Anal. Calcd for C_3H_6BrI (248.90): C, 14.48; H, 2.43; Br, 32.11; I, 50.99. Found: C, 14.55, 14.94, 14.74; H, 2.45, 2.53, 2.47; Br, 33.4;[18] I, 50.61, 50.65.

1-Chloro-1-iodoethane.—This compound was synthesized analogously beginning with α-chloropropionic acid: yield 21%, nmr data in text. Identified by spectral comparison with an authentic sample prepared by the addition of hydrogen iodide to vinyl chloride.[7]

Acknowledgment.—Support by the National Science Foundation is gratefully acknowledged.

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(18) These data were obtained from the difference of a total halide determination and the specific iodine analysis assuming the identity of the second halogen atom.

Direct Fluorination.[1] Addition of Fluorine to Indenes and Acenaphthylenes

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Direct addition of F_2 to olefins at −78° has been shown to produce vicinal difluorides in good yields. Vicinal F–F coupling constants exhibit an angular dependence similar to H–H and H–F coupling constants.

The addition of molecular fluorine to simple unsubstituted olefins as a preparative procedure for vicinal difluorides has received little attention. Additions to perhalo olefins,[2a] vinyl acetate,[2b] and diethyl fumarate[2c] have been successful. It seemed possible that the large heat of reaction could be removed by working at low temperature and thereby eliminating the usual problems of charring, substitution, etc., usually associated with elemental fluorine.

In view of our interest in the synthetic utilization of reactive reagents such as OF_2,[3] which could be completely controlled at −78°, a similar procedure was adopted for pure undiluted fluorine. It was found that direct addition of fluorine will occur in good yield at −78° and that the process is of synthetic utility for the preparation of certain vicinal difluorides.

Experimental Section

Materials.—The fluorine was obtained from Allied Chemical Corp. and passed through a sodium fluoride HF scrubber prior to use. The 2-methylindene[4a] and 1-methylacenaphthylene[4b] were prepared according to established procedures. The physical properties and spectral characteristics were in agreement with those of the original authors. Freon 11 (CCl_3F) and 4A Molecular Sieve[5] were carefully dried before use. The indene was carefully fractionated and stored under nitrogen. The acenaphthylene was used as received from Aldrich Chemical Co.

Apparatus.—The fluorination reactor and auxilliary equipment were constructed entirely of Pyrex with the exception of stirring vanes, which were of Teflon. The reactor was a cylindrical vessel (30 × 300 mm) fitted with a side arm and a topmounted magnetically driven stirrer. The inner magnet was sealed with Pyrex to avoid exposure to fluorine. The stirrer was driven with standard magnetic driving assembly used for spinning-band columns. The reactor was separated from the fluorine reservoir (usually 1 l.) by a single stopcock which was used to meter the flow of fluorine. Manometers were placed on both the reactor and reservoir side of the stopcock to monitor the course of the addition. Kel-F 40 grease[6] was used as stopcock lubricant and Kel-F^{10} oil[6] was used to protect the mercury manometers. The fluorine reservoir was loaded just prior to use from a standard remote fluorine-handling facility.

Procedure.—The olefin was diluted tenfold with Freon 11 (CCl_3F), and slurried with an equal weight (to olefin) of finely ground anhydrous 4A Molecular Sieve.[5] The mixture was vigorously stirred, cooled to −78°, and thoroughly degassed. The fluorine was slowly metered into the reactor above the stirred solution in such a manner as to keep the pressure of fluorine below 50 mm. The exact stoichiometric amount of fluorine could be controlled by varying the volume or pressure of the reservoir bulb. The uptake of fluorine was usually complete to within the vapor pressure of Freon 11 at −78° (~3 mm).

1,2-Difluoro-2-methylindan.—2-Methylindene (2.60 g, 20 mmoles) was fluorinated at −78° in the manner described above with 20 mmoles of fluorine. The uptake of fluorine was smooth and complete within 2 hr. The fluorine partial pressure never exceeded 50 mm at any time. The solvent was distilled away leaving a colorless oil which rapidly darkened upon exposure to air. Rapid low temperature[7] elution on anhydrous silica gel at 15° produced 0.94 g of *trans*-1,2-difluoro-3-methylindan. Continued elution with 3:1 pentane–methylene chloride afforded 0.51 g of *cis*-1,2-difluoro-2-methylindan. Both isomers decomposed when vacuum distilled. The complete spectral properties are listed in the discussion along with assignment of structure.

