tion a more favorable pathway than the oxidation of a single substrate.

The oxidation of a single molecule of a substrate, *e.g.*, isopropyl alcohol, leads to an unstable and very reactive chromium(IV) species.[21] One can certainly expect that the reaction would be greatly facilitated if chromium(VI) could be reduced directly to chromium(III), thus avoiding the formation of the energetically unfavorable chromium(IV). The presence of the molecule of oxalic acid within the complex offers such a possibility. We thus propose that the unusual reactivity is due to the fact that the reaction represents a direct three-electron reduction of chromium(VI) to chromium(III) coupled with the formation of a very stable molecule of carbon dioxide and of a relatively stable free radical, $\cdot CO_2H^-$ or $\cdot CO_2H$.

This mechanism is strongly supported by the observation that the two products, acetone and carbon dioxide, are formed in exactly equimolar ratios in the presence of a free-radical trap. The ratio does not depend on the relative concentration of isopropyl alcohol and oxalic acid in the solution. Thus no intermediate chromium species is produced in the reaction which would have a long enough lifetime to react with a molecule in its surrounding. Instead, one would have to assume that it reacts entirely with the oxalic acid molecule present in the complex. Thus, one would have to postulate the formation of a very short-lived chromium(IV)–oxalic acid intermediate for which no evidence of kinetic independence could be obtained. The proposed mechanism, in which such an intermediate is never formed but chromium(VI) is reduced directly to chromium(III) in the rate-limiting step, not only correctly predicts the product ratio and its independence of the composition of the solution, but also offers a very attractive interpretation of the unusual two-substrate activated complex and of the high rate of the cooxidation reaction. To the best of our knowledge, the cooxidation of oxalic acid and isopropyl alcohol by chromic acid presents the first case where there is valid ground to believe that a one-step three-electron oxidation is taking place.

Some data can be quoted to support the assumption of the stability of the $\cdot CO_2^-$ or $\cdot CO_2H$ radicals. The C–H bond dissociation energy for formic acid is 90 kcal/mol, which is 14 kcal/mol lower than that of the C–H bond in methane and 1 kcal/mol lower than for the tertiary C–H bond in isobutane. This indicates that the $\cdot CO_2H$ radical should be more stable than the *tert*-butyl radical.[22] A similar value can be derived from the bond dissociation energies for the C–C bonds of ethylbenzene and phenylacetic acid. The energies for breaking of the bonds which would lead to a benzyl radical as one fragment and to a methyl or carboxyl radical as the other fragment are 70 and 55 kcal/mol, respectively, indicating that the $\cdot CO_2H$ radical is 15 kcal/mol more stable than the methyl radical.[23] The $\cdot CO_2^-$ radical ion is stable enough to permit its formation and direct observation in the gas phase,[24] as well as the use of CO_2 as scavenger for solvated electrons in radiation chemistry.[25]

Acknowledgment. The authors wish to thank Dr. E. A. Gislason for helpful discussions.

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(22) S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965).
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Mechanism for the Reaction of Lead Tetraacetate and Hydrogen Fluoride with Olefins

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Abstract: A mechanism for the reaction of the lead tetraacetate–hydrogen fluoride reagent with olefins has been proposed. From a mechanistic analysis of the possible paths leading to the formation of the products from the reactions of 1,1-diphenylethylene and norbornene with this reagent, it is proposed that a transient intermediate lead–ligand addition product is first formed in these reactions. Breaking of the lead–carbon bond yields cationic intermediates which result in the observed products. The nature of the rearrangement products in both reactions necessitates the formation of carbonium ion species, and the stereochemistry of the products formed in the norbornene reaction is best explained by a cis-exo-2,3-metal–ligand addition to this olefin as the first step in the reaction sequence.

The fluorination of an olefin by lead tetraacetate and hydrogen fluoride was first reported 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 obtained in 28% yield. Accompanying the fluorinated material, deoxybenzoin was obtained in a 15% yield. These authors proposed that lead tetrafluoride was the active halogenating reagent and assigned the structure 1,2-difluoro-1,1-di-

(1) O. Dimroth and W. Bockemüller, *Chem. Ber.*, 64, 516 (1931).

phenylethane to the difluoride. The difluoride obtained by Dimroth and Bockemüller has subsequently properly been reassigned the structure 1,1-difluoro-1,2-diphenylethane.[2]

Dimroth's method was used by Bowers and coworkers[3] in the fluorination of pregnenolone acetate (**1**), and they were able to obtain a 27% yield of the *cis*-5,6-difluoro derivative **2** and 63% recovered **1**. In order to rationalize the stereochemistry of the adduct, a cis molecular addition mechanism was proposed.

Bornstein, *et al.*,[4] have repeated the older work on the fluorination of 1,1-diphenylethylene. These results were essentially the same as those of the earlier workers. However, when the reaction was run at −40° for 10 min, not only were deoxybenzoin and 1,1-difluoro-1,2-diphenylethane (**3**) found but also 1,4-difluoro-1,1,4,4-tetraphenylbutane (**5**) was isolated in a 25% yield. The following free-radical sequence proposed by Bornstein to rationalize these findings is shown in Scheme I.

Scheme I

i. $Ph_2C{=}CH_2 \xrightarrow[HF]{Pb(OAc)_4} \underset{\mathbf{4}}{Ph_2\dot{C}FCH_2}$

ii. $2\underset{\mathbf{4}}{Ph_2\dot{C}FCH_2} \longrightarrow \underset{\mathbf{5}}{Ph_2CFCH_2CH_2CFPh_2}$

iii. $Ph_2\dot{C}FCH_2 \longrightarrow Ph\dot{C}FCH_2Ph$

iv. $Ph\dot{C}FCH_2Ph \xrightarrow{F\cdot} \underset{\mathbf{3}}{PhCF_2CH_2Ph}$

Recently Bornstein and Skarlos[5] have shown that lead tetrafluoride will not react with 1,1-diphenylethylene in the absence of glacial acetic acid. These authors suggested that the active fluorinating reagent is lead(IV) diacetate difluoride, and have convincingly demonstrated that this reagent, when synthesized, gives the same difluoride upon reaction with 1,1-diphenylethylene as does the lead tetraacetate–hydrogen fluoride reagent.

The mechanistic conclusions reached by Bornstein regarding the formation of compounds **3** and **5**, and the lack of explanation in these mechanisms for the formation of deoxybenzoin, bear some comment, and have prompted us to further investigate the reaction with other olefins. The formation of the dimer **5** was taken by the previous workers[4] as evidence for a free-radical intermediate, although the radical formed is the least stable of the two possible. Similarly, it can be proposed that a cationic species can lead to dimeric products although the first formed cation would likewise be the least stable of the two possible structures.

$$Ph_2C\overset{+}{F}CH_2 + Ph_2C{=}CH_2 \longrightarrow Ph_2CFCH_2CH_2\overset{+}{C}Ph_2 \xrightarrow{F^-} \mathbf{5}$$

Both paths are equally probable and might both arise from a likely organometallic precursor, **6**, by either homolytic (b) or heterolytic (a) cleavage of the lead–carbon bond, or even more probably by the nucleophilic displacement of lead by the olefin (c) (Scheme II).

