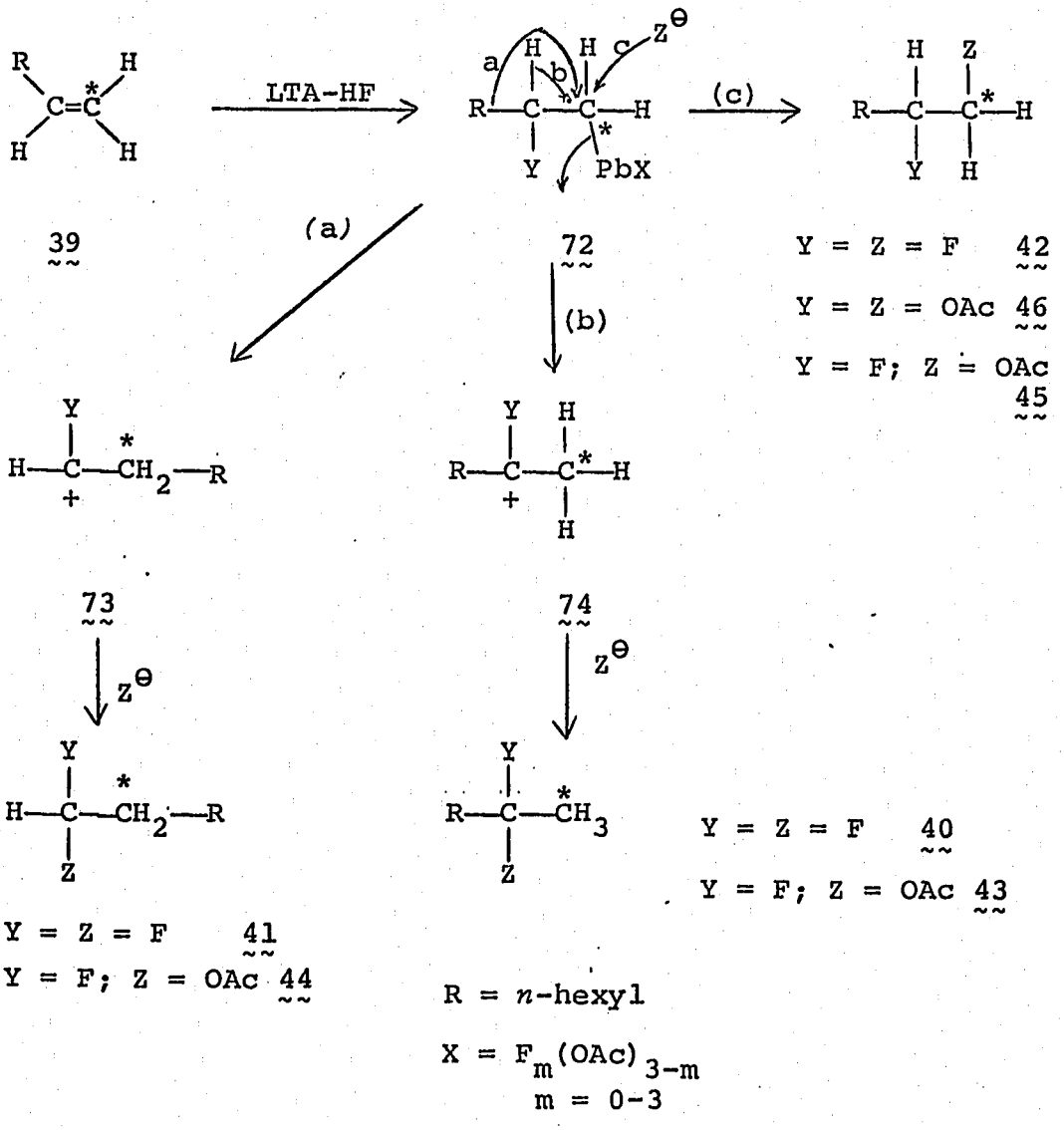
Observed Products

X = $F_m(OAc)_{3-m}$

m = 0-3

Preliminary work on this system indicated that some of the products formed could best be explained *via* alkyl and hydrogen migration. In order to determine the correctness of the suggested mechanism, 1-octene specifically labelled with ^{13}C in the one position was synthesized. The mechanism which can readily rationalize the formation of the observed products and the position of the carbon-13 label is shown in Scheme XXI.

SCHEME XXI



The products can again be rationalized by a mechanism which procedes *via* the initial lead-ligand adduct, 72. The adduct 72 arises from Markovnikov addition analogous to that seen in the reaction of LTA-HF with 1,1-diphenylethylene. The intermediate can then react by the three paths shown in Scheme XXI.

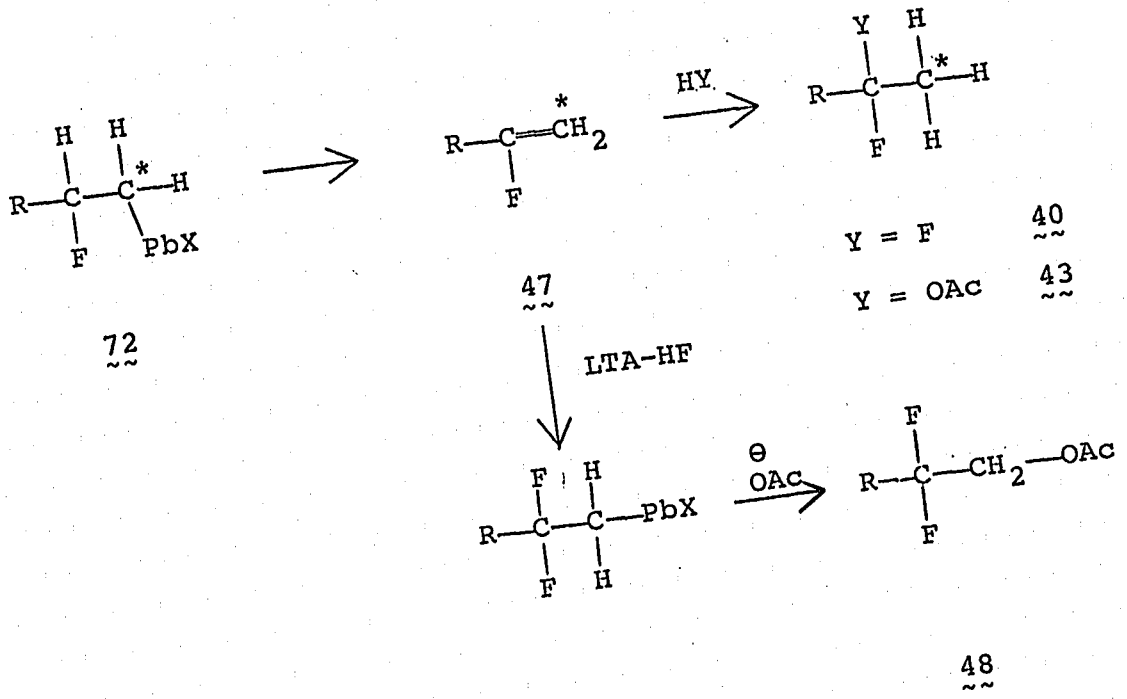
Path a shows heterolysis of the lead-carbon bond with concomitant migration of the alkyl group formally to leave the cation, 73, which is then attacked by a nucleophile to give the products 41 and 44.

Path b shows heterolysis of the lead-carbon bond with coincident migration of the hydrogen formally to leave cation 74 which is attacked by a nucleophile to give compounds 40 and 43.

Path c represents a direct displacement mechanism leading to the compounds 42, 45, and 46.

An alternate pathway to get to the 2,2-disubstituted products 40 and 43 is shown in Scheme XXII. The addition of HF to the olefin is a competing pathway in the reaction of LTA-HF with norbornene. The product arising from addition of HF to 1-octene, 2-fluorooctane, was not observed in this reaction. However, the olefin 47 may well be activated towards protonation since there is evidence that a fluorine atom directly attached to a carbonium ion stabilizes the carbonium ion (see below). A choice

SCHEME XXII



72 47 40 43 48

R = *n*-hexyl

X = $F_m(OAc)_{m-3}$

m=0-3

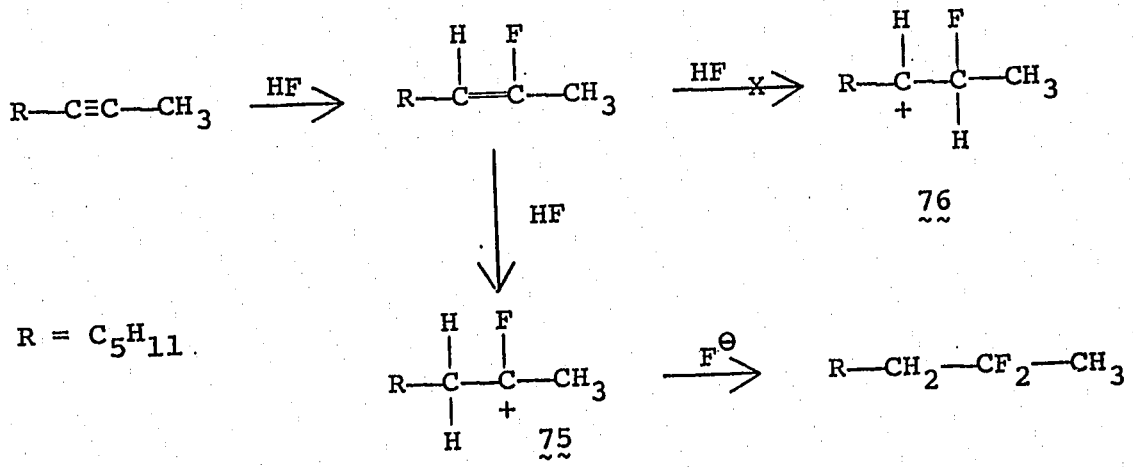
between the pathway of Scheme XXI and the pathway shown in Scheme XXII cannot be made at this time. To make this choice, the olefin 47 should be synthesized and subjected to the reaction conditions. An analysis of the products formed from this reaction may then offer a choice between these two pathways. A possible synthesis of 47 is outlined in the Appendix.

The formation of the minor product 1-acetoxy-2,2-difluorooctane (48), is rationalized as arising from the

reaction of the LTA-HF reagent with olefin 47 (Scheme XXII). Undoubtedly the appearance of other minor products obtained from the reaction (see Figure III) could be rationalized as arising in this manner.