Anal. Calcd for $C_{10}H_{10}F_2$: C, 71.41; H, 5.99. Found for *cis:* C, 71.33; H, 6.20. Found for *trans:* C, 70.81; H, 6.36.

1,2-Difluorindan.—Indene (5.1 g, 44 mmoles) was fluorinated at −78° with 45 mmoles of fluorine within 1 hr. The partial pressure of fluorine in the reactor was maintained below 50 mm. Removal of solvent produced the adduct as a colorless oil which was immediately chromatographed on silica gel. The difluoride (2.0 g, 29% yield) was eluted with a 1:1 pentane–methylene chloride mixture. No evidence of the other isomer was indicated by fluorine nmr of the crude product before chromatography. Spontaneous decomposition of a purified sample was noted after standing for 10 days at 25°.

Anal. Calcd for $C_9H_8F_2$: C, 70.12; H, 5.23. Found: C, 69.74; H, 4.98.

1,2-Difluoroacenaphthene.—The olefin (6.0 g, 39 mmoles) was fluorinated in a manner described above at −78° with 44 mmoles of F_2. Care was taken to ensure that the partial pressure of F_2 was maintained below 40 mm. Upon removal of the solvent the colorless oil was immediately chromatographed at 15° on anhydrous silica gel with 4:1 pentane–methylene chloride. The first fractions contained 0.82 g (11% yield) of *trans*-1,2-difluoroacenaphthene, mp 40.5–42.5°. This fraction was contaminated with 1,1,2-trifluoroacenaphthene which proved impossible to remove completely.

Continued elution with 4:1 pentane–methylene chloride afforded 2.60 g (35% yield) of *cis*-1,2-difluoroacenaphthene, mp 105° (petroleum ether, bp 60–80°). Spectral details are discussed in the results section.

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(1) This work was sponsored under Army Ordnance Contract DA-01-021 ORD-11878 (Z) Modification No. 15.

(2) (a) W. T. Miller, J. O. Stoffer, G. Fuller, and A. C. Currie, *J. Am. Chem. Soc.*, **86**, 51 (1964). (b) A. Yu. Yakubovich, S. M. Rozenshtein, and V. A. Ginsberg, U.S.S.R. Patent 162,825; *Chem. Abstr.*, **62**, 451*g* (1965). (c) A. Y. Yakubovich, V. A. Ginsberg, S. M. Rozenshtein, and S. M. Smirnov, U.S.S.R. Patent 165,162; *Chem. Abstr.*, **62**, 9018*g* (1965).

(3) R. F. Merritt and J. K. Ruff, *J. Am. Chem. Soc.*, **86**, 1392 (1964); *J. Org. Chem.*, **30**, 328 (1965).

(4) (a) E. R. Alexander and A. Mudrak, *J. Am. Chem. Soc.*, **73**, 59 (1951). (b) L. Fieser and J. Cason, *ibid.*, **62**, 432 (1940).

(5) Trademark of Union Carbide Corp.

(6) Trademark of Minnesota Mining and Manufacturing Co. The grease must be thoroughly purged of unsaturated volatile impurities by heating at 125° at 0.01 mm for 12 hr.

(7) All elution chromatographic columns were fitted with water jackets through which coolant was passed during the separations.