Scheme II

$Ph_2CFCH_2Pb^{IV}(F)_x(OAc)_y$

6, $x, y = 0$–3

$$\xrightarrow{a} Ph_2C\overset{+}{F}CH_2 + (F^- \text{ or } {}^-OAc) + Pb^{II}(F)_x(OAc)_y$$

$$\xrightarrow{b} Ph_2C\dot{F}CH_2 + \cdot Pb^{III}(F)_x(OAc)_y$$

$$\xrightarrow[Ph_2C=CH_2]{c} Ph_2\overset{+}{C}CH_2CH_2CFPh_2$$

The possibility that addition of **6** to the olefin gives a new lead alkyl intermediate which could then lead to the product by analogous pathways can also be proposed.

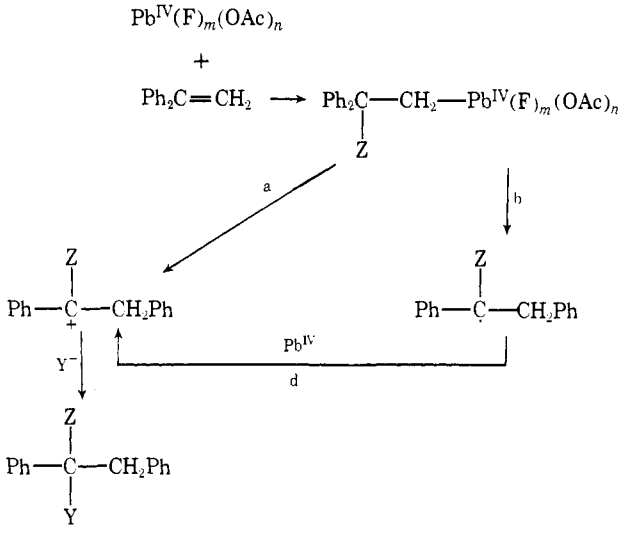
The reaction path can be further complicated by the intrusion of the well-documented and facile interconversion of a radical to a cationic intermediate by Pb(IV).[6]

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

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

On the basis of a transient lead addition intermediate the remaining reaction product **3** and the formation of a precursor to deoxybenzoin can easily be rationalized (Scheme III) by the inclusion of a concomitant phenyl

Scheme III



Z, Y = F or OAc
$m, n = 0$–3

migration at an appropriate step in the reaction scheme, while if an oxidation–reduction sequence (d) takes place it may be prior to or after the migration of the phenyl group.

Metal–ligand addition compounds are well documented as intermediate species in the reactions of thallic acetate[7] and nitrate[8] with olefins, in oxymercuration reactions,[9] and have been suggested as intermediates in

(2) J. Bornstein and M. R. Borden, *Chem. Ind. (London)*, 441 (1958).
(3) A. Bowers, P. G. Holton, E. Denot, M. C. Loza, and R. Urquiza, *J. Amer. Chem. Soc.*, **84**, 1050 (1962).
(4) J. Bornstein, M. R. Borden, F. Nunes, and H. I. Tarlin, *ibid.*, **85**, 1609 (1963).
(5) J. Bornstein and L. Skarlos, *ibid.*, 90, 5044 (1968).
(6) (a) J. K. Kochi, *ibid.*, 87, 3609 (1965); (b) J. K. Kochi, J. D. Bachu, and T. W. Bethea III, *ibid.*, **89**, 6538 (1967); (c) R. O. C. Norman and C. B. Thomas, *J. Chem. Soc. B*, 771 (1967).
(7) (a) K. C. Pande and S. Winstein, *Tetrahedron Lett.*, 3393 (1964), and references cited therein; (b) R. J. Ouellette, G. Kordosky, C. Levin, and S. Williams, *J. Org. Chem.*, **34**, 4104 (1969), and references cited therein.
(8) E. C. Taylor and A. McKillop, *Accounts Chem. Res.*, **3**, 338 (1970).
(9) (a) T. G. Traylor and A. W. Baker, *J. Amer. Chem. Soc.*, **85**, 2746 (1963), and references cited therein; (b) H. J. Lucas, F. R. Hepner, and S. Winstein, *ibid.*, 61, 3102 (1939); (c) T. G. Traylor, *Accounts Chem. Res.*, **2**, 152 (1969).

Table I. Nmr Spectral Data for 2,7-Dihalonorbornanes

Compound	τ, C_2–H	Mult	J, cps	τ, C_7–H	Mult	$W_{1/2}$, cps	J, cps
17	5.50	d^m	58	5.01	d	5	58
2-*exo*-Br-7-*anti*-Br	6.07	t		5.57	s	4	
2-*exo*-F-7-*anti*-Br	5.14	d^t	52	5.81	s	4	
20	5.37	d^m	57	5.32	d	4	56
2-*exo*-Cl-7-*syn*-Cl	6.22	m		6.18	s	4.5	
2-*exo*-Br-7-*syn*-Br	6.10	m		6.07	s	4.5	
2-*exo*-F-7-*syn*-Br	5.3	d^m	60	6.13	s	4	

the oxidation reactions of lead tetraacetate[6c,10] with olefins.

In the reaction of styrene with lead tetraacetate[6c] both homolytic and heterolytic pathways, as well as an oxidation of a benzyl radical to its corresponding carbonium ion by Pb^{IV}, have been evoked to rationalize the reaction products.

The oxidation of the bicyclic olefin norbornene (**14**) has been used as a mechanistic probe to elucidate the mechanism and stereochemistry of oxymercuration,[9a] thallic acetate,[7a] and lead tetraacetate[10a] 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 path proceeding *via* cationic intermediates.

We would like to report in this publication our work on the mechanism for the reaction of this reagent with two of the unsaturated hydrocarbons that we have studied.

Results and Discussion

Reaction of 1,1-Diphenylethylene. 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[4] except that aliquot samples of the reaction mixture in solvent methylene chloride (rather than chloroform), containing an internal standard, Freon 112, were quenched at varying reaction times. The reaction mixtures were then subjected to glpc analysis. A reaction that had been run for 1 min showed only three volatile components. A comparison of the glpc retention times of the materials indicated that besides starting material the major product was 1,1-difluoro-1,2-diphenylethane. The starting material had reacted to 90%, and the ratio of the major product and the minor product was 1.6:1.

A second fraction that was quenched after 45 min showed that all of the starting material had reacted and that a 51% yield of the major product was formed; the minor product now appeared to have been partially transformed into a third product having an identical retention time with that of deoxybenzoin. The ratio of the difluoride to the deoxybenzoin plus its precursor remained unchanged at all reaction times. When the difluoride was subjected to the reaction conditions it was found to be unreactive.