The compounds 1,1-difluorooctane (41) and 1-acetoxy-1-fluorooctane (44) make up 49% of the products obtained from the LTA-HF reaction with 1-octene. The only satisfactory pathway leading to these compounds is shown as pathway a in Scheme XXI. The alkyl migration formally leaves a primary carbonium ion stabilized by a geminal fluorine atom. The stabilization of a carbonium ion by a geminal fluorine atom is suggested by the addition of HF to acetylenes which invariably leads to geminal difluorides. For example, the addition of HF to 2-octyne resulted in a 87:13 mixture of 2,2-difluorooctane and 3,3-difluorooctane.[60] A probable Scheme to account for this observation is shown in Scheme XXIII.

SCHEME XXIII



The product formation suggests that the carbonium ion 75 is more stable than the alternate carbonium ion 76.

In electrophilic aromatic substitution, it is found that fluorobenzene reacts only slighly slower than benzene.[61] Fluorine acts as an *ortho-para* director. These results indicate that electron donation is important for fluorine, even more important than for the other halides despite the fact that these are more polarizable. A plausible reason for this could be the shortness of the C-F bond in aromatic systems (shorter than the carbon-carbon double bond [62]) and the similar size of the carbon and fluorine p-orbitals. These same arguments could be used to explain the stability of the species 73 and 74.

The formation of geminal fluoro acetates has not been previously reported although a number of geminal chloro and bromo acetates have been isolated.[63] It was found that primary geminal halo acetates were more stable toward hydrolysis than secondary geminal halo acetates.[64] These same workers [65] reported that secondary geminal halo esters decompose upon standing at room temperature. It would appear, from an examination of these data, that the geminal halo acetates derived from aldehydes are more stable than those derived from ketones. The instability of these types of compounds has also been observed in this work. It was found that 1-acetoxy-1-fluorooctane could quite readily be isolated whereas 2-acetoxy-2-

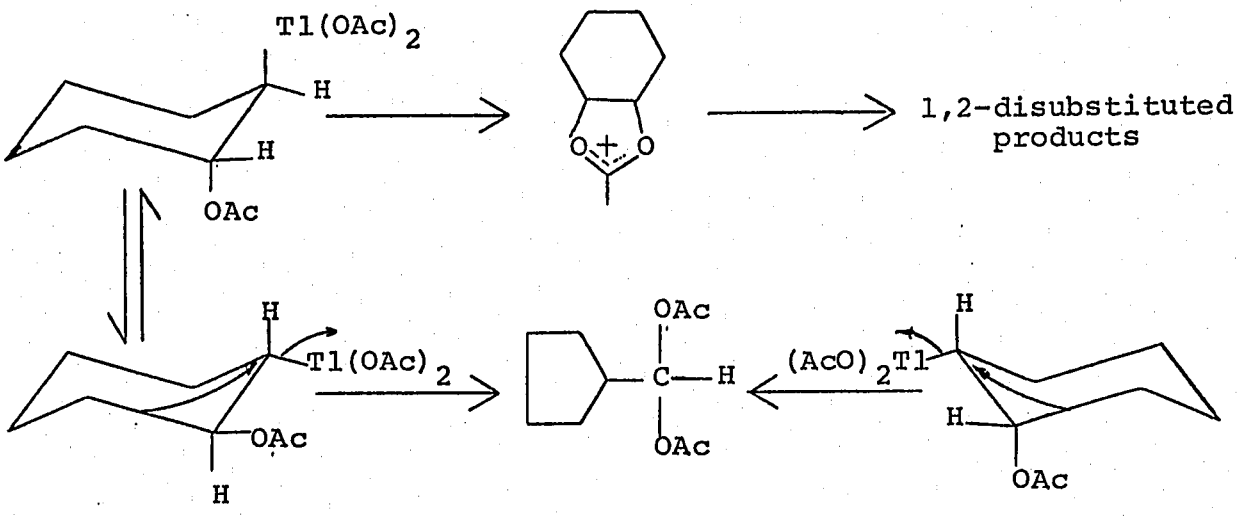
fluorooctane was more difficult to isolate while the isolation of 1-acetoxy-1-fluoro-1,2-diphenylethane was only partially successful. A mechanistic rationale explaining the instability of the geminal fluoro acetates is not available at this time.

Unifying Concept

It has been well established that oxymercuration of unstrained olefins gives *trans* mercury-acetate addition products but oxymercuration of strained bicyclic olefins gives *cis* mercury-acetate addition products.[41c] To account for this behavior, it has been postulated[41c] that addition to unstrained olefins goes by carbonium ion pathways, cationic complexes, or termolecular additions while additions to strained rigid olefins go through a molecular *cis* addition pathway. Similarly, the addition of thallic acetate to norbornene[39a] also gave a *cis* addition product. Addition of thallic acetate to cyclohexene[66] gave 1,2-disubstituted products, a ring contracted product and an allylic oxidation product.

The formation of the 1,2-disubstituted products can best be explained by an initial *trans* addition of thallium and acetate across the double bond followed by heterolysis of the thallium-carbon bond with acetoxy participation and the formation of an acetoxonium ion (Scheme XXIV). The stereochemistry of these products could be controlled

SCHEME XXIV



by solvent. In "dry" solvents, the products had the *trans* stereochemistry while in "wet" solvents the products had primarily the *cis* stereochemistry. Thus this reaction is analogous to the "wet" and "dry" Prévost reaction [67] which does proceed *via* an acetoxonium ion. The ring contraction product could arise from a *trans* or a *cis* addition to the double bond. This product requires that the thallium be in an equatorial position as shown in Scheme XXIV.

As has been pointed out, the products obtained from the reaction of LTA-HF with the bicyclic olefins, norbornene and dibenzobicyclo[2.2.2]octadiene can best be explained as arising from an initial *cis* addition of lead and a ligand to the double bond. The products arising from the LTA oxidation of norbornene are also best explained by the

initial *cis* addition of lead and an acetate across the double bond*. The stereochemistry of the LTA oxidation of cyclopentadiene can also be controlled in the same

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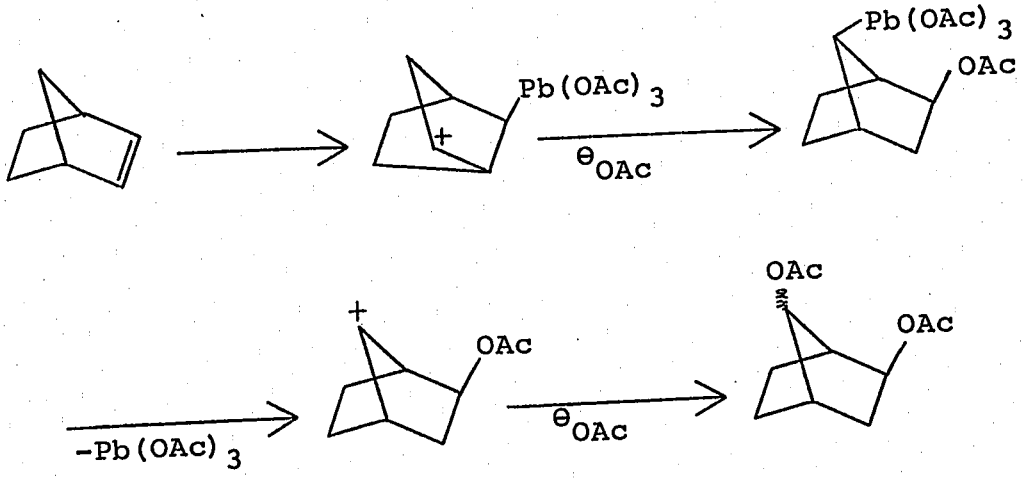
* This mechanistic pathway differs from that proposed by Alder.[42a] Alder's mechanism, shown in Scheme XXV, is less appealing as it requires the formation of a carbonium ion in the C-7 position. This is unfavorable since the bond angle in norbornane is normally 97° [68], while a carbonium ion, being sp^2 hybridized desires a bond angle of 120°.

SCHEME XXV

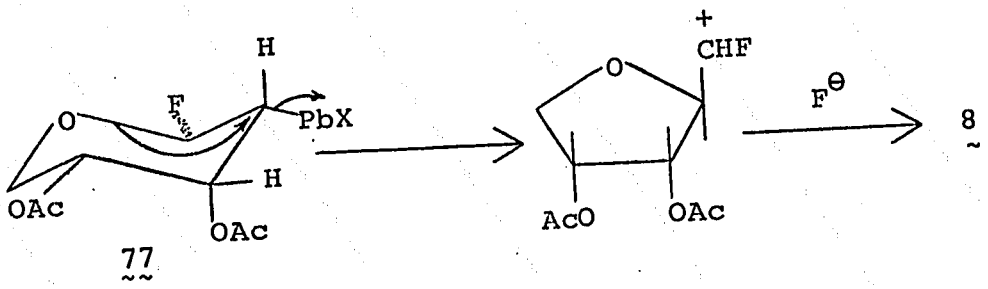


fashion as the Prévost reaction [69] again suggesting that the reaction goes *via* a cyclic acetoxonium ion. The formation of this ion requires an initial *trans* addition of lead and an acetoxy group followed by lead-carbon bond heterolysis with acetoxy participation.

The present work does not allow a statement on the stereochemistry of an initial lead-ligand addition product that would be obtained from the LTA-HF reaction with unstrained olefins. This will be the subject of future work. However, in the light of the above discussion and the results obtained in this work, an alternate pathway to that proposed by Bowers for the fluorination of pregnenolone acetate, 1, to give the *cis*-5α,6α-difluoro compound 2 (see Scheme I - page 5) can be proposed. Assuming that the stereochemistry of the difluoro compound 2 is correct (as it has not been rigorously established), the reaction could proceed *via* an initial *trans* addition of lead and a fluorine to give a *trans* 5α-fluoro-6β-lead species which would be the normal ionic addition product of this compound.[8] This would be followed by a second step, the displacement of the lead by another fluorine to give the *cis*-5α,6α-difluoride, 2.

Similarly, the difluorinated ring contraction product 8, obtained from the reaction of the unsaturated sugar, di-O-acetyl-D-arabinal (7), with LTA-HF could arise by the mechanism shown in Scheme XXVI.

SCHEME XXVI



The first step of the reaction would be the formation of the lead-ligand addition product 77, by Markovnikov addition. The stereochemistry of the initial addition product is of no consequence in this particular case. To get the observed ring contraction product 8, the lead must be in an equatorial position and *cis* to the acetoxy groups.

Thus the postulated mechanism derived from the results of this work can satisfactorily account for all the observations made concerning the LTA-HF reaction with a number of structurally different olefins.