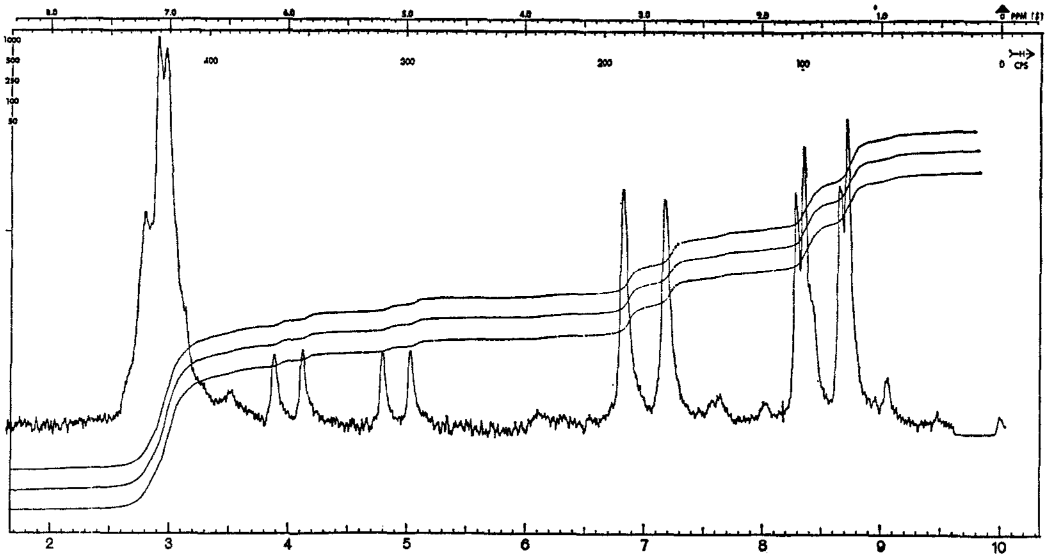

Figure 1.—Isomer A.

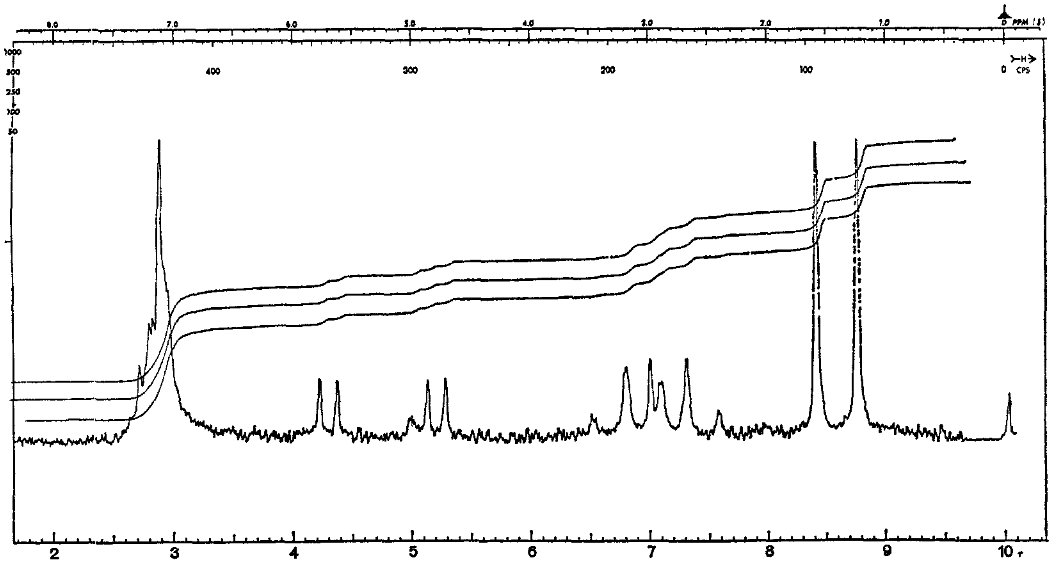

Figure 2.—Isomer B.

Anal. Calcd for $C_{12}H_8F_2$: C, 75.78; H, 4.24. Found for *cis:* C, 75.44; H, 3.99. Found for *trans:* C, 75.10; H, 4.16.

1-Fluoroacenaphthylene.—*cis*-1,2-Difluoroacenaphthene (mp 105°, 0.125 g) was dissolved in 20 ml of absolute ethanol containing 0.25 g of KOH. The mixture was refluxed under nitrogen for 1 hr to produce a bright yellow solution. The ethanol was removed *in vacuo* and the residue was extracted twice with ether. Removal of the ether produced a yellow oil which would not solidify and decomposed upon attempts to distil it *in vacuo.*

The proton and F^{19} nmr spectra are discussed in the results section. The ultraviolet spectrum was quite similar to acenaphthylene and contained the following peaks, λ_{max}, mμ (log ϵ): 341 (3.64), 333 (3.65), 318 (3.93), 277 (2.23), 251 (3.77), 227 (4.64) (EtOH).