The three products of the reaction mixture were collected by preparative glpc, and the identification of the difluoride and the deoxybenzoin was confirmed by a comparison of their ir spectra with those of authentic materials. The ir spectrum of the precursor of deoxybenzoin showed the characteristic absorption of an acetate carbonyl at 1758 cm^{-1}. 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) was consistent with a $C_{16}H_{14}O_2$ ion, which we have assigned to the mass of the parent ion minus hydrogen fluoride or acetic acid. A tentative structure 1-acetoxy-1-fluoro-1,2-diphenylethane (**7a**) or 1,1-diacetoxy-1,2-diphenylethane (**7b**) has been assigned to the precursor of deoxybenzoin. The precursor could have one of the nine possible structures **7**–**12**.

$PhC(OAc)(Y)CH_2Ph$ **7a**, Y = F **b**, Y = OAc	$Ph_2C{=}CH(OAc)$ **10**
$PhCH(OAc)CHPh(Y)$ **8a**, Y = F **b**, Y = OAc	$Ph_2C(OAc)CH_2Y$ **11a**, Y = F **b**, Y = OAc
$Ph(OAc)C{=}CHPh$ **9**	Ph_2CFCH_2OAc **12**

The enol acetate **9** was prepared and subjected to the reaction conditions. No trace of deoxybenzoin or 1,1-difluoro-1,2-diphenylethane (**3**) was observed. Since on mechanistic ground **8a,b**, **10**, and **11a,b** can only yield deoxybenzoin *via* the intermediacy of **9** or its protonated analog, these compounds can also be eliminated as the structure of the deoxybenzoin precursor. Structure **12**, to yield deoxybenzoin, must proceed through the intermediacy of the protonated form of **9** or through an intermediate which could equally as well yield **3**. Since the ratio of **3** to deoxybenzoin plus its precursor remained constant throughout the course of the reaction, **12** could also be eliminated.

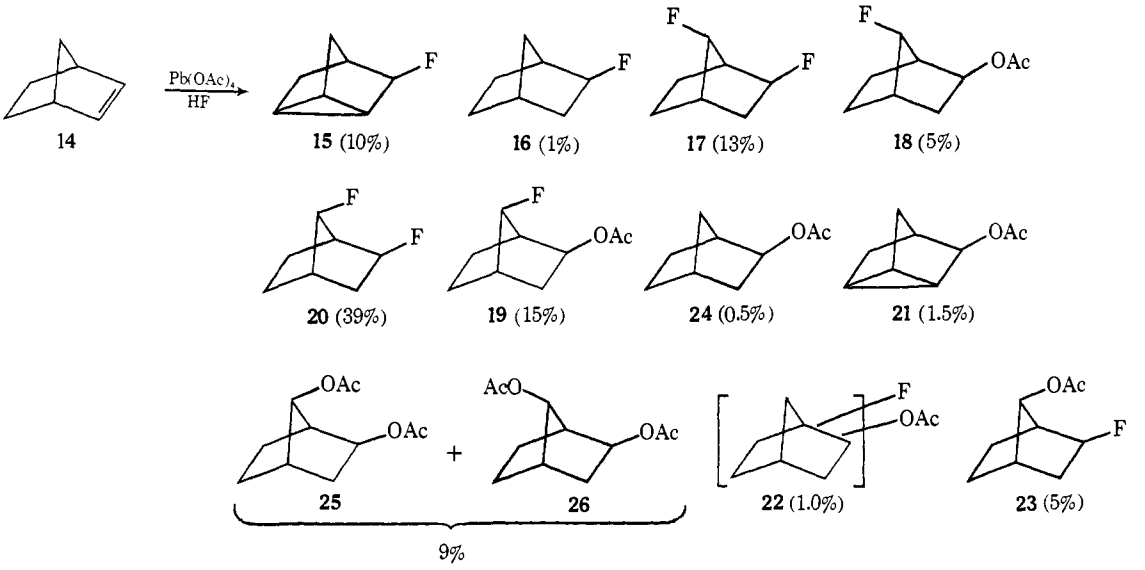
At the conclusion of the reaction (125 min) in addition to **3** and deoxybenzoin, small amounts of 3-methyl-1,1,3-triphenylindan (**13**), 1%, and 1,4-difluoro-1,1,4,4-tetraphenylbutane (**5**), 1.5%, were observed. These products had, likewise, previously been reported by Bornstein.[4]

The mechanism for the formation of **5** could as easily result in the formation of 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 be formed in *ca.* the same or lower yields than **5** (1.5%), no attempt was made to identify these products.

Reaction of $Pb(OAc)_4$–HF with Norbornene. Norbornene was treated with the lead tetraacetate–hydrogen fluoride reagent and gave a 101% yield of 11 major products (>1%) (**15**–**23** and **25**–**26**) and several minor products (<1%); see Scheme IV. Analysis of the re-

(10) (a) K. Alder, F. H. Flock, and H. Wirtz, *Chem. Ber.*, **91**, 609 (1958); (b) R. O. C. Norman and C. B. Thomas, *J. Chem. Soc. B*, 604 (1967), and references cited therein.

Scheme IV



action mixture by glpc, using an added internal standard, gave the yields, based on the norbornene used, which are listed in Scheme IV.

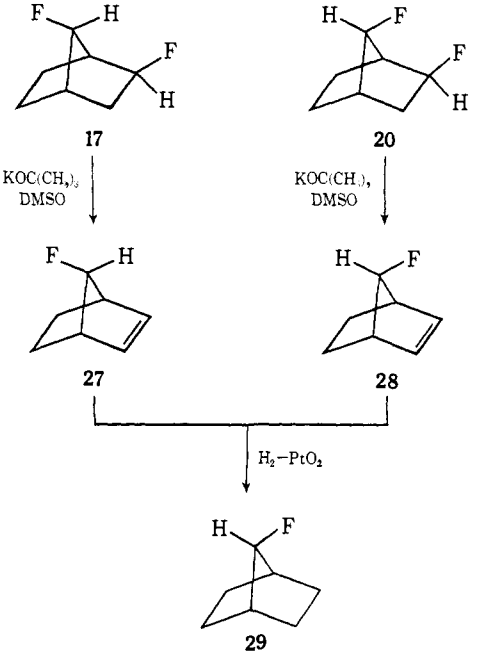
The products of the reaction were collected by preparative glpc. The structures of compounds **15**, **16**, **21**, and **24** were assigned by a comparison of their ir spectra with those of authentic samples. Compounds **25** and **26** were isolated as a 3:1 mixture (nmr integration) from the reaction of $Pb(OAc)_4$ with **14** in acetic acid. The ir and nmr spectra of this mixture were identical with those of the materials having the same retention time isolated from the reaction of $Pb(OAc)_4$–HF with **14** (see Experimental Section).