EXPERIMENTAL

Materials

Lead tetraacetate (LTA) was obtained from Alpha Inorganics and recrystallized from acetic acid/acetic anhydride prior to use. Anhydrous hydrogen fluoride (HF) was obtained from Matheson, distilled, and used without further purification. Methylene chloride (reagent grade) was distilled from phosphorus pentoxide prior to use. 1,1-Diphenylethylene was obtained from Aldrich Chemical Co. and purified by distillation through a one ft Vigreaux column under reduced pressure. The fraction boiling from 126-127° at 6.5 mm Hg was collected and shown by gas liquid partition chromatography (glpc) to contain three minor impurities (<2%). In subsequent reactions these impurities did not react to any extent. Norbornene was obtained from Aldrich Chemical Co. and purified by glpc (25 ft by 3/8 in SE-30 on Chromosorb W A/W) prior to use. 1-Octene was research grade material (certified 99.73 mole per cent pure) obtained from Phillips Petroleum Co. and used without futher purification. Carbon-13 enriched barium carbonate (analysis 61.2 atom per cent C-13) was obtained from Bio-Rad Laboratories. "Freon 112" was obtained from DuPont and distilled before use: bp 90.5° (710 mm).

Glpc Analysis

Throughout the course of this work, two glpc columns were used for both analytical and preparative purposes. These were a 10 ft by 0.25 in 10% SE-30 on Chromosorb W A/W column and a 10 ft by 0.25 in 10% Carbowax 20M on Chromosorb W column. These will be referred to as Column A and Column B respectively.

Reaction of 1,1-Diphenylethylene with LTA/HF

In a 500 ml polyethylene bottle, previously dried in a vacuum oven at 45°, equipped with a "Teflon" coated magnetic stirring bar and protected by a calcium sulfate drying tube, was prepared a solution of 50 g (0.11 mole) LTA in 100 ml dry methylene chloride. This solution was cooled to 0° and 6 ml (0.3 mole) HF was added. The resultant solution was stirred at 0° for one hour. To this was added in one portion, a 55 ml pre-cooled (0°) dry methylene chloride solution, 1.06 M in 1,1-diphenylethylene and 0.29 M in "Freon 112". The resultant reaction mixture was stirred for 1 minute at 0° and then quenched by pouring the mixture into a cold (0°) saturated potassium carbonate solution. The organic layer was filtered through "Celite Filter Aid"; the aqueous layer was extracted with methylene chloride, the combined organic phases were washed in succession with water, saturated sodium bicarbonate solution, water, and finally dried over anhydrous sodium sulfate. The reaction mixture was then subjected to glpc analysis

(Column A linearly programmed from 100° to 300° at 6° per minute). Analysis revealed that 90% of the starting material had reacted and that two major volatile products had formed. The product with the shortest retention time was shown to be 1,1-difluoro-1,2-diphenylethane, 3, by comparison of its retention time and infrared (ir) spectrum with those of an authentic sample. From a calibration curve obtained by plotting the mole ratio of 3/"Freon 112" against the area ratio of 3/"Freon 112" (see Appendix for an example), it was found that 0.028 mole of compound 3 had been formed. The other major volatile component was isolated by preparative glpc: ir (CCl_4) ν 1760, 1211, 1097, 700 cm^{-1}. The mass spectrum showed the highest m/e at 238 with a satellite m/e at 239 which was 18% of m/e 238 indicative of a C_{16} structure. Two minor products were observed which were shown to have the same retention time as 3-methyl-1,1,3-triphenylindane and 1,4-difluoro-1,1,4,4-tetraphenylbutane. The abundance of these materials was estimated by area measurements and found to represent *ca.* 1% and 1.5% of the volatile products.

The above procedure was repeated for 5, 45, and 125 minute reaction times. See Table I for the results of these reactions. In these reactions it was found that the second major component partially decomposed to a third compound which upon isolation proved to be deoxybenzoin by comparison of its ir spectrum with that of an authentic

sample.

A solution of 21.6 g (0.117 mole) of 1,1-diphenylethylene in 200 ml dry methylene chloride was added to a cold (0°), stirred solution of 100 g (0.23 mole) LTA and 12 ml (0.6 mole) HF in 200 ml dry methylene chloride in the manner described previously. The reaction was quenched after 5 minutes reaction time and treated as described. The bulk of the solvent was removed by distillation through an 8 in Vigreaux column. The oily residue was kept at 0° overnight and the precipitate which formed was collected by filtration, sparingly washed with methylene chloride, and recrystallized from hexane to yield 0.35 g (1.5%) of 1,4-difluoro-1,1,4,4-tetraphenylbutane: mp 172-173° with decomposition*; nmr (DMSO-d_6) τ 2.68 (singlet, 20 H), 6.72 (singlet, 4 H); m/e 398.1844 (calcd. for $C_{28}H_{24}F_2$: 398.1846).

The residue was steam distilled. The first 1500 ml of distillate was extracted with ether. The ether layer

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* Various melting point determinations of this compound resulted in melting points ranging from 160° to 200° but always very sharp and always accompanied by decomposition to a yellow oil. Bornstein [11] observed this same behavior and showed that the decomposition product was 1,1,4,4-tetraphenyl-1,3-butadiene.

was dried over anhydrous sodium sulfate. Glpc analysis revealed that compound 3 was the main component of the distillate. The ether was removed to yield a solid residue which was recrystallized from methanol to yield 6.5 g (25%) of white crystals: mp 65-66° (lit.[1] 66°); nmr spectrum was identical to that reported[70]; ^{19}F nmr ($CDCl_3$) 95.85 ppm ($CFCl_3$) (triplet, J = 16 cps).

The second 1500 ml of distillate was extracted with ether. The ether was dried over anhydrous sodium sulfate. Glpc analysis revealed that deoxybenzoin was the main component of the distillate. The ether was removed to yield an oily residue which was crystallized from methanol to yield 1.8 g (10%) of white crystals shown to be deoxybenzoin by melting point, mixture melting point and comparison of its ir spectrum with that of an authentic sample.

On completion of the distillation, 5 g of polymeric material remained. The composition of this material was not analysed.

Reaction of α-Stilbenol Acetate (10) with LTA/HF

Compound 10 was prepared by the method described by Barnes[71]: mp 101-104° (lit. 101°). A solution of 2.00 g (0.010 mole) "Freon 112" and 2.50 g (0.0105 mole) of 10 in 25 ml dry methylene chloride was added to a cold (0°), stirred solution of 10 g (0.022 mole) LTA and 1.2 ml

(0.06 mole) HF in 25 ml of dry methylene chloride in the manner described previously. The reaction was quenched after 125 minutes and treated as described previously. Glpc analysis (Column A linearly programmed from 100-300° at 6° per minute) revealed that 47% of the starting material had reacted and one volatile product had been formed. When deoxybenzoin was added to the reaction mixture, a new peak was observed in the glpc chart showing that the product was not deoxybenzoin. Thin layer chromatography (0.1 mm silica gel GF plate eluted with 10% $CHCl_3/CCl_4$) showed that three products had been formed all having longer retention times than deoxybenzoin.

Reaction of Norbornene (12) with LTA/HF

A solution of 10.6 g (0.114 mole) 12 and 4.05 g (0.020 mole) "Freon 112" in 100 ml dry methylene chloride was pre-cooled to -47° (*m*-xylene slush). This was added to a stirred solution of 35 g (0.081 mole) LTA and 5 ml (0.25 mole) HF in 200 ml dry methylene chloride at -78° in the manner previously described. The reaction was quenched after one minute and the reaction mixture was treated in the manner previously described. The reaction mixture was analysed by glpc (Column A linearly programmed from 50° to 200° at 8° per minute). From a calibration curve obtained by plotting the mole ratio of 12/"Freon 112"

against the area ratio of 12/"Freon 112", it was found that 0.048 mole of 12 had reacted. From a calibration curve constructed as described (Appendix) using compound 16 and "Freon 112", it was found that compounds 13, 14, 15, and 16 represent 63% of the products (based on the amount of 12 consumed). From a calibration curve constructed as described (Appendix) using compound 20 and "Freon 112", it was found that compounds 17, 18, 19, 20, 21, 22, 23, and 24 represent 38% of the products. For the amount of each compound present see Table II. The products of the reaction were collected by preparative glpc (Column B programmed from 100-200°).

2-*exo*-7-*anti*-Difluoronorbornane (15)

Compound 15 is a volatile, white, waxy solid: mp (sealed capillary) 107-110°; ir (CCl_4) ν 1059, 1078 cm^{-1} (C-F stretch)[72]; nmr (CCl_4) see Figure 1; ^{19}F nmr (CCl_4) 42.49 ppm (C_6F_6) (doublet of multiplets, J_d = 58 cps); m/e 132.0749 (calcd for $C_7H_{10}F_2$: 132.0750). *Anal.* Calcd for $C_7H_{10}F_2$: C, 63.62; H, 7.63. Found: C, 63.67; H, 7.58.

7-*anti*-Fluoronorbornene (25)

To a 50 ml flask fitted with a magnetic stirrer and a reflux condenser was added 233 mg (1.7 mmole) of 15 dissolved in 20 ml of dry dimethyl sulfoxide (DMSO). To this was added 380 mg (3.4 mmole) of potassium *tert*-

butoxide. This mixture was heated to 120° with stirring for 24 hours. Since the product of the reaction was expected to be volatile, the exit of the reflux condenser was connected to a Dry Ice cold trap. At the completion of the reaction, the contents of the cold trap were dissolved in ether and added to the cooled DMSO solution. The reaction mixture was poured into 50 ml of saturated aqueous sodium chloride solution and extracted with ether by liquid-liquid extraction for 24 hours. The exit of the reflux condenser was again connected to a Dry Ice cold trap to trap any volatile material. The ethereal layer was washed with water and dried over anhydrous sodium sulfate. The bulk of the ether was removed by distillation through an 8 in Vigreaux column. The residue was analysed by glpc (Column B at 50°) and found to contain only 2 volatile components. These were collected by preparative glpc (same column and conditions as above) and found to be *tert*-butyl alcohol (ir) and compound 25. Compound 25 is a volatile, white, waxy solid: mp (sealed capillary) 56-57°; ir (CS_2) ν 3060, 1040, 709 cm^{-1}; nmr (CCl_4) τ 4.05 (quartet, J = 2.2 cps, 2 H), 5.82 (doublet of broadened singlets, J_d = 60 cps, $W_{\frac{1}{2}}$ = 4 cps, 1 H), 7.31 (quartet, J = 2.2 cps, 2 H), 8.2 (multiplet, 2 H), 8.9 (multiplet, 2 H); m/e $(M-F)^+$ 93.0704 (calcd for C_7H_9: 93.0704).