Anal. Calcd for $C_{12}H_7F$: C, 84.69; H, 4.15. Found: C, 84.17; H, 4.37.

1,2-Difluoro-1-methylacenaphthene.—1-Methylacenaphthylene (5.0 g, 30 mmoles) was fluorinated in Freon 12 at −120° with 30 mmoles of F_2. Silica gel chromatography at 15° produced 1.2 g (20% yield) of *cis* adduct as a colorless nondistillable oil which would spontaneously decompose at room temperature within 2 hr. Spectral details are included in the discussion.

1-Fluoro-2-methylacenaphthylene.—The 1-methylacenaphthylene adduct was treated with ethanolic KOH in a similar manner as the acenaphthylene adduct. The yellow product was a nondistillable, nonsublimable unstable oil whose structure is indicated by its nmr spectra as noted in the discussion.

Results and Discussion

The controlled fluorination of 2-methylindene proceeded smoothly at −78° to afford 1,2-difluoro-2-methylindan in an isolated yield of 43%. The *cis* and *trans* difluorides were separated by elution chromatography on anhydrous silica gel at 15°.

After isolation, the structures of the two isomers were assigned according to their nmr spectra, an interpretation of which is outlined in this paper.

The isomers, A and B, will be discussed in order of appearance from silica gel when eluted with a 3:1 (v/v) pentane–methylene chloride solution. The proton nmr spectra of A and B are given as Figures 1 and 2. The geminal H–F coupling (J = 56 cps) appears to be normal[8] and the multiplet centered at δ 5.3–5.5 is assigned to the benzilic proton at position 1. Note that the vicinal HF coupling of this proton to the C-2 fluorine atom is 15 cps in isomer A and 9 cps in isomer B.

On the basis of this evidence alone and the assumption that HF coupling constants follow a trend of angular dependence analogous to that of H–H coupling constants,[9] the isomer A which contains the larger coupling constant is *trans* adduct and, therefore, B is *cis* adduct. The ring geometry is assumed nearly planar[10] making $<\mathrm{HF}_{vic} \sim 90°$ for the *cis* adduct and $<\mathrm{HF}_{vic} \sim 0°$ for the *trans* adduct. A lack of nmr spectral changes associated with conformational isomerization was found from $-85°$ to $+40°$, and tends to confirm the near planar structure.

The protons of the methyl group on position 2 are coupled with the C-2 fluorine atom, J = 22 cps. This value is essentially the same for both isomers A and B. However, the methyl protons in A are further coupled by 4 cps to another single nucleus. This is presumed to be a long-range effect between the methyl protons and the fluorine atom on position 1 of the ring. This effect is expected to be the greatest when the two interacting groups are in the configuration demanding the closest proximity. This condition is best satisfied with the *trans* adduct or isomer A, while B is of necessity the *cis* adduct in agreement with the assignment from vicinal H–F coupling considerations.

The benzilic methylene groups appear as an ABX case in each spectrum and could be completely analyzed[11] in the case of compound B. The upfield proton couples with the fluorine atom at C-2 (J_{AX} = 18.6 cps). The downfield proton coupling is slightly smaller (J_{BX} = 17.6 cps). The downfield proton is further coupled with a value of about 2 cps to another spin ½ nucleus, presumed to be the fluorine atom at C-1. This coupling should be favored when the proton and fluorine atoms involved are on the same side of the ring; a further support for the F,F *cis* structure of isomer B.