Compounds **17** and **20** were shown to be difluoronorbornanes by their microanalyses and nmr (^1H and ^{19}F) spectra. It was evident from the integrated nmr spectra that both difluorides had two nonequivalent fluorine atoms each attached to a carbon having a single hydrogen. The base-promoted dehydrofluorination of **17** and **20** yielded two different monosubstituted norbornenes **27** and **28** (see Scheme V). The nmr spectra of **27** and **28** both showed two vinyl protons, thus establishing that their hydrofluorinated precursors were not vicinal difluorides. The hydrogenation of both **27** and **28** yielded the same monofluoronorbornane, **29**, firmly establishing that both **20** and **17** are 2,7-difluoronorbornanes and that compound **29** must be 7-fluoronorbornane (see Scheme V). The stereochemistry of the substituents in compounds **20**, **17**, **27**, and **28** could be established from their nmr spectra, and their structural assignments as well as that of **29** could likewise be confirmed spectrally. The chemical evidence demands that **17** and **20** must be one of either four sets of isomeric pairs (syn-exo and anti-exo, syn-exo and anti-endo, anti-exo and syn-endo, syn-endo and anti-endo) of epimeric difluorides.

The nmr spectra of **17** and **20** could be compared with those of their halogen analogs; see Table I.

Of the two hydrogens geminate to a fluorine in both **17** and **20**, the low-field absorption can be assigned to the C_7 hydrogen by analogy with the assignments made for their halogen analogs.[11]

Scheme V



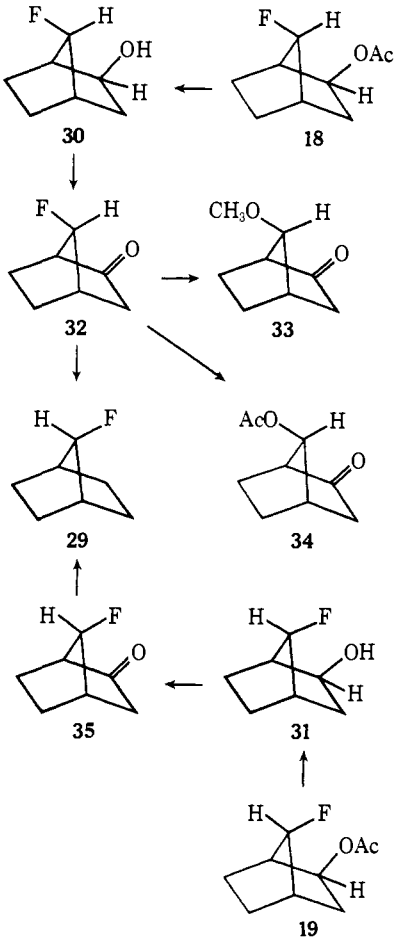
The endo C-2 proton of **17** shows a large geminal coupling due to the fluorine to give the doublet, J_d = 58 cps, vicinal couplings due to the exo and endo C-3 protons, a small vicinal coupling due to the C-1 proton, and a long-range coupling due to the anti C-7 fluorine (W effect), causing each branch of the doublet to appear as a multiplet. Similar couplings for the endo C-2 proton are seen for all of the other compounds listed in Table I.

Having established the stereochemistry at C-2 for both **17** and **20**, and also having obtained an indication of the C-7 stereochemistry, an analysis of the nmr spectra of the epimeric dehydrohalogenation products of these difluorides allows a yet firmer assignment of the stereochemistry at C-7 for each of the isomers.

A comparison of the nmr spectrum of **27** and **28** shows the C-7 proton absorption of the anti epimer to

(11) The authors wish to thank Professor E. W. Warnhoff for making the spectra of the bromine-containing analogs of **17** and **20** available to us prior to their publication. See F. H. Dean, D. R. Marshall, E. Warnhoff, and F. L. M. Pattison, *Can. J. Chem.*, **45**, 2279 (1967); D. R. Marshall, J. R. Robinson, P. Reynolds-Warnhoff, and E. W. Warnhoff, *ibid.*, **49**, 885 (1971).

Scheme VI



be centered at τ 5.82 (J_d = 60 cps). The shift of the C-7 proton absorption to a higher field in the case of the anti isomer is expected since the C-7 proton is shielded by the double bond in the case of a variety of simple anti 7-substituted norbornene derivatives.[12]

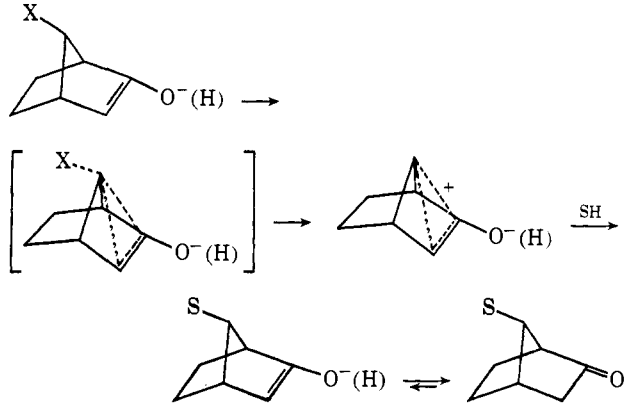
Further support for the stereochemical assignments of **27** and **28** was obtained from their mass spectral fragmentation patterns. Mass spectral analysis of **28** showed a molecular ion at *m/e* 112; however, the first major fragmentation peak of compound **28** was *m/e* 97 (M − 15).

In the case of the fragmentation of **27**, the base peak is *m/e* 93 (M − 19), indicating a stable ion formed by the loss of the fluorine atom. No parent peak was observed. Presumably the loss of fluorine in **27** is assisted by the anti-olefinic double bond, analogous to the stabilization which takes place upon the solvolysis of *anti*-7-norbornenyl derivatives.[13]

Of the four fluoro acetates **18**, **19**, **22**, and **23**, only **18** and **19** could be separated and isolated. Fluoro acetate **23** could be collected admixed with a minor amount of **19**. Microanalysis of the mixture gave a correct analysis for a fluoro acetate. A nmr spectrum of **23** was consistent with 2-*exo*-fluoro-7-*syn*-acetoxynorbornane, but this assignment must remain speculative.

Compounds **18** and **19** were both converted to 7-fluoronorbornane (**29**) by the reactions shown in Scheme VI, thus establishing the structures of both to be isomeric 7-fluoro-2-acetoxynorbornanes. The stereochemistry at C-7 for the two fluoro acetates was established both chemically and by nmr.

Whitham has shown that 7-*anti*-chloronorbornan-2-one solvolyzed with MeOH–MeO$^-$ to give exclusively 7-*anti*-methoxynorbornan-2-one while the epimeric 7-*syn*-chloronorbornan-2-one did not react under these reaction conditions.[14] Gassman has observed a rate enhancement of 10^7 for the solvolysis of 7-*anti*-hydroxynorbornan-2-one *p*-toluenesulfonate over 7-norbornyl *p*-toluenesulfonate.[15] The sole product of 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 back side, and furthermore, this participation results in the maintenance of stereochemistry prior to nucleophilic attack by solvent.