2-*exo*-7-*syn*-Difluoronorbornane (16) and its Dehydrofluorination to 7-*syn*-Fluoronorbornene (26)

Compound 16 is a volatile, white, waxy solid: mp (sealed capillary) 95-97°; ir (CCl_4) ν 1050, 1083 cm^{-1} (C-F stretch); nmr (CCl_4) see Figure II; ^{19}F nmr (CCl_4) 42.57 ppm (C_6F_6) (doublet of multiplets, J_d = 56 cps); m/e 132.0749 (calcd for $C_7H_{10}F_2$: 132.0750). *Anal.* Calcd for $C_7H_{10}F_2$: C, 63.62; H, 7.63. Found: C, 63.33; H, 7.46.

Dehydrofluorination was effected as for 15. Glpc analysis (Column B at 50°) showed three volatile components. These were collected by preparative glpc and shown to be *tert*-butyl alcohol (ir), compound 16 (ir), and compound 26. Compound 26 is a volatile, white waxy solid: mp (sealed capillary) 56-57.5°; ir (CS_2) ν 3065, 1045, 711 cm^{-1}; nmr (CCl_4) τ 4.02 (singlet, 2 H), 5.53 (doublet of broadened singlets, J_d = 57 cps, $W_{\frac{1}{2}}$ = 4 cps, 1 H), 7.19 (singlet, 2 H), 8.35 (multiplet, 2 H), 9.0 (multiplet, 2 H); m/e 112.0692 (calcd for C_7H_9F; 112.0688).

Hydrogenation of 25 and 26

To each of the residues obtained above was added 0.1 g Adams Catalyst. The flask was cooled with ice and the contents stirred under one atmosphere of hydrogen for three hours. The catalyst was filtered off and the reaction mixture analyzed by glpc (Column B at 50°). Both 25 and 26 gave the same hydrogenation product, 7-fluoronorbornane

(27) in 100% yield (determined by glpc using an internal standard). Compound 27 is an extremely volatile, white, waxy solid: mp (sealed capillary) 106-107°; ir (CS_2) ν 1040 cm^{-1}; nmr (CCl_4) τ 5.31 (doublet of broadened singlets, J_d = 57 cps, $W_{½}$ = 4 cps, 1 H), 7.8 - 8.9 (10 H); m/e 114.0845 (calcd for $C_7H_{11}F$: 114.0845). Samples of 27 from both sources gave identical ir spectra.

The Norbornylfluoro Acetates

All the fluoro acetates had very similar glpc retention times. A microanalysis of the mixture was taken. *Anal.* Calcd for $C_9H_{13}FO_2$: C, 62.77; H, 7.61. Found: C, 62.69; H, 7.77. The acetates were collected by preparative glpc (Column B at 180°). It was possible to collect 7-*syn*-acetoxy-2-*exo*-fluoronorbornane (22) admixed with a small amount of 7-*anti*-acetoxy-2-*exo*-fluoronorbornane (21), and it was possible to collect 2-*exo*-acetoxy-7-*anti*-fluoronorbornene (19) and 2-*exo*-acetoxy-7-*syn*-fluoronorbornane (20) in the pure state.

Fluoro Acetate 22

Compound 22 is a colorless liquid ir (CCl_4) ν 1745, 1242, 1063 cm^{-1}; nmr (CCl_4) τ 5.44 (doublet of multiplets, J_d = 52 cps, 1 H), 5.46 (broadened singlet, $W_{½}$ = 5 cps, 1 H), 8.06 (singlet, 3 H) 7.3 - 9.2 (8 H).

Fluoro Acetate 19

Compound 19 is a colorless liquid: ir (CCl_4) ν 1750, 1233 cm^{-1}; nmr (CCl_4) τ 5.00 (doublet of broadened singlets, J_d = 58 cps, $W_{1/2}$ = 4.5 cps, 1 H), 5.55 (multiplet, 1 H), 8.09 (singlet, 3 H), 7.6 - 8.9 (8 H).

Compound 19 was reduced to 7-*anti*-fluoro-2-*exo*-norborneol (28) with lithium aluminum hydride (LAH). In a typical reaction 133 mg (0.77 mmole) of 19 was dissolved in 10 ml of anhydrous ether. This solution was added slowly to a solution of 20 mg LAH in anhydrous ether. After addition of the ester the excess LAH was decomposed with water saturated ether. The resultant mixture was poured into 20 ml of 6 N HCl solution. The layers were separated and the aqueous portion extracted with ether. The combined ether fractions were washed in succession with water, saturated sodium bicarbonate solution, water, and finally dried over anhydrous sodium sulfate. The ether was removed by distillation through an 8 in Vigreaux column. The yield of 28 was 95 mg (94%). Compound 28 was purified by glpc (Column B at 130°) and sublimed at 40° at 0.1 mm Hg. Compound 28 is a white, waxy solid: mp (sealed capillary) 126.5 - 129°; ir (CCl_4) ν 3630 cm^{-1}; nmr (CCl_4) τ 5.12 (doublet of broadened singlets, J_d = 57 cps, $W_{1/2}$ = 5 cps, 1 H), 6.35 (multiplet, 1 H), 6.53 (singlet 1 H), 7.5 - 9.1 (8 H); ^{19}F nmr (CCl_4) see Table V. *Anal.* Calcd for $C_7H_{11}FO$: C, 64.59; H, 8.52. Found: C, 64.36; H,

8.36.

Oxidation of 28 to 7-*anti*-Fluoronorbornan-2-one (30)

The oxidation was carried out using Brown's method.[73] By this procedure, 96 mg (0.74 mmole) of 28 afforded 92 mg (96%) of 30. Compound 30 was purified by glpc (Column B at 130°) and sublimation (40° at 0.1 mm Hg). Compound 30 is a white, waxy solid: mp (sealed capillary) 104-106°; ir (CCl_4) ν 1751 cm^{-1}; nmr (CCl_4) τ 5.20 (doublet of broadened singlets, J_d = 56 cps, $W_{1/2}$ = 5 cps, 1 H), 7.2 - 8.6 (8 H). *Anal.* Calcd for C_7H_9FO: C, 65.61; H, 7.07. Found: C, 65.59; H, 7.15.

Solvolysis of 30 to 7-*anti*-Methoxynorbornan-2-one (32) and 7-*anti*-Acetoxynorbornan-2-one (33).

To 1.6 ml of 3% sodium methoxide-methanol solution was added 26 mg (0.2 mmole) of 30. This solution was sealed in an ampoule and heated to 75° for 11 hours. Glpc analysis (Column A at 130°) revealed two volatile components. The minor one (*ca.* 5%) was shown by retention time to be 30. The other material, 95%, was collected by preparative glpc (same column and conditions as above) and shown to be 32 by comparison of its ir and nmr spectra with those of the authentic material.[23]

The acetolysis of 30 was carried out by dissolving 139 mg (1.1 mmole) of this material in 10 ml dried acetic

acid (heated under reflux with acetic anhydride and catalytic amounts of sulfuric acid followed by distillation). This solution was buffered with 100 mg (1.2 mmole) of fused sodium acetate. The mixture was sealed in an ampoule and placed in a 150° bath for 800 hours. The reaction mixture was cooled and poured into 20 ml of ether. The ether solution was washed several times with water, 10% sodium bicarbonate solution, water, and finally dried over anhydrous sodium sulfate. Analysis of the reaction mixture by glpc (Column B linearly programmed from 100 to 170° at 10° per minute) showed that two components were present in the ratio 1:4. Both compounds were collected by preparative glpc (same column and conditions as above). The smaller component proved to be unreacted 30 (ir) while the larger component was shown to be 33 by a comparison of its ir spectrum with that of the authentic material.[24]

The ether was carefully removed by distillation through an 8 in Vigreaux column. By the integration of the nmr spectrum of the mixture, with an added standard, it was shown that 33 had been formed in 72% yield.

Reduction of 30 to 27

The reduction of the carbonyl function to a methylene group was carried out by the preparation of the thio-ketal of 30 followed by its heating to reflux with Raney Nickel in the manner described by van Tamelen.[74] The exit of the reflux condenser was connected to a Dry Ice cold trap.

Glpc analysis (Column B at 50°) with an added external standard revealed that only one volatile product was formed in *ca.* 60% yield. The reduction product was isolated by preparative glpc (same column and conditions as above) and was found to have an ir spectrum identical to that of 27.

Fluoro Acetate 20 and its Derivatives

Compound 20 is a colorless liquid: n_D^{25}= 1.4544; ir (CCl_4) ν 1740, 1244, 1052 cm^{-1}; nmr (CCl_4) τ 5.32 (doublet of broadened singlets, J_d = 56 cps, $W_{\frac{1}{2}}$ = 5 cps, 1 H), 5.36 (triplet, J = 5 cps, 1 H), 8.06 (singlet, 3 H), 7.6 - 9.1 (8 H).

The LAH reduction of 144 mg (0.84 mmole) of 20 by the procedure described above, yielded 92 mg (84%) of 7-*syn*-fluoro-2-*exo*-norborneol (29). Compound 29 is a white, waxy solid: mp (sealed capillary) 132-134°; ir (CCl_4) ν 3600, 1089, 1052 cm^{-1}; nmr (CCl_4) τ 5.17 (doublet of doublets, J = 56 cps, J = 2 cps, 1 H), 6.25 (broad singlet, $W_{\frac{1}{2}}$ = 14 cps, 1 H), 7.5 - 9.2 (9 H); ^{19}F nmr (CCl_4) see Table V. *Anal.* Calcd for $C_7H_{11}FO$: C, 64.59; H, 8.52. Found: C, 64.37; H, 8.59.

The oxidation of 47 mg (0.22 mmole) of 29 by Brown's method yielded 35 mg (76%) of 7-*syn*-fluoronorbornan-2-one (31). Compound 31 is a white, waxy solid: mp (sealed capillary) 115-118°; ir (CCl_4) ν 1751 cm^{-1}; nmr (CCl_4) τ 5.10 (doublet of quadruplets, J_d = 56 cps, J_q = 2 cps, 1H), 7.3 - 8.7 (8 H). *Anal.* Calcd for C_7H_9FO: C, 65.61; H, 7.07.

Found: C, 65.72; H, 7.01.

The attempted base promoted solvolysis of 31 yielded only unreacted 31.

Acetolysis of 31 was carried out under the identical conditions as for the acetolysis of 30. The reaction was run for 750 hours. Glpc analysis (Column B linearly programmed from 100-170° at 10° per minute) of the reaction mixture revealed that aside from the starting material, 31, (*ca.* 90%) four new products were formed in a total yield of *ca.* 10%. The isolation and characterization of these products was not attempted.