The fluorine nmr spectra are given in Figure 3. The low-field multiplet centered at ϕ[12] +146.3 in A and ϕ +163.3 in B is assigned to the fluorine atom geminal to the methyl group. The doublet centered at ϕ +177.5 in A and ϕ +190.4 in B is the fluorine atom at C-1. The vicinal fluorine–fluorine coupling constant of B is about 8 cps while that of A is too small to measure. The trend in magnitude of vicinal fluorine–fluorine coupling constants, as observed in substituted ethanes, is that the *trans* value is less than the gauche value.[13,14] Therefore the *cis* adduct should possess the larger F–F coupling constant and assignment of structure B as *cis* is possible and consistent with the other nmr interpretations.

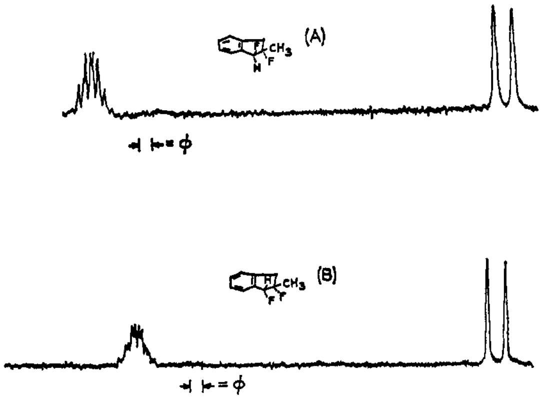

Figure 3.

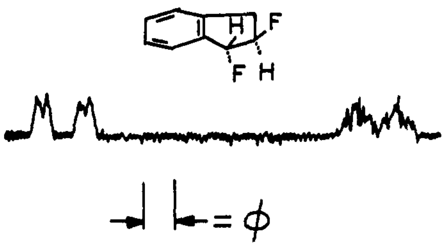

Figure 4.

The case of indene was next examined with the hope that the information obtained from the spectrally simpler 2-methyl derivative would lead to the structural assignment of isomers by nmr.

The addition was smooth at $-78°$ and the difluoride was isolated by silica gel chromatography in a yield of 32%, and proved to be composed of a single isomer. The fluorine nmr spectrum is reproduced as Figure 4 and consists of two sets of multiplets centered at ϕ +196.3 and 200.5. The lower field group represents the fluorine atom at C-1 with the normal *gem*-HF coupling of 56 cps. Further coupling to two other spin 0.5 nuclei with values of 16 and ~4 cps are also apparent. Homonuclear decoupling experiments were successful in reducing this group to a doublet of doublets (J_{HF} = 56, 16 cps) and showing the J_{FF} vicinal to be of the order of 4 cps. The magnitude of this coupling when compared to that found in the 2-methyl derivative is intermediate in value and not useful. The vicinal HF coupling of 16 cps is comparable to that found for the *trans* isomer of the difluoro-2-methylindan. The structure of the difluoride of indene formed exclusively is presumably *trans* if the geometry of the two systems is equivalent.

The case of acenaphthene presents certain desirable structural and spectroscopic features as its halogenation products are well known.[15,16] The acenaphthylene could be smoothly fluorinated to 1,2-difluoroacenaphthene with no evidence of polymerization. It was possible to separate the two isomers, which appeared in the ratio of 1:3.2 *trans*:*cis*, with silica gel elution chromatography. The lower melting isomer (mp 40.5–42.5°) is tentatively assigned the *trans* configuration while the higher melting isomer (mp 105°) is assigned the *cis*.[16] This perhaps unjustified assignment will

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(8) J. A. Pople, *Mol. Phys.*, **1**, 216 (1958).

(9) J. B. Lambert and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 3891 (1965).

(10) The proton nmr spectrum of *trans*-1,2-dibromoindan [S. Winstein and R. M. Roberts, *ibid.*, **75**, 2297 (1953)] can be analyzed by inspection to yield the following vicinal coupling constants: J_{trans} = 1.5 cps and J_{cis} = 5.0 cps. A comparison with the *cis* and *trans* constants of the camphane diols [F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961)] in which $J_{cis} \sim$ 8–9.0 cps ($<\sim 0°$) and J_{trans} = 2.0 cps ($<\sim 120°$) shows the qualitative similarity of the geometries. Substituent effects are expected to cause variations in the absolute values and angles involved.

(11) K. B. Wiberg and B. J. Nist, "The Interpretation of NMR Spectra," W. A. Benjamin, Inc., New York, N. Y., 1962.