When the fluoro ketone **32**, derived from **18**, was subjected to solvolysis in methanol–sodium methoxide at 75° for 11 hr, a 95% yield of a single methoxy ketone **33** was obtained. Compound **33** had the same ir and nmr spectra as those of an authentic sample of 7-*anti*-methoxynorbornan-2-one.[16] When **32** was subjected to acetolysis in dry acetic acid at 150° for 800 hr, a single product was formed, 75% reaction, whose ir spectrum was identical with that of 7-*anti*-acetoxynorbornan-2-one[17] (**34**). When the fluoro ketone **35** was subjected to the same reaction conditions, the methanolysis gave only unreacted starting material, while acetolysis conditions showed only approximately 10% reaction and yielded four products.

The nmr (^{1}H and ^{19}F) spectra of **30** and **31** were taken with and without added 2,2,6,6-tetramethylheptadioneeuropium (III), 5%. The absorption spectra for the two fluoro alcohols are tabulated in Table II with and without added Eu^{III} complex.

The results of the solvolysis reactions of **32** and **35**, and their chemical conversion, establish the stereochemistry of the C-7 fluorine as anti in compounds **18**, **30**, and **32**, and syn in compounds **19**, **31**, and **35**. The large pseudo-contact shift observed for the syn-7 proton in **30** compared with the much smaller shift observed for the anti-7 proton in **31** establishes the

(12) B. Franzus, W. C. Baird, Jr., N. F. Chamberlain, T. Hines, and E. I. Snyder, *J. Amer. Chem. Soc.*, 90, 3721 (1968), and references therein.

(13) (a) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *ibid.*, 77, 4183 (1955); (b) S. Winstein and C. Ordronneau, *ibid.*, 82, 2084 (1960).

(14) J. T. Lamb and G. H. Whitham, *Chem. Commun.*, 400 (1966).

(15) P. G. Gassman and J. L. Marshall, *J. Amer. Chem. Soc.*, 88, 2599 (1966).

(16) The authors are indebted to Professor G. H. Whitham for furnishing us the spectrum of the authentic compound, 33.

(17) The authors are indebted to Professor P. G. Gassman for furnishing us the spectrum of the authentic compound, 34.

Table II. Chemical Shifts (^{1}H and ^{19}F, 60 Mc) of **30** and **31** with and without Added Eu^{III} Complex

Compound	$\tau(C_7\text{–}H)$ (J_d, cps)	$\tau(C_2\text{–}H)$	$(C_7\text{–}F)^a$ (J_d, cps)
30	5.12 (57)	6.35	210.1 (57)
30 + Eu^{III} complex	3.94 (57)	0.75	210.4 (57)
31	5.17 (54)	6.25	200.7 (54)
31 + Eu^{III} complex	4.70 (54)	1.72	199.9 (54)

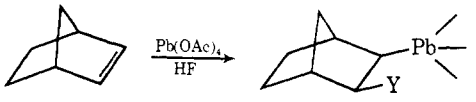
[a] Parts per million from $CFCl_3$.

close proximity of the complexed alcohol[18] to the indicated proton, and therefore establishes the structure of **30** to be 7-*anti*-fluoro-2-*exo*-norborneol and **18** to be its acetylated derivative.

The stereochemistry of the C-2 acetate and hydroxyl in compounds **19** and **31** was assigned on the basis of the observed pseudo-contact shifts between the Eu^{III} alcohol complex and the syn fluorine and anti proton. The shift as observed in the fluorine spectra is larger than that for the corresponding anti fluoro isomer and the C-7 proton shift is smaller than that observed in compound **30**. It seems unreasonable to expect Eu^{III} shift of the magnitude observed in **31** if the hydroxyl group were in the endo configuration, far removed from the C-7 substituents.[19]

It is of interest that the magnitude of the pseudo-contact shift for the anti 7-fluoride is shifted upfield, a phenomenon not understood at this time.

Mechanism of the Reaction of $Pb(OAc)_4$–HF with Norbornene. Metal–ligand additions to norbornene, oxymercuration,[9a] and oxythallation[7a] lead to stable cis–exo molecular addition products. By analogy the products of the lead tetraacetate–hydrogen fluoride reaction can also be satisfactorily rationalized as being derived from the cis–exo addition product **36**. Since



36
Y = F or OAc

all of the isolated disubstituted products of the reaction are rearranged 2,7-disubstituted norbornanes, and since no free radical rearrangements of norbornyl systems have been reported at ordinary temperatures,[20] a homolysis of the lead–carbon bond, if it takes place, must be rapidly followed by an oxidation step to yield a cationic intermediate, which then can undergo rearrangement. No evidence for or against this process is available at this time.

The intermediate **36** can lead to products *via* the reaction paths shown in Scheme VII. Path a leads to the nortricyclyl products **15** and **21** *via* loss of a proton. The formation of nortricyclyl products during addition reactions to norbornene has precedence since ionic additions to this olefin generally lead to significant amounts of substituted nortricyclenes.[21] In independent experiments it was shown that both nortricyclyl fluoride and nortricyclyl acetate were stable under the reaction conditions.

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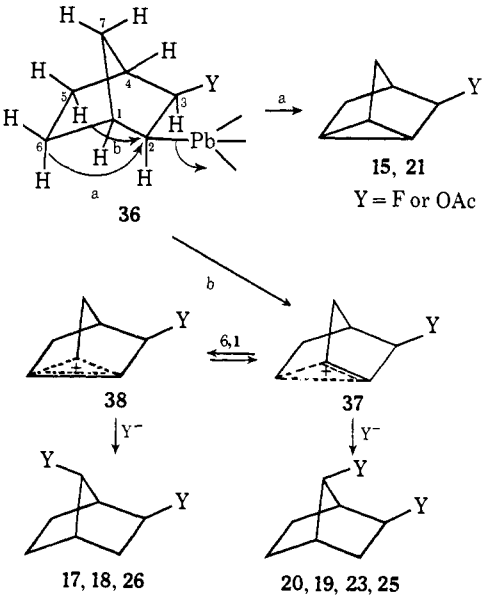
(21) R. C. Fahey, *Top. Stereochem.*, **3**, 250 (1968).

Scheme VII



Path b, by assisted heterolysis of the carbon–lead bond, leads to a norbornyl cation **37** which is attacked by a nucleophile at the most electrophilic carbon, C-1, to give rearranged *syn*-7-*exo*-2-disubstituted norbornanes **20**, **19**, **23**, and **25**. The substituted norbornyl cation **37** can alternatively undergo a competitive 6,1-hydride shift to give cation **38**, which upon nucleophilic attack at the more positively charged C-6 center (*i.e.*, that furthest away from the electronegative substituent) will yield *anti*-7-*exo*-2-disubstituted norbornanes **17**, **18**, and **26**. The 6,1-hydride shift has recently been established as leading to product in a number of ionic addition reactions of norbornene.[11]

The formation of small amounts of compounds **16** and **24** must obviously have arisen by the acid-catalyzed addition of the elements of hydrogen fluoride or acetic acid to **14**.