The reduction of the carbonyl in 31 to a methylene group by van Tamelen's method gave a 60% yield of only one volatile product (glpc analysis). The ir spectrum of this reduction product proved to be identical to that of 27.

Nmr Analysis of the Fluoro Alcohols 28 and 29

An nmr sample was prepared using 168 mg (1.3 mmole) of 29 dissolved in 0.5 ml CCl_4. Both the proton and ^{19}F nmr were taken. Then a total of 40 mg (5.7×10^{-2} mmole) of *tris*(dipivalomethanato)europium ($Eu(DPM)_3$) was added and the spectra were again obtained. Similarly a solution of 104 mg (0.8 mmole) of 28 in 0.5 ml CCl_4 was prepared and the proton and ^{19}F nmr were obtained. Then a total of 30 mg (4×10^{-2} mmole) of $Eu(DPM)_3$ was added and the spectra were

again obtained. In both cases the mole ratio of substrate: $Eu(DPM)_3$ was *ca.* 1:0.05. The nmr spectra were taken on a Varian A 56/60 Spectrophotometer. See Table V for results.

Preparation and Reaction of Nortricyclylfluoride (13) and LTA - HF

Compound 13 was prepared as reported by Hanack and Kaiser[75]: mp (sealed capillary) 52-54° (lit. 51-53°); ir (CH_2Cl_2) ν 3080, 815, 803 cm^{-1}; nmr (CCl_4) τ 5.42 (doublet of triplets, J_d = 58 cps, J_t = 2.3 cps, 1 H), 7.4 - 8.9 (8 H); m/e 112.0668 (calcd for C_7H_9F: 112.0668). *Anal.* Calcd for C_7H_9F: C, 74.97; H, 8.09; F, 16.94. Found: C, 75.09; H, 8.04, F, 17.04.

A solution, pre-cooled to -78°, of 222 mg (2 mmole) of 13 and 306 mg (1.5 mmole) of "Freon 112" in 4 ml dry methylene chloride was added to a stirred solution of 900 mg (2 mmole) of LTA and 0.2 ml (10 mmole) of HF in 10 ml dry methylene chloride at -78°. This mixture was stirred at -78° for a period of one hour, quenched, and treated in the usual manner. It was found, by glpc analysis (Column A at 80°), that the area ratio of 13:"Freon 112" was 0.91 ± 0.03 before the reaction and 0.87 ± 0.03 after the reaction. Some products were formed but in amounts too small to be isolated and characterized. The peak designated as 13 was reisolated and shown to be the original material by comparison of its ir spectrum with

that of the authentic material.

Reaction of Nortricyclylacetate (17) with LTA - HF

Compound 17 was prepared as described by Cristol.[76]

A solution, pre-cooled to -78°, of 320 mg (2.11 mmole) 17 and 343 mg (1.68 mmole) "Freon 112" in 10 ml of dry methylene chloride was added to a stirred solution of 900 mg (2 mmole) LTA and 0.2 ml (10 mmole) HF in 10 ml of dry methylene chloride cooled to -78°. This mixture was stirred at -78° for a period of one hour, quenched, and treated in the usual manner. It was found, by glpc analysis (Column A at 130°), that the area ratio of 17:"Freon 112" was 1.47 ± 0.03 before the reaction and 1.47 ± 0.11 after the reaction. The peak designated as 17 was reisolated and its ir spectrum was found to be identical to that of the authentic material.

Preparation of 2-*exo*-7-*syn*-Diacetoxynorbornane (24) and 2-*exo*-7-*anti*-Diacetoxynorbornane (23)

The method of preparation was that suggested by Alder.[42a] To a suspension of 100 g (0.23 mole) LTA in 700 ml acetic acid was added a solution of 11.2 g (0.119 mole) 12 in 100 ml of acetic acid. The resultant mixture was stirred for one hour at room temperature and then allowed to stand overnight. The reaction mixture was poured into 1500 ml of water and extracted with

methylene chloride. The methylene chloride solution was washed several times with water, saturated sodium bicarbonate solution, and finally dried over anhydrous sodium sulfate. Glpc analysis (Column B programmed from 30 - 100°) showed two product peaks. The smaller one (7.4% based on peak areas) was shown to be 17 by comparison of its retention time and ir spectrum with those of the authentic material. The larger peak (92.6%) was shown by nmr integration to be a mixture of compounds 24 and 23 in the ratio of 3:1. A microanalysis of the mixture was taken. *Anal.* Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.30; H, 7.59.

Preparation of 2-*exo*-Fluoronorbornane (14)

A solution of 2 g (0.021 mole) 12 in 100 ml methylene chloride was pre-cooled to -47° (*m*-xylene slush). The solution was added to 10 ml (0.5 mole) of HF at -78° and stirred for 15 minutes. The reaction mixture was poured into a cold, 0°, saturated sodium carbonate solution. The layers were separated and the aqueous layer was extracted with methylene chloride. The combined organic portions were washed with water and dried over anhydrous sodium sulfate. The bulk of the solvent was removed by distillation through an 8 in Vigreaux column. Compound 14 was collected by preparative glpc (Column A at 70°). Compound 14 is a volatile, white, waxy solid: mp (sealed

capillary) 49-51°. The nmr of 14 is identical to that published for 2-*exo*-fluoronorbornane .[16] Integration of a nmr spectrum of the reaction mixture showed that 14 was present in 60% yield.

Preparation of 2-*exo*-Norbornylacetate (18)

Compound 18 was prepared from its alcohol by acetylation with acetic anhydride-sodium acetate.[77] By this method, 2-*exo*-norborneol yielded 79% of 18: bp 88-91° at 20 mm Hg (lit.[78] 89-90° at 20 mm Hg); ir (CCl_4) ν 1740, 1260 cm^{-1}. Glpc analysis (10 ft by 0.25 in 10% SF-96 on Chromosorb W column at 140°) showed only one peak.

Reaction of Dibenzobicyclo[2.2.2]octadiene (34) with LTA-HF

The olefin (34) was prepared by the method described by Cristol.[29] The reaction was run in the manner described previously for the reaction of 1,1-diphenylethylene. A cold (0°) solution of 1.15 g (0.0056 mole) 34 dissolved in 10 ml of dry methylene chloride was added to a cold (0°) stirred solution of 2.0 g (0.0045 mole) LTA and 0.3 ml (0.015 mole) HF in 20 ml of dry methylene chloride. The reaction was quenched after 30 minutes and treated in the manner previously described. The solvent was removed by rotary evaporation. The residue (1.41 g) was taken up in methylene chloride and spotted on two one meter preparative thin layer chromatography plates (0.5 mm Silica

Gel GF) and eluted with reagent grade chloroform (stabilized with 0.75% ethanol). On development, four bands - A, B, C, and D (in order of decreasing mobility) appeared. These were individually extracted from the Silica Gel by means of a Soxhlet extractor using methylene chloride as solvent. The solvent was removed by rotary evaporation.

Compound A was recrystallized from ethanol to yield 0.61 g (0.0030 mole) of white crystals shown to be the olefin 34 by melting point, mixture melting point and comparison of its ir with that of the authentic material.

Compound B was recrystallized from Skelly B to yield 0.20 g (32% based on 34 consumed) of a white crystalline solid: mp 152-153°. Nmr analysis showed this compound to be 4-*exo*-8-*syn*-difluorodibenzobicyclo[3.2.1]octadiene 35 (see Results Section). *Anal.* Calcd for $C_{16}H_{12}F_2$: C, 79.32; H, 4.99. Found: C, 79.47, H, 5.12.

Compound C was recrystallized from Skelly B to yield 0.22 g (30% based on 34 consumed) of a white crystalline solid: mp 136.5 - 137°; ir (CCl_4) 1740, 1238 cm^{-1}; m/e 282.1054 (calcd for $C_{18}H_{15}FO_2$: 282.1056). Nmr analysis showed this compound to be 4-*exo*-acetoxy-8-*syn*-fluorodibenzobicyclo[3.2.1]octadiene 36 (see Results Section). *Anal.* Calcd for $C_{18}H_{15}FO_2$: C, 76.58, H, 5.36. Found: C, 76.53, H, 5.33.

Compound D was recrystallized from Skelly B to yield 0.20 g (24% based on 34 consumed) of a white crystalline

solid: mp 170-171° (lit[79] 168-170°). The nmr spectrum was identical to that published for 4-*exo*-8-*syn*-diacetoxy-dibenzobicyclo[3.2.1]octadiene (see Table VI Results Section).

Solvolysis of Compound 35

Compound 35-51 mg (0.21 mmole) was dissolved in 6 ml dry glacial acetic acid and sealed in an ampoule. This was heated at 115° for 576 hours. The reaction mixture was poured into 20 ml water and extracted with chloroform. The organic layer was washed with water, saturated sodium bicarbonate solution, and dried over anhydrous sodium sulfate. The solvent was removed by rotary evaporation and the residue was studied by nmr (see Results Section).

Reaction of 1-Octene (39) with LTA-HF

The reaction was carried out using the same procedure as that described for the reaction of 1,1-diphenylethylene with LTA-HF. By this procedure, a solution of 5.01 g (0.0446 mole) 39 and 3.71 g (0.0182 mole) "Freon 112" in 50 ml of dry methylene chloride, pre-cooled to 0°, was added to a stirred solution of 40 g (0.09 mole) LTA and 5.4 ml (0.27 mole) HF in 200 ml of dry methylene chloride at 0°. The resultant mixture was stirred at 0° for 30 minutes, then quenched and treated as previously described. The reaction mixture was subjected to glpc analysis (Column A linearly programmed from 80-275° at 8° per minute). On

the basis of the ratio of 39:"Freon 112" before and after the reaction, 0.0433 mole (97%) of 39 had reacted and 7 major products (>2%) and a number of minor products (<2%) were formed (see Table VIII and Figure III). The molar amounts of the fluorinated octanes were determined from a calibration curve constructed as described using 1,1-difluorooctane (41) and "Freon 112" while the molar amounts of the acetates were determined from a calibration curve constructed as described using 1-acetoxy-2-fluorooctane (45) and "Freon 112" (see Appendix). The products were isolated by preparative glpc using Column A under the same conditions as described above.