(12) F^{19} nmr spectra are given in values of ϕ (parts per million from $\mathrm{CCl_3F}$ as internal standard).

(13) S. L. Manatt and D. D. Elleman, *J. Am. Chem. Soc.*, **84**, 1305 (1962).

(14) R. K. Harris and N. Sheppard, *Trans. Faraday Soc.*, **59**, 606 (1963).

(15) B. Campbell, *J. Chem. Soc.*, **107**, 918 (1915); M. Blumenthal, *Ber.*, **7**, 1092 (1874).

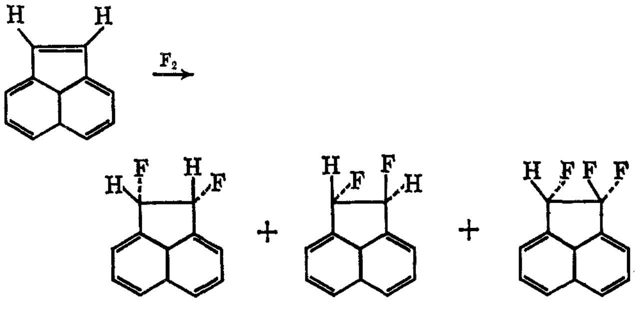
(16) S. J. Cristol, F. R. Stermitz, and P. S. Ramey, *J. Am. Chem. Soc.*, **78**, 4939 (1956). The isomeric 1,2-dichloroacenaphthalenes follow: *cis*, mp 116°; *trans*, mp 68°.

be shown to be correct and consistent with earlier data upon examination of the nmr spectra. An additional factor is that the order of elution is mp 40° isomer prior to mp 105° material. In the indene system, the *trans* isomer was eluted from silica gel before the *cis* isomer. Similar column, solvent, etc., conditions were used for the two adduct series.

The F^{19} nmr spectrum of both isomers is a typical example of an AA'XX' case. The ethylene bridge portion of the proton spectrum is identical with the F^{19} spectrum as is demanded by this case. The spectra were solved by a combination of nmr-EN and nmr-IT computer programs[17] utilizing approximate couplings observable from the 1,1,2-trifluoroacenaphthene and 1,2-difluoro-1-methylacenaphthene spectra which will be discussed in a later section. The F^{19} resonances were arbitrarily centered at −9000 cps and the proton resonances at +9000 cps to ensure $\delta_{HF} \gg J_{HF}$; a similar procedure[9] has been used for calculations involving both H^1 and F^{19}. Differences between observed and calculated spectra were generally <0.3 cps; the major contribution to this error arises from the difficulty of measuring the HR-40 F^{19} spectra with the accuracy of the A-60 proton spectra.

It can be readily seen that the apparent angular dependence of proton-proton coupling is also appearing with proton-fluorine and fluorine-fluorine coupling (Chart I). The relative values *trans/cis* for J_{HH} = 0.7/5.1, J_{HF} = 5.2/19.4, and J_{FF} = 0.1/16.4 clearly show that relative magnitudes of vicinal fluorine-fluorine coupling constants can be predicted by knowledge of the geometry and conversely, the geometry can be predicted by the relative magnitudes of the fluorine-fluorine coupling constants.

CHART I



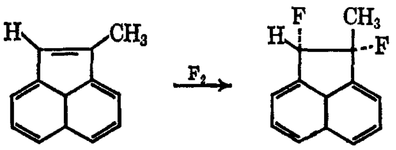
	J, cps		
J_{FF} (*cis*)	16.4	...	9.8
J_{FF} (*trans*)	...	0.1	1.2
J_{FF} (*gem*)	...	...	265.3
J_{HF} (*cis*)	...	19.4	12.8
J_{HF} (*trans*)	5.2	...	1.2
J_{HF} (*gem*)	54.6	52.2	53.9
J_{HH} (*cis*)	5.1	...	...
J_{HH} (*trans*)	...	0.7	...

The X-ray crystal structure of acenaphthene[18] has shown the geminal H-H angle to be 99° as slightly less than tetrahedral. The influence of fluorine substitution on this angle is not known but the effect is not expected to be large.