Experimental Section

Materials. The lead tetraacetate (LTA) was obtained from Alfa 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 1-ft Vigreux column under reduced pressure. The fraction boiling from 126 to 127° (6.5 mm) was collected and shown by gas–liquid phase 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 preparative glpc prior to use. Freon 112 was distilled before use, bp 90.5° (710 mm).

Reaction of 1,1-Diphenylethylene with LTA–HF. i. A 55-ml methylene chloride solution, 1.06 *M* in 1,1-diphenylethylene and 0.29 *M* in Freon 112, was cooled to 0°. This was added to a stirred cold, 0°, solution of 50 g (0.113 mol) of LTA and 6 ml (0.3 mol) of HF in 100 ml of methylene chloride in a 500-ml polyethylene bottle. The reaction was quenched, after 1-min reaction time, by pouring the reaction 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, and the combined organic phases were washed in succession with water, saturated sodium bicarbonate solution, and water and finally dried over anhydrous sodium sulfate. The reaction mixture was then subjected to glpc analysis (10 ft × 0.25 in. 10% SE-30 on Chromosorb W column programmed from 100 to 300°). 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 ir spectra with those of an authentic sample. By the internal standard method,[22] 0.028 mol (48%) of **3** was found to have been formed. The molar amount **3** was determined from a calibration curve of the mole ratio of **3**/Freon 112 *vs.* the area ratio of **3**/Freon 112. The other major volatile component was isolated by preparative glpc: ir (CCl_4) ν 1758, 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.

ii. A second reaction carried out for 5 min showed by glpc analysis that 93% of the starting material had reacted. The second volatile component had partially decomposed to a third compound which upon isolation proved to be deoxybenzoin by comparison of its ir spectrum to that of an authentic sample.

iii. A third reaction carried out for 45 min showed that all of the starting material had reacted and that 0.029 mol (51%) of **3** had been formed (glpc analysis).

iv. A fourth reaction run for 125 min showed that the ratio of the area of **3** to the combined areas of deoxybenzoin and its precursor remained unchanged in all reactions, 1.63 ± 0.05 (1 min), 1.50 ± 0.05 (125 min). The amount of deoxybenzoin increased at the expense of its precursor throughout the course of the reaction. Two minor products were observed which were shown to have the same retention times as **13** and **5**. The abundance of these materials was estimated by area measurements and found to represent *ca.* 1 and 1.5% of the volatile products.

Reaction of α-Stilbenol Acetate (9) with LTA–HF. Compound **9** was prepared by the method described by Barnes, *et al.*, mp 101–104° (lit.[23] 101°). A solution of 2.00 g (0.010 mol) of Freon 112 and 2.50 g (0.0105 mol) of **9** in 25 ml of methylene chloride was cooled to 0°. The solution was added to a cold, 0°, stirred solution of 10 g (0.022 mol) of LTA and 1.2 ml (0.06 mol) of HF in 25 ml of methylene chloride. The reaction was quenched after 125 min. Glpc analysis revealed that 47% of the starting material had reacted and one volatile product was observed. When deoxybenzoin was added to the reaction mixture, a new peak was observed 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 the product had a longer retention time than deoxybenzoin.

Reaction of Norbornene (14) with LTA–HF. A solution of 10.6 g (0.114 mol) of **14** and 4.05 g (0.02 mol) of Freon 112 in 100 ml of methylene chloride was precooled to −47° (*m*-xylene slush) and added to a stirred solution of 35 g (0.081 mol) of LTA and 5 ml (0.25 mol) of HF at −78°. The reaction was quenched after 1 min. Glpc analysis (10 ft × 0.25 in. 10% SE-30 column programmed from 50 to 200°) showed that 0.048 mol of **14** had reacted. The molar amount was determined, as described above, from a calibration curve of **14** *vs.* Freon 112. Compounds **15**, **16**, **17**, and **20** represent 63% of the total products while compounds **18**, **19**, **21**, **22**, **23**, **24**, **25**, and **26** represent 38% of the reaction products. These figures were arrived at by calibration of **20** and **19** *vs.* Freon 112. The products were collected by preparative glpc (10 ft × 0.25 in. 10% Carbowax 20M column).

2-*exo*,7-*anti*-Difluoronorbornane (17). Compound **17** is a volatile, white, waxy solid: mp (sealed capillary) 107–110°; ir (CCl_4) ν 1059, 1078 cm^{-1} (C–F stretch);[24] nmr (CCl_4) τ 5.01 (doublet of broadened singlets, J_d = 58 cps, $W_{1/2}$ = 5 cps, 1 H), 5.50 (doublet of multiplets, J_d = 58 cps, 1 H), 7.4–9.0 (8 H); ^{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 (27). To a 50-ml flask fitted with a magnetic stirrer and a reflux condensor was added 233 mg (1.7 mmol) of **17** dissolved in 20 ml of dry dimethyl sulfoxide (DMSO). To this was added 380 mg (3.4 mmol) of potassium *tert*-butoxide. This mixture was heated to 120° with stirring for 24 hr. The exit of the reflux condensor was connected to a Dry Ice cold trap. After 24 hr the contents of the cold trap was dissolved in ether and added to the DMSO solution. The reaction mixture was poured into 50 ml of a saturated aqueous sodium chloride solution and extracted with ether by liquid–liquid extraction for 24 hr. The exit of the reflux condensor was again connected to a cold trap. 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. Vigreux column. The residue was analyzed by glpc (10 ft × 0.25 in. column 10% Carbowax 20M on Chromosorb W) and found to contain only two volatile components, one of which was *tert*-butyl alcohol (ir), the other being **27**. Compound **27** 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, $W_{1/2}$ = 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 (20) and Its Dehydrohalogenation to 7-*syn*-Fluoronorbornene (28). Compound **20** 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) τ 5.32 (doublet of broadened singlets, J_d = 56 cps, $W_{1/2}$ = 4 cps, 1 H), 5.37 (doublet of multiplets, J_d = 57 cps, 1 H), 7.4–9.1 (8 H); ^{19}F (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 **17**. Glpc analysis showed three volatile components, one of which was *tert*-butyl alcohol (ir), the other **20** (ir), and the remaining one compound **28**. Compound **28** 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, $W_{1/2}$ = 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 27 and 28. To each of the residues obtained above was added 0.1 g of Adams catalyst. The flask was cooled with ice and the contents stirred under 1 atm of hydrogen for 3 hr. The catalyst was filtered off and the reaction mixture analyzed by glpc (Carbowax column at 50°). Both **27** and **28** gave the same hydrogenation product, 7-fluoronorbornane (**29**), in 100% yield (determined by glpc using an internal standard). Compound **29** 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, $W_{1/2}$ = 4 cps, 1 H), 7.8–8.9 (10 H); *m/e* 114.0845 (calcd for $C_7H_{11}F$: 114.0845). Samples of **29** from both sources gave identical ir spectra.