2,2-Difluorooctane (40)

The yield of compound 40 was 0.0057 mole (13.2% based on the consumption of 39). An authentic sample of compound 40 was prepared by the addition of HF to 1-octyne at -78° as described by Grosse and Linn.[32*] Compound 40 is a colorless liquid: bp 136° at 700 mm (lit.[80] 136° at 760 mm); n_D^{20} = 1.3776 (lit.[80] n_D^{20} = 1.3766); nmr ($CFCl_3$) τ 8.1 (multiplet, 2 H), 8.48 (triplet, J = 18 cps, 3 H),

* This reaction, as reported[32], is extremely exothermic and care must be exercised in carrying out this procedure.

8.65 (multiplet, 8 H), 9.09 (triplet, J = 5 cps, 3 H); ^{19}F nmr ($CFCl_3$) 126.99 ppm (sextet, J = 18 cps).

The glpc retention time and the spectral data of synthetic 40 were found to be identical to those of compound 40 isolated from the reaction of LTA-HF with 39.

1,1-Difluorooctane (41)

The yield of compound 41 was 0.0148 mole (34.2%). Compound 41 is a colorless liquid: bp 133° at 690 mm; n_D^{20} = 1.3831; nmr (CCl_4) τ 4.29 (triplet of triplets, J = 57 cps, J = 5 cps, 1 H), 8.1 (multiplet, 2 H), 8.7 (multiplet, 10 H), 9.11 (triplet, J = 5 cps, 3 H); ^{19}F nmr (CCl_4) see Results Section; m/e 150.1220 (calcd for $C_8H_{16}F_2$: 150.1220). *Anal.* Calcd for $C_8H_{16}F_2$: C, 63.92; H, 10.73. Found: C, 63.56; H, 10.70.

1,2-Difluorooctane (42)

The yield of compound 42 was 0.0024 mole (5.5%). Compound 42 is a colorless liquid: bp 147° at 690 mm; n_D^{20} = 1.3929; nmr (CCl_4) τ 5.5 (multiplet), 5.62 (doublet of doublets of doublets, J = 49 cps, J = 22 cps, J = 4.5 cps - the combined signals at τ 5.5 and 5.62 integrated for 3 H), 8.35 (multiplet, 2 H), 8.62 (multiplet, 8 H), 9.08 (triplet, J = 5 cps, 3 H); ^{19}F (CCl_4) see Results Section. *Anal.* Calcd for $C_8H_{16}F_2$: C, 63.92; H, 10.73. Found: C, 64.17; H, 10.94.

2-Acetoxy-2-fluorooctane (43)

The yield of compound 43 was 0.0013 mole (3.0%). Compound 43 is a colorless unstable liquid; ir (CCl_4) see Table X; nmr (CCl_4) τ 8.00 (singlet, 3 H), 8.34 (doublet, J = 19 cps, 3 H), 8.7 (multiplet, 10 H), 9.10 (triplet, J = 5 cps, 3H).

When neat 43 was reinjected on the glpc column (Column A at 180°), it completely decomposed to a new compound. The decomposition product was isolated and shown to be 2-octanone by comparison of its ir and nmr spectra with those of an authentic sample.

1-Acetoxy-1-fluorooctane (44)

The yield of compound 44 was 0.0065 mole (15.0%). Compound 44 is a colorless liquid: n_D^{20} = 1.4101; ir (CCl_4) see Table X; nmr (CCl_4) τ 3.77 (doublet of triplets, J_d = 56 cps, J_t = 5 cps, 1 H), 7.96 (singlet, 3 H), 8.3 (multiplet, 2 H), 8.7 (multiplet, 10 H), 9.12 (triplet, J = 5 cps, 3 H); ^{19}F nmr (CCl_4) see Results Section. *Anal.* Calcd for $C_{10}H_{19}FO_2$: C, 63.13; H, 10.07. Found: C, 62.91; H, 9.78.

Isolation of 1-Acetoxy-2,2-difluorooctane (48)

Both compounds 42 and 43 would decompose when the glpc column flooded. When this happened, compound 48 could be isolated (see Figure III). Compound 48 is a clear colorless

liquid: ir (CCl_4) see Table X; nmr (CCl_4) τ 5.84 (triplet, J = 12 cps, 2 H), 7.93 (singlet, 3 H), 8.5 (multiplet, 2 H), 8.7 (multiplet, 8 H), 9.12 (triplet, J = 5 cps, 3 H); ^{19}F nmr (CCl_4) see Results Section.

1-Acetoxy-2-fluorooctane (45)

The yield of compound 45 was 0.0053 mole (12.2%). Compound 45 is a colorless liquid: n_D^{25} = 1.4144 (lit.[35] n_D^{25} = 1.4134); ir (CCl_4) see Table X; nmr (CCl_4) τ 5.5 (doublet of multiplets, J = 50 cps, 1 H), 5.95 (doublet of doublets, J = 23 cps, J = 3 cps, 2 H), 7.97 (singlet, 3 H), 8.3 (multiplet, 2 H), 8.7 (multiplet, 8 H), 9.11 (triplet, J = 5 cps, 3 H); ^{19}F nmr (CCl_4) 187.38 ppm ($CFCl_3$) (multiplet). *Anal.* Calcd for $C_{10}H_{19}FO_2$: C, 63.13; H, 10.07. Found: C, 63.40; H, 10.17.

Preparation of 1,2-Octanediol

The synthesis of 1,2-Octanediol was achieved by the method described by Swern.[81] By this method, 20 g (0.18 mole) 39 gave 10.2 g (39%) of the diol: bp 135-136° at 9 mm (lit. 135-136° at 10 mm); n_D^{20} = 1.4494; ir (neat) ν 3450, 1075, 1040 cm^{-1}; nmr (CCl_4) τ 5.44 (multiplet, 2 H), 6.54 (multiplet, 3 H), 8.67 (multiplet, 10 H), 9.11 (triplet, J = 5 cps, 3 H).

Preparation of 1,2-Diacetoxyoctane (46)

To 2 g (0.014 mole) of the diol prepared above dis-

solved in 30 ml benzene, was added 4.8 g (0.056 mole) of freshly fused sodium acetate and 5 ml (0.050 mole) of acetic anhydride. This mixture was heated on a steam bath for 5 hours and then heated under vigorous reflux for an additional hour. The reaction mixture was cooled and poured into water. Enough sodium carbonate was added to neutralize the mixture. The mixture was transferred into a separatory funnel, the layers were separated, the aqueous layer was extracted with benzene, the combined organic portions were washed with water, and dried over anhydrous sodium sulfate. The benzene was removed by distillation through an 8 in Vigreaux column to yield 2.7 g (84%) of 46. Compound 46 was further purified by preparative glpc (Column A at 230°). Compound 46 is a colorless liquid: n_D^{20} = 1.4304; ir (CCl_4) see Table X; nmr (CCl_4) τ 5.05 (multiplet, 1 H), 5.97 (multiplet, 2 H), 8.02 (singlet, 6 H), 8.7 (multiplet, 10 H), 9.12 (triplet, J = 5 cps, 3 H). *Anal.* Calcd for $C_{12}H_{22}O_4$: C, 62.58; H, 9.63. Found: C, 62.90; H, 9.38.

The yield of compound 46 from the reaction of LTA-HF with 39 was 0.0029 mole (6.7%). The glpc retention time and the spectral data of synthetic 46 were found to be identical to those of compound 46 isolated from the reaction of LTA-HF with 39.

Preparation of 1-^{13}C-1-Acetoxyoctane

To 0.9 g (0.038 g-atom) magnesium turnings was added dropwise, with stirring, a solution of 5.4 g (0.030 mole) 1-bromoheptane in 100 ml of anhydrous ether. The Grignard reagent thus formed was carbonated with the carbon dioxide released from 3 g (0.015 mole) of carbon-13 enriched barium carbonate when it was treated with concentrated sulfuric acid. The procedure used for the carbonation reaction has been outlined in "Isotopic Carbon" for the synthesis of acetic acid-1-^{14}C.[82] Upon completion of the carbonation reaction, the reaction mixture was hydrolysed by the addition of 10 ml of concentrated sulfuric acid. The layers were separated and the ether layer was washed several times with water. The aqueous wash was saturated with sodium chloride and extracted with ether. The combined ether portions were extracted with saturated sodium bicarbonate solution. The aqueous extract was carefully neutralized with concentrated hydrochloric acid, saturated with sodium chloride, and extracted with ether. The ether solution was dried over anhydrous sodium sulfate.

The above procedure was repeated until a total of 15 g (0.075 mole) of carbon-13 enriched barium carbonate had been converted to octanoic acid. The octanoic acid was not isolated.

The ethereal solution (300 ml) of octanoic acid,

obtained above, was added dropwise, with stirring, to 5.2 g (0.14 mole - greater than two-fold excess) of LAH dissolved in 400 ml of anhydrous ether. When addition was completed, the reaction mixture was heated under reflux for four hours and then allowed to stand overnight. The excess LAH was destroyed by careful dropwise addition, with stirring, of water saturated ether. The reaction mixture was then treated with 200 ml 6N hydrochloric acid solution. The layers were separated and the organic phase was washed in succession with water, saturated sodium bicarbonate solution, water and finally dried over anhydrous sodium sulfate. The bulk of the ether was removed by distillation through an 8 in Vigreaux column.

The alcohol formed was not isolated but was treated with 9.7 ml (0.13 mole) of acetyl chloride added in a dropwise manner. When the initial reaction had subsided, enough of an aqueous 20% sodium hydroxide solution was added, in a dropwise fashion, to render the reaction mixture just alkaline to litmus. The layers were separated and the aqueous layer was extracted with ether. The combined ether portions were washed with water and dried over anhydrous sodium sulfate. Removal of the ether by distillation through an 8 in Vigreaux column resulted in 12 g (92% based on barium carbonate) of 1-^{13}C-1-acetoxyoctane: ir (neat) ν 1740, 1235 cm^{-1}.

Preparation of 1-^{13}C-1-Octene

The acetate prepared above was pyrolysed following the procedure of Wibaut.[83] By this method, 3.7 g (47%) 1-^{13}C-1-octene was isolated. The glpc retention time and ir spectrum were found to be identical to those of compound 39. For ^{13}C nmr see page 118.

Reaction of 1-^{13}C-1-Octene with LTA-HF

The reaction was run in an identical manner to that described above. Thus a solution of 3.7 g (0.033 mole) of 1-^{13}C-1-octene in 40 ml of dry methylene chloride was added to a cold (0°), stirred solution of 30 g (0.066 mole) of LTA and 3.9 ml (0.2 mole) of HF in 150 ml of dry methylene chloride. The reaction was quenched after 30 minutes reaction time and treated in the usual manner. Glpc analysis revealed that the product distribution was identical to that obtained from the reaction carried out with unlabelled material. The bulk of the solvent was removed by distillation through an 8 in Vigreaux column. Upon standing this solution changed color from pale yellow to dark brown. Glpc analysis of the dark brown solution revealed that the signals corresponding to compounds 43 and 44 had disappeared. A new signal having a retention time of about one minute longer than that of compound 42 (see Figure III) had appeared. The decomposition products were isolated, but not separated, by preparative glpc (Column A at 130°).