Both isomers could be dehydrofluorinated with KOH in ethanol to a single yellow fluorine-containing compound assigned the structure 1-fluoroacenaphthylene. The proton nmr spectra contained a singlet at δ 6.33 with an integrated intensity of one-sixth that attributed to the aromatic protons. The fluorine nmr spectrum contained a single peak at ϕ +134.4. A very small *cis* vicinal HF coupling is to be expected in light of earlier work with substituted fluoroethylenes.[19]

To further ensure the placement of the two fluorine atoms, 1-methylacenaphthylene was prepared by a standard Grignard procedure from acenaphthenone.[4b] The fluorine adduct of this olefin was easily prepared and appeared to consist of a single isomer (*cis*) as judged from the F^{19} nmr spectrum of the crude product. The values of the coupling constants which are given in Chart II compare favorably with those observed for the *cis*-acenaphthylene adduct. The small HF vicinal coupling of 5 cps can only arise from a *trans* vicinal orientation of proton and fluorine atoms. The large (16 cps) FF vicinal coupling is comparable to that observed (16.4 cps) in the *cis* adduct of acenaphthylene.

CHART II



	J, cps
J_{FF}	16
J_{HF} (*vic*)	5
J_{HF} (*vic*-CH_3)	22
J_{HF} (*gem*)	54

The methyl group resonances appears as a doublet (*J* = 22 cps) with the normal (free rotation) vicinal HF coupling value. Each member of the doublet is further coupled (*J* = 1.5 cps) to another spin 0.5 nucleus and is presumably the *trans*-β-fluorine atom. The placement of the fluorine atoms is thus unambiguous at the 1 and 2 positions.

The elimination of HF from the 1-methylacenaphthylene adduct is possible with KOH in ethanol. The product, a yellow low-melting solid, may be easily identified by its nmr spectrum as 1-fluoro-2-methylacenaphthylene. The proton spectrum contained only aromatic and vinylogous methyl protons (ratio 2:1). The methyl protons appeared as a doublet (J_{HF} = 2.8 cps) centered at δ 2.18 which show the small coupling with the β-fluorine atom. The vinyl fluorine atom appears an unresolved band at ϕ +143.7 with a width at half-height of 9 cps.

The other two standard procedures for the preparation of vicinal difluorides are lead tetrafluoride[20] and phenyliodosodifluoride.[21] Both of these methods were tested on acenaphthylene to assess their stereochemical mode of addition but neither reaction produced material sufficient for an F^{19} nmr spectrum.

Summary and Conclusions

It has been shown that the low-temperature addition of undiluted elemental fluorine to aliphatic olefins is a smooth and controllable process. The examples tested

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[17] J. D. Swalen and C. A. Reilly, *J. Chem. Phys.* **37**, 21 (1962).

[18] H. W. W. Ehrlich, *Acta Cryst.*, **10**, 699 (1957).

[19] H. M. McConnell, C. A. Reilly, and A. D. McLean, *J. Chem. Phys.*, **24**, 479 (1956).

[20] O. Dimroth and W. Bockemüller, *Ber.*, **64B**, 516 (1931).

[21] W. Bockemüller, *ibid.*, **64B**, 522 (1931).

to date are indicative of its potential synthetic utility for the preparation of vicinal difluorides.

Work is continuing to assess the conditions necessary for control of the stereochemistry as well as to provide additional data on vicinal F–F coupling constants in other cycloalkene adducts. The latter are quite necessary to establish empirical correlations of fluorine coupling constants to dihedral angles.

Low-temperature fluorination coupled with F^{19} nmr may prove to be a useful diagnostic tool for structure determination.

Acknowledgment.—We are grateful to Mr. Morris Howard for technical assistance, Mrs. Carolyn Haney for nmr spectra, and Mr. Robert Watkins for infrared spectra.

Nucleophilic Substitution on a Hexachloronorbornadiene

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Sodium methylmercaptide effects stepwise displacement of two chlorine atoms in 5-phenyl-1,2,3,4,7,7-hexachloronorbornadiene (1). Treatment of the bis-substitution product with aged Raney nickel results in selective removal of only one methylthio group. These experiments are discussed briefly in relation to the problem of nucleophilic substitutions on vinyl halides, especially in dipolar aprotic solvents.