Fluoronorbornyl Acetates. All the fluoro acetates had very similar retention times by glpc. 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. It was possible to collect 2-*exo*-acetoxy-7-*anti*-fluoronorbornane (**18**) and 2-*exo*-acetoxy-7-*syn*-fluoronorbornane (**19**) in the pure state.

Fluoro Acetate 18. Compound **18** 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 **18** was reduced to 7-*anti*-fluoro-2-*exo*-norbornanol (**30**) with $LiAlH_4$. In a typical reaction 133 mg (0.77 mmol) of **18** was dissolved in 10 ml of anhydrous ether. The solution was added slowly with stirring to a solution of 20 mg of $LiAlH_4$ in anhydrous ether. After the addition of the ester the excess $LiAlH_4$ was decomposed with water-saturated ether. The resultant mixture was poured into 20 ml of 6 *N* HCl. The solvent layers were separated and the aqueous portion extracted with ether. The combined ether fractions were washed successively with water, saturated sodium bicarbonate solution, and water, and finally dried over anhydrous sodium sulfate. The ether was removed by distillation through an 8-in. Vigreux column. The yield of **30** was 95 mg (94%). Compound **30** was purified by glpc and sublimed at 40° (0.1 mm). Compound **30** 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 II. *Anal.* Calcd for $C_7H_{11}FO$: C, 64.59; H, 8.52. Found: C, 64.36; H, 8.36.

Oxidation of 30 to 7-*anti*-Fluoronorbornan-2-one (32). The oxidation was carried out using Brown's method.[25] By this procedure, 96 mg (0.74 mmol) of **30** affords 92 mg (96%) of **32**. Compound **32** 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

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(25) H. C. Brown and C. P. Garg, *J. Amer. Chem. Soc.*, **83**, 2952 (1961).

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 32 to 7-*anti*-Methoxynorbornan-2-one (33) and 7-*anti*-Acetoxynorbornan-2-one (34). To 1.6 ml of 3% sodium methoxide–methanol solution was added 26 mg (0.2 mmol) of **32**. The solution was sealed in an ampoule and heated to 75° for 11 hr. Glpc analysis (10% SE-30 on A/W Chromosorb W at 130°) revealed two volatile components. The minor one (*ca.* 5%) was identified by retention time to be **32**. The other material, 95%, was collected and shown to be **33** by the comparison of its ir and nmr spectra with those of the authentic material.[16]

The acetolysis of **32** was carried out by dissolving 139 mg (1.1 mmol) in 10 ml of 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 mmol) of fused sodium acetate. The mixture was sealed in an ampoule and placed in a 150° bath for 800 hr. The reaction mixture was cooled, and the solution was poured into 20 ml of ether. The ether layer was washed several times with water, 10% sodium bicarbonate, and then water, and finally dried over anhydrous sodium sulfate.

Analysis of the reaction mixture by glpc (10% Carbowax 20M on A/W Chromosorb W programmed at 100–170°) showed that two components were present in the ratio 1:4. Both compounds were collected by preparative glpc. The smaller component proved to be unreacted **32** (ir) while the larger component was shown to be **34** by a comparison of its ir spectrum with that of the authentic material.[17]

The ether was carefully removed by distillation through an 8-in. Vigreux column. By the integration of an nmr spectrum of the mixture, with an added standard, it was shown that **34** was formed in 72% yield.

Reduction of 32 to 29. The reduction was carried out as described by van Tamelen.[26] Since the reduction product is volatile, the reflux condenser is connected to a Dry Ice cold trap. Glpc analysis with an added external standard revealed that only one volatile product was formed in *ca.* 60–70% yield. The reduction product, isolated by preparative glpc, had an ir spectrum identical with that of **29**.

Fluoro Acetate 19. Compound **19** is a colorless liquid: $n^{25}D$ 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, $W_{1/2}$ = 5 cps, 1 H), 5.36 (triplet, J = 5 cps, 1 H), 8.06 (singlet, 3 H), 7.6–9.1 (8 H). The $LiAlH_4$ reduction of 144 mg (0.84 mmol) of **19** yielded 92 mg (84%) of 7-*syn*-fluoro-2-*exo*-norbornanol (**31**). Compound **31** 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, respectively, 1 H), 6.25 (broad singlet, $W_{1/2}$ = 14 cps, 1 H), 7.5–9.2 (9 H); ^{19}F nmr (CCl_4), see Table II. *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 mmol) of **31** by Brown's method yielded 35 mg (76%) of 7-*syn*-fluoronorbornan-2-one (**35**). Compound **35** 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, 1 H), 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 base promoted solvolysis of **35** yielded only unreacted **35**.

Acetolysis of **35** was carried out under the identical conditions as for acetolysis of **32**. The reaction was run for 750 hr. Glpc analysis of the reaction mixture revealed that aside from the starting material, **35** (*ca.* 90%), four new products were formed. Their total yield was *ca.* 10%.

The reduction of the carbonyl in **35** to a methylene group gave a 60–70% yield of only one volatile product (glpc analysis). The ir spectrum of this reduction product proved to be identical with that of **29**.

Nmr Analysis of the Fluoro Alcohols 30 and 31. An nmr sample was prepared using 168 mg (1.3 mmol) of **31** dissolved in 0.5 ml of CCl_4. Both the proton and ^{19}F nmr were taken. Then a total of 40 mg (5.7×10^{-2} mmol) of 2,2,6,6-tetramethylheptadioneeuropium(III) (Euroshift) was added and the spectra were again obtained. Similarly a solution of 104 mg (0.8 mmol) of **30** in 0.5 ml of CCl_4 was prepared and the proton and ^{19}F nmr were obtained. Then a total of 30 mg (4×10^{-2} mmol) of Euroshift was added and the spectra were again obtained. In both cases the mole ratio of substrate/Euroshift was *ca.* 20. The nmr spectra were taken on a Varian A 56/60 spectrophotometer. See Table II for results.

Preparation and Reaction of Nortricyclyl Fluoride (15) and LTA–HF. Compound **15** was prepared as reported by Hanack and Kaiser:[27] 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 (multiplet, 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, precooled to −78°, of 222 mg (2 mmol) of **15** and 306 mg (1.5 mmol) of Freon 112 in 4 ml of methylene chloride was added to a stirred solution of 900 mg (2 mmol) of LTA and 0.2 ml (10 mmol) of HF in 10 ml of methylene chloride at −78°. This mixture was stirred at −78° for a period of 1 hr, quenched, and treated in the usual manner. It was found, by glpc analysis, that the area ratio of **15**/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 collected and characterized. The peak designated **15** was collected and shown to be the original material by comparison of its ir spectrum with that of the authentic material.