Isolation of 1-^{13}C-2-Octanol and 2-^{13}C-1-Octanol

To 200 mg (5 mmole) of LAH dissolved in 5 ml of anhydrous ether, was added dropwise, with stirring, a solution of 252 mg of the decomposition products, described above, in 15 ml of anhydrous ether. The reaction mixture was treated in the manner already described. Glpc analysis (Column A at 130°) revealed that two volatile products had been formed. The area ratio of the 2-octanol to the 1-octanol was found to be the same as the area ratio, before decomposition, of compound 43 to compound 44. The reduction products were isolated by preparative glpc (same column and conditions as above) and their nmr spectra were recorded (see Results and Discussion section).

Carbon-13 Nmr Studies

Carbon -13 nmr spectra were determined using a Bruker Scientific HFX-8 spectrometer operating in conjunction with a Frabri-Tek-1074/PDP-8L fast Fourier transform signal averager. The samples, isolated from glpc, were dissolved in deuteriochloroform and tetramethylsilane (TMS) was added as an internal reference. Chemical shifts were calculated relative to the internal TMS signal and for purposes of comparison may be converted to the benzene scale (TMS to benzene, 128.54 ppm). For ^{13}C nmr spectral data of the carbon-13 enriched compounds 40, 41, 42, and 45 see Table IX.

Carbon-13 Nmr Spectrum of Compound 39

Compound 39 showed proton decoupled carbon-13 resonances at 139.63, 114.65, 34.50, 32.45, 29.61, 29.51, 23.22, and 14.29 ppm. The carbon-13 nmr of 1-^{13}C-1-octene showed only one proton decoupled carbon-13 resonance at 114.65 ppm. This signal appeared as a nominal triplet (J = 154 cps) in the proton coupled ^{13}C nmr spectrum thereby confirming that the ^{13}C enriched carbon was in the C-1 position.

Carbon-13 Nmr Spectrum of Compound 41

The proton-decoupled carbon-13 nmr spectrum of compound 41 showed resonances at 131.30 (triplet, J = 237 cps), 34.41 (triplet, J = 19 cps), 32.06 (singlet), 29.09 (singlet), 29.07 (triplet, J = 32 cps), 22.90 (singlet), 22.42 (triplet, J = 5 cps), and 14.14 (singlet) ppm. The proton-decoupled spectrum of ^{13}C enriched compound 41 showed that only the resonance at 34.41 ppm was enhanced (see Table IX for results).

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A P P E N D I X

The construction and use of a calibration curve for the determination of molar amounts of products in a reaction mixture can most simply be illustrated by an actual example. The example chosen is the calibration of 1,1-difluorooctane (41) and "Freon 112".

Solutions with known molar amounts of "Freon 112" and compound 41 were prepared and subjected to glpc analysis using Column A 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 analysis of the reaction mixture obtained from the LTA-HF reaction with 1-octene.

A stock solution of 0.486 g (0.00238 mole) of "Freon 112" in 10 ml of methylene chloride was prepared. One ml of this solution was transferred into a solution of 0.118 g (0.000785 mole) of compound 41 in 5 ml of methylene chloride. For the resultant solution, the mole ratio of 41/"Freon 112" was 3.30. The observed area ratio of 41/"Freon 112" was 3.64 $\pm$ 0.07. This procedure was repeated using solutions obtained by successive additions of 1 ml aliquots of the "Freon 112" stock solution to the mixture described above. The results are tabulated in Table IX.

TABLE XI

Glpc Calibration of 1,1-Difluorooctane and "Freon 112"

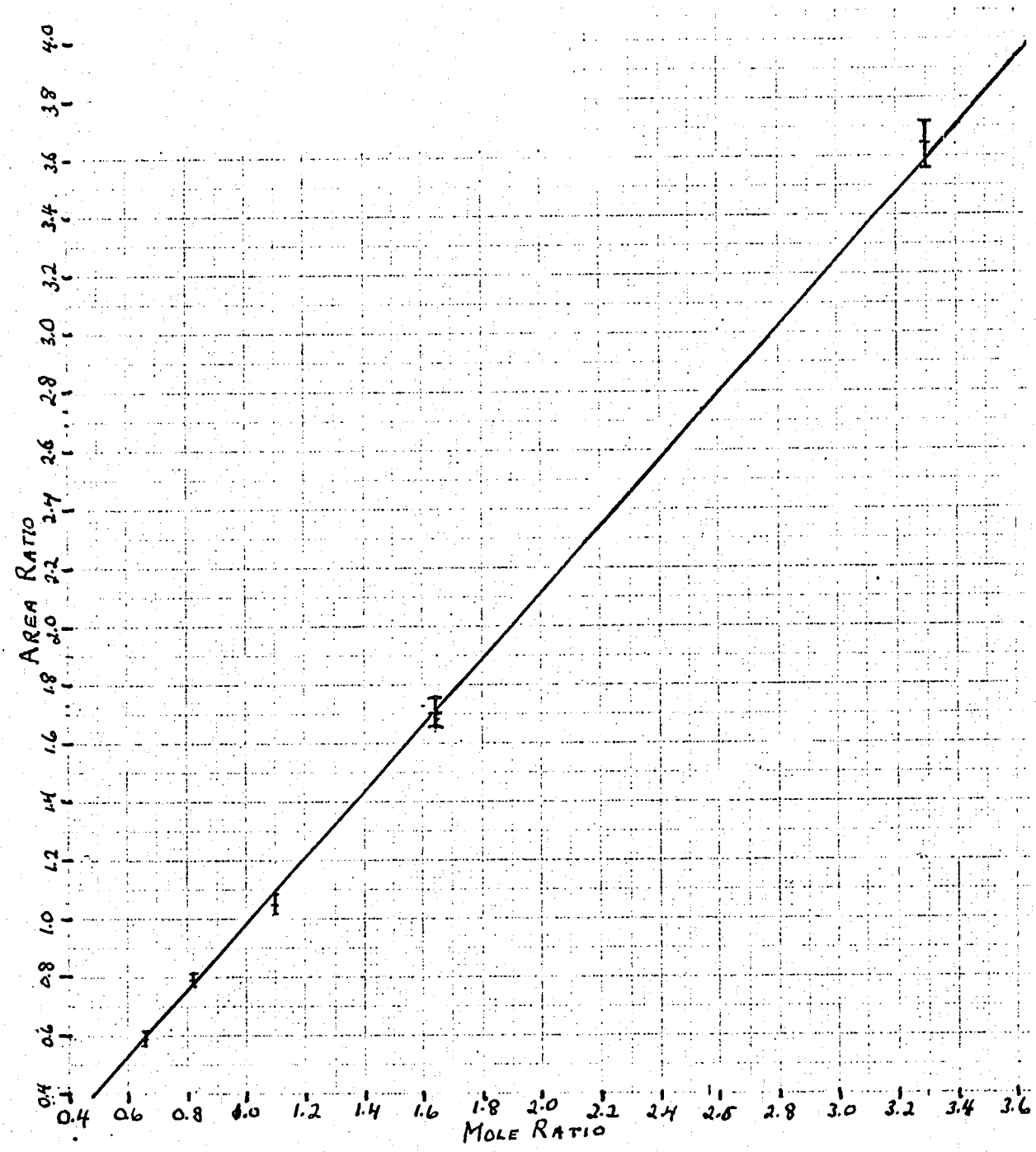
Mole Ratio	3.30	1.65	1.10	0.82	0.66
Area Ratio	3.64±0.07	1.70±0.05	1.05±0.03	0.79±0.02	0.59±0.02

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

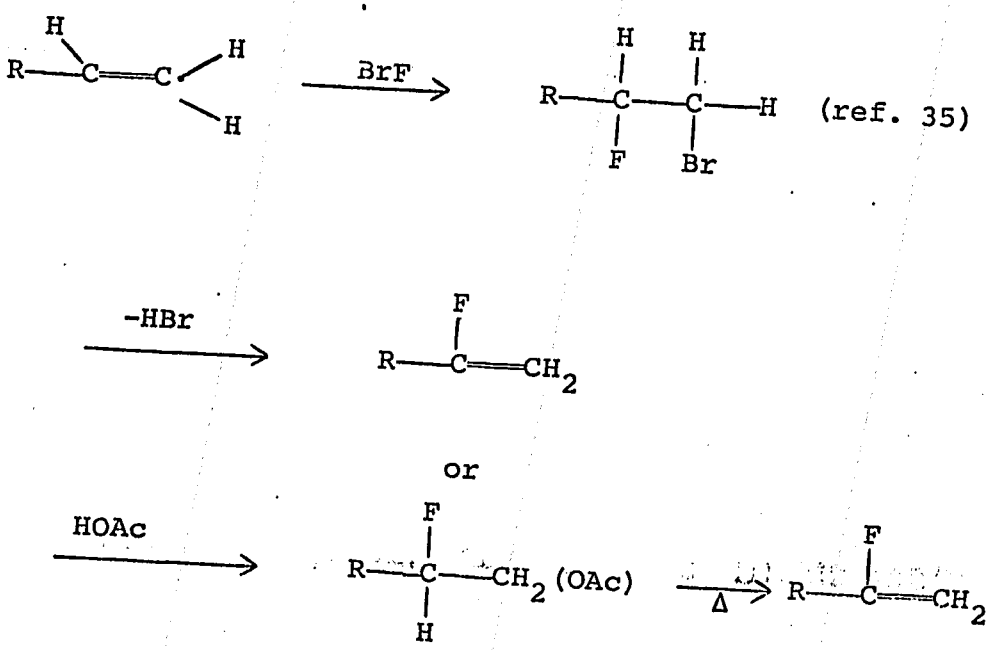
From the reaction mixture of the LTA-HF reaction with 1-octene (see Experimental Section) it was found that the area ratio of 41/"Freon 112" was 0.76 ± 0.02. From the calibration curve, the mole ratio corresponding to this area ratio is 0.81 ± 0.02. Since 0.0364 mole of "Freon 112" was added to the reaction mixture, the molar amount of 41 formed is (0.81 ± 0.02) x 0.0182 = 0.0148 ± 0.0003. Therefore the percent of 41 formed, based on the consumption of 1-octene, is 34.2 ± 1. It was assumed that the other difluorides obtained from the reaction would have the same response on the glpc detector as 41. Therefore the molar amounts of these compounds were calculated using the calibration curve shown in Figure IV.