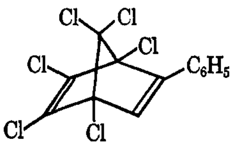
The reactions of vinyl halides with nucleophiles have been the object of considerable recent interest.[2] Truce[2a] has found that nucleophilic substitutions on *cis*-1,2-dichloroethylene by thiolates occur by an elimination-addition sequence involving chloroacetylene as an intermediate. On the other hand, an addition–elimination sequence was implicated in the transformation of vinylidene chloride into *cis*-di-*p*-tolylmercaptoethylene by *p*-toluenethiolate.[2b] We have been interested in the synthesis of norbornadienone thioketals as possible precursors of dithiocarbenes.[3] In attempts to prepare such species, we have observed facile substitution by the addition–elimination process in a *cis*-1,2-dichloroethylene which cannot undergo prior dehydrohalogenation to an acetylene.

5-phenyl-1,2,3,4,7,7-hexachloronorbornadiene (1) has been prepared by McBee[4] in 21% yield from the reaction between hexachlorocyclopentadiene and phenyl acetylene, in the absence of solvent. By operating with toluene as diluent, we have obtained 1 in 42% yield (63% based upon recovered hexachlorocyclopentadiene). Although we initially obtained this material as a viscous liquid, as did McBee,[4] it later crystallized, mp 96–98°. Its nmr spectrum consisted of singlets at τ 2.65 and 3.45, relative areas 5:1. When 1 was allowed to react with 2 equiv of sodium methylmercaptide for 8 hr at 0–25° in dimethylformamide, a new compound was isolated in good yield. Its nmr spectrum (singlets at τ 2.68, 3.53, and 7.53, relative areas 5:1:3, respectively) and microanalysis indicated substitution by a single S-methyl group.

It was clear from spectral evidence that no gross skeletal change had occurred during this substitution. The compound exhibited infrared absorption for the trisubstituted double bond at 12.38 μ and vinylic resonance in the nmr at τ 3.53; for 1 the corresponding values are 12.38 μ and τ 3.45. In a number of 7,7-dialkoxy-5-phenyl-1,2,3,4-tetrachloronorbornadienes prepared by Lemal and coworkers[3f] the trisubstituted double bond is observed in the narrow range of 12.35–12.45 μ, and vinylic resonance in the nmr region occurs between τ 3.45 and 3.65. Further evidence for retention of the 2-phenylnorbornadiene skeleton in the substitution product was provided by ultraviolet spectral data. Maxima are exhibited by 1 at 285, 254, and 223 mμ (ϵ 3300, 8920, and 11,500, respectively). 7,7-Dimethoxy-1,2,3,4-tetrachloro-5-phenylnorbornadiene[3f] has maxima at 275, 247, and 218 mμ (ϵ 2940, 9100, and 10,300, respectively). The monomethylthio-substituted product exhibits ultraviolet absorption maxima at 268 and 228 mμ (ϵ 8070 and 11,620).

Analogy with the reaction of sodium methoxide with 1[4,3a–c] would suggest substitution at the bridge to afford 2 or 3 (Chart I). In view of Truce's observations[2b] on the reaction of vinylidene chloride with

CHART I



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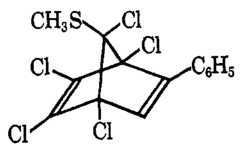

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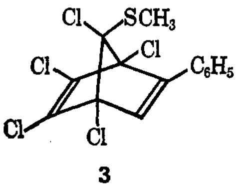

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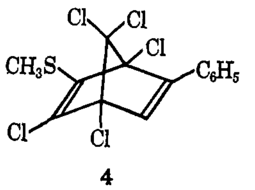

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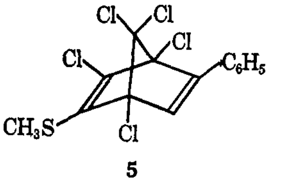

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