Reaction of Nortricyclyl Acetate (21) with LTA–HF. Compound **21** was prepared as described by Cristol, *et al.*[28] A solution, precooled to −78°, of 320 mg (2.11 mmol) of **21** and 343 mg (1.68 mmol) of Freon 112 in 10 ml of methylene chloride was added to a stirred solution of 900 mg (2 mmol) of LTA and 0.2 ml (10 mmol) of HF in 10 ml of methylene chloride cooled to −78°. This mixture was stirred at −78° for a period of 1 hr, quenched, and treated in the usual manner. It was found, by glpc analysis, that the area ratio of **21**/Freon 112 was 1.47 ± 0.03 before the reaction and 1.47 ± 0.11 after the reaction. The peak designated **21** was collected and its ir spectrum was found to be identical with that of the authentic material.

Preparation of 2-*exo*,7-*syn*-Diacetoxynorbornane (25) and 2-*exo*,7-*anti*-Diacetoxynorbornane (26). The method of preparation was that suggested by Alder, *et al.*[10a] To a suspension of 100 g (0.23 mol) of LTA in 700 ml of acetic acid was added a solution of 11.2 g (0.119 mol) of **14** in 100 ml of acetic acid. The resultant mixture was stirred for 1 hr 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 and saturated sodium bicarbonate solution, and finally dried over anhydrous sodium sulfate. Glpc analysis (10% SE-30 A/W, Chromosorb W programmed from 30 to 100°) showed two product peaks. The smaller one (7.4% based on peak areas) was shown to be **21** by comparison of its retention time and ir spectrum with those of the authentic material. The larger peak (92.6%) was shown by nmr to be a mixture of compounds **25** and **26** in the ratio 3:1. (For physical constants, ir, and nmr of **25** and **26**, see Baird and Buza.[29]) 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 (16). A solution of 2 g (0.021 mol) of **14** in 100 ml of methylene chloride was precooled to −47° (*m*-xylene slush). The solution was added to 10 ml (0.5 mol) of HF at −78° and stirred for 15 min. The reaction mixture was poured into a saturated sodium carbonate solution. The aqueous and organic layers were separated and the aqueous layer was extracted with methylene chloride. The combined organic phases were washed with water and dried over anhydrous sodium sulfate. The bulk of the solvent was removed by distillation through an 8-in. Vigreux column. Compound **16** was collected by preparative glpc (10 ft × 0.25 in. 10% SE-30, Chromosorb W, 70°). Compound **16** is a volatile, white, waxy solid: mp (sealed capillary) 49–51°. The nmr of **16** is identical with that published for 2-*exo*-fluoronorbornane.[30] Integration of a nmr of the reaction mixture showed that **16** was present in 60% yield.

Preparation of 2-*exo*-Norbornyl Acetate (24). Compound **24** was prepared from its alcohol by acetylation with acetic anydride–sodium acetate.[31] By this method 2-*exo*-norborneol yielded 79% of **24**: bp 88–91° (20 mm) [lit.[32] 89–90° (20 mm)]; ir (CCl_4) ν

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1740, 1260 cm^{-1}. Glpc analysis (10 ft × 0.25 in. 10% SF-96, Chromosorb W, 140°) showed only one peak.

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Mechanisms of Chlorination by Hypochlorous Acid. The Last of Chlorinium Ion, Cl^+ [1]

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Abstract: Based on product formation, the chlorination of anisole, $CH_3OC_6H_5$ (AnH), by hypochlorous acid, HOCl, follows the rate law $d[AnCl]/dt = k'[HOCl]^2 + k''[H_3O^+][HOCl]^2 + k'''[AnH][H_3O^+][HOCl]$ in aqueous solutions containing perchloric acid ($H_3O^+ + ClO_4^-$), sodium perchlorate, and 0.01 *M* silver perchlorate. At 0.60 *M* ionic strength and 25° the rate constants are 0.124 M^{-1} sec^{-1}, 3.06 M^{-2} sec^{-1}, and 0.478 M^{-2} sec^{-1}, respectively. Terms second order in HOCl represent rate-determining formation of chlorine monoxide, Cl_2O, while the term first order in HOCl may result from a termolecular reaction or a reaction of AnH with hypochlorous acidium ion, H_2OCl^+, formed in a prior equilibrium step. An observed zero-order decomposition of HOCl explains the complex titrimetric rate based on HOCl. No term in the rate law is consistent with rate-determining formation of chlorinium ion, Cl^+. It is now extremely improbable that Cl^+ is significantly involved in any thermal reaction ever studied in solution.

The relatively unreactive hypochlorous acid,[2] HOCl, can be converted into more reactive chlorinating agents by catalytic anions, such as Cl_2 by Cl^- ion,[3] chlorine monoxide, Cl_2O, by ClO^- ion,[4] and ClOAc by acetate ion.[5] This mode of nucleophilic catalysis in the presence of acid is supported by the independently determined rate of Cl_2 formation,[6] and by formation constants for Cl_2O[7] and ClOAc[8] that allow for reasonable concentrations of these proposed intermediates. In the presence of sulfuric and perchloric acids, chlorination rates of benzene, toluene, and sodium α-toluenesulfonate are consistent with formation of the more reactive hypochlorous acidium ion, H_2OCl^+.[9]

The most reactive chlorinating agent should presumably be the chlorinium ion, Cl^+, a species that was proposed to explain the kinetics of chlorination of olefins and aromatic compounds by HOCl in aqueous solution at 25°.[10] Titrimetric rate expressions[10] included a contribution that was first order in HOCl, first order in H_3O^+, but independent of the concentration and nature of the organic substrate, and interpreted as rate-determining formation of Cl^+ from HOCl in a manner analogous to nitration *via* the nitronium ion NO_2^+ from HNO_3. Isotope effects in H_2O *vs.* D_2O solution are inconsistent with an alternative proposal of rate-determining formation of H_2OCl^+,[11] and in accord with this Cl^+ proposal. The Cl^+ mechanism has been publicized in many excellent textbooks.[12] However, thermodynamic arguments show that Cl^+ is highly unstable relative to coordinated species.[13] For dissociation of Cl_2 to Cl^+ and Cl^- in water at 25°, the estimated equilibrium constant is 10^{-40}, from which it can be calculated that $[Cl^+]$ is less than 10^{-40} *M* under conditions where the zero-order dependence on organic substrate was observed. From 1955 to 1967 this dilemma persisted as an outstanding challenge to physical organic chemistry; seemingly *no* mechanistic interpretation could be devised consistent with all of the facts.

The present work was undertaken to resolve this apparent conflict between kinetics, best explained by Cl^+ as an intermediate, and thermodynamics showing that the concentration of Cl^+ is too low to be kinetically significant.[14] We decided to study the chlorination, by HOCl in H_2O solution, of anisole, $CH_3OC_6H_5$, here-

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