Similar calibration curves were constructed for the other systems studied by glpc.

FIGURE IV Glpc Calibration Curve (Mole Ratio *vs* Area Ratio) for 1,1-Difluorooctane and "Freon 112".



Proposed Synthesis of 2-Fluoro-1-octene



The Reaction of 2-Fluoro-1-octene with LTA-HF

The synthesis of 2-fluoro-1-octene (47) was carried out as outlined in Scheme XXVII. The elimination reaction gave two compounds in a 1:1 ratio. The compound with the

SCHEME XXVII

$$R\text{-}CH{=}CH_2 \xrightarrow{\text{"BrF"}} R\text{-}CHF\text{-}CH_2Br \xrightarrow[MeOH]{NaOCH_3}$$

$$R\text{-}\overset{F}{\overset{|}{C}}{=}CH_2$$

47

R = n-hexyl.

shorter glpc retention time decolourized a bromine solution and was shown to be 2-fluoro-1-octene on the basis of its nmr and ir spectra and its microanalysis. The product with the longer glpc retention time was not characterized but is presumably 1-bromo-2-octene.

The nmr spectrum of 2-fluoro-1-octene (47) shows a doublet at τ 5.48 (J = 2 cps, 1 H), a doublet of doublets at τ 6.03 (J = 34 cps, J = 2 cps, 1 H), and a doublet of triplets at τ 7.86 (J_d = 16 cps, J_t = 6 cps, 2 H). By a comparison of the observed multiplicity of the resonance at τ

5.48 with standard spectra reported in the literature (which are similar in structure to compound 47) the τ 5.48 resonance may be assigned to the C-1 hydrogen which is *cis* to the fluorine atom. The magnitude of the geminal proton-proton spin-spin coupling in terminal olefins is reported to be from 0 to 3 cps.[84] The magnitude of this coupling is observed to be 2 cps in compound 47. The *cis* fluorine-proton spin-spin coupling constant is reported to be from 1 to 8 cps.[84] This coupling is unresolved in the nmr spectrum of compound 47. The resonance at τ 6.03 may be assigned to the C-1 hydrogen which is *trans* to the fluorine atom. The *trans* fluorine-hydrogen spin-spin coupling constant in an olefin is reported to be from 12 to 40 cps.[84] Thus the large coupling constant (34 cps) may be assigned to the *trans* fluorine-proton spin-spin coupling while the small coupling constant (2 cps) may be assigned to geminal proton-proton spin-spin coupling in the terminal olefin 47. The signal at τ 7.86 may be assigned to the C-3 methylene protons. These protons will be split into a doublet (J = 16 cps) by a vicinal C-2 fluorine atom and split into a triplet (J = 6 cps) by the C-4 methylene protons. The nmr data is consistent with that expected for 2-fluoro-1-octene.

The ir spectrum of the fluoro olefin shows carbon-carbon double bond stretching at 1660 cm^{-1} which is indicative of a terminal olefin.[38]

The synthetic 2-fluoro-1-octene (47) had an

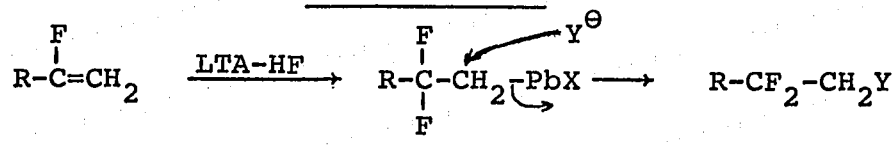
identical glpc retention time as the compound assumed to be 2-fluoro-1-octene obtained from the reaction of 1-octene with LTA-HF (see Figure 3, page 45). The fluoro olefin obtained from the reaction of 1-octene with LTA-HF could only be obtained admixed with 2,2-difluorooctane (40). All of the absorption bands present in the ir spectrum of synthetic 47 were also present in the mixture of 40 and 47 obtained from the LTA-HF reaction with 1-octene. These observations firmly establish that 2-fluoro-1-octene is indeed a product obtained in the reaction of LTA-HF with 1-octene.

Synthetic 2-fluoro-1-octene was treated with LTA-HF in a manner identical to that described for the LTA-HF reaction with 1-octene. Glpc analysis revealed that all of the starting olefin had reacted and that two products were formed in a 1:2.5 ratio. When 2,2-difluorooctane (40) was added to the reaction mixture a new "peak" was observed in the glpc chart thereby showing that 40 is not formed by the addition of HF to 47. This indicates that the compound 40 is probably formed by a 2,1-hydride shift as shown in Scheme XXI, pathway b (page 78). Compound 40 cannot arise by the alternate pathway suggested in Scheme XXII (page 80).

The products of the LTA-HF reaction with 47 were isolated by preparative glpc. The major product, having the longer retention time, was shown to have the identical

glpc retention time as 1-acetoxy-2,2-difluorooctane (48) (see Figure III, page 45) and had a superimposible nmr spectrum with compound 48. This shows that the formation of compound 48 in the LTA-HF reaction with 1-octene can be rationalized as shown in Scheme XXII (page 80). The minor product, having the shorter retention time, appears from the nmr spectrum to be 1,2,2-trifluorooctane (78). The nmr spectrum of 78 shows a doublet of triplets at τ 5.67 (J_d = 57 cps, J_t = 11 cps, 2 H). This resonance may be assigned to the C-1 protons on the basis of their chemical shift and multiplicity. The large coupling constant can be assigned to the geminal proton-fluorine spin-spin coupling while the small coupling constant can be assigned to the vicinal proton-fluorine spin-spin coupling. A more complete structural analysis is not available at this time. The formation of these products (48 and 78) can be rationalized as shown in Scheme XXXIII.

SCHEME XXXIII



R = n-hexyl X = $F_m(OAc)_{3-m}$ m = 0-3 Y = F (78) Y = OAc (48)

EXPERIMENTAL

Preparation of 1-Bromo-2-fluorooctane

The method used was similar to that described by Pattison and coworkers.[35] To 60 ml (3 moles) of HF at -80° was added 200 ml of cold, -80°, anhydrous diethyl ether. To this mixture was added, alternately, with stirring, (30 g; 0.11 mole) 1,3-dibromo-5,5-dimethylhydantoin (obtained from Arapahoe Chemical Co.) and a cold, -80°, solution of (30 g; 0.27 mole) 1-octene in 100 ml of anhydrous ether over a period of 45 minutes. The mixture was stirred at -80° for 3 hours and then allowed to stand at this temperature for an additional 10 hours. The reaction mixture was allowed to warm up to room temperature and was then slowly poured into a cold, 0°, saturated solution of potassium carbonate. The organic layer was separated and the aqueous layer was extracted with ether. The combined ether layers were washed in succession with water, saturated sodium bicarbonate solution, water, and finally dried over anhydrous sodium sulfate. The ether was removed and the residue was distilled under reduced pressure to yield 26 g (53%) of 1-bromo-2-fluorooctane: bp 89-91° at 12 mm (lit.[35] 90° at 16 mm); n_D^{25} = 1.4437 (lit.[35] n_D^{25} = 1.4423); nmr (CCl_4) τ 5.47 (doublet of multiplets, J = 48 cps, 1 H), 6.60 (doublet of doublets, J = 18 cps, J = 6 cps, 2 H), 8.1 (multiplet, 2 H), 8.65 (multiplet, 8 H), 9.08 (triplet, J = 5 cps, 3 H); ^{19}F nmr (CCl_4) 185.99 ppm ($CFCl_3$) (multi-

plet).

Preparation of 2-Fluoro-1-octene

To 10 g (0.047 mole) of the 1-bromo-2-fluorooctane prepared above was added 2.8 g (0.052 mole) of sodium methoxide and 15 ml of methanol. This mixture was heated to reflux with stirring for 8 hours. The reaction mixture was cooled and diluted with water and extracted with ether. The aqueous phase was saturated with sodium chloride and extracted with ether. The combined ether portions were washed with water and dried over anhydrous sodium sulfate. Glpc analysis (column A linearly programmed from 100-250° at 10° per minute) revealed that 85% of the 1-bromo-2-bromooctane had reacted (estimated from peak area measurements) and two products were formed in a 1:1 ratio. The product with the shorter retention time was isolated by preparative glpc and shown to be 2-fluoro-1-octene: bp 132° at 690 mm; n_D^{25} = 1.4011; ir (CCl_4) ν 1660 cm^{-1}; nmr (CCl_4) τ 5.48 (doublet, J = 2 cps, 1 H), 6.03 (doublet of doublets, J = 34 cps, J = 2 cps, 1 H), 7.86 (doublet of triplets, J_d = 16 cps, J_t = 6 cps, 2 H), 8.65 (multiplet, 8 H), 9.08 (triplet, J = 5 cps 3 H); ^{19}F nmr (CCl_4) 93.48 ppm ($CFCCl_3$) (multiplet). *Anal.* Calcd for $C_8H_{15}F$: C, 73.79; H, 11.61. Found: C, 73.57; H, 11.58.

Reaction of 2-Fluoro-1-octene (47) with LTA-HF

This reaction was run in an identical manner as that described for the reaction of 1-octene with LTA-HF. By this procedure, a solution of 0.99 g (0.0076 mole) 47 and 0.98 g (0.0048 mole) "Freon 112" in 10 ml of dry methylene chloride, pre-cooled to 0°, was added to a stirred solution of 7 g (0.016 mole) LTA and 1 ml (0.05 mmole) HF in 35 ml of dry methylene chloride at 0°. The resultant mixture was stirred at 0° for 30 minutes, then quenched and treated as previously described. Glpc analysis (column A linearly programmed from 80° to 275° at 8° per minute) revealed that all of compound 47 had reacted and that two compounds were formed. The larger component (70% by peak area measurement) had an identical glcp retention time and nmr spectrum as 1-acetoxy-2,2-difluoro-octane. *Anal.* Calcd for $C_{10}H_{18}F_2O_2$: C, 57.67; H, 8.71. Found: C, 58.00: H, 9.17. The smaller component (30% by peak area measurement) had a nmr spectrum which is consistant for 1,2,2-trifluorooctane: nmr (CCl_4) τ 5.67 (doublet of triplets, J_d = 57 cps; J_t = 11 cps, 2 H), 8.2 (multiplet, 2 H), 8.65 (multiplet 8 H), 9.09 (triplet, J = 5 cps, 3 H).