In some runs, a second slow-moving alcohol was obtained in ~5% yield, mp 144–147°; it showed no cyclopropane absorption in the nmr and it was not investigated.

4β,5-Methano-3-cholestanone (3a).—To an ice-cooled solution of 220 mg (0.55 mmole) of alcohol **2a** in 20 ml of CP acetone, through which nitrogen was bubbled, there was added, dropwise, 0.15 ml (10% excess) of a 2.67 *M* solution of Jones reagent.[5] The magnetically stirred mixture was allowed to react at 0° for 5 min, methanol was added, and the mixture was poured into ice–water. The precipitate was filtered, washed with water, dried under reduced pressure, and chromatographed on 5.7 g of alumina (activity III). Hexane eluted 16 mg (7%) of dimer **4a** and hexane–benzene eluted 135 mg (61%) of ketone **3a**. The solid was recrystallized from aqueous methanol and from methanol: mp 89.0–89.5°; $[\alpha]^{22}D$ +71° (*c* 1.05); ν_{max} 1665 cm^{-1}; λ_{max}^{EtOH} 200 mμ (ε 6400), 277 mμ (ε 45), λ_{max}^{hexane} 187 mμ (ε 8100); ORD (positive Cotton effect) [φ] +5590° (304 mμ), [φ] −6780° (252 mμ); nmr τ 9.22 (singlet, C_{18}), 8.82 (singlet, C_{19}).

Anal. Calcd for $C_{28}H_{46}O$ (mol wt, 398.65): C, 84.35; H, 11.63. Found: C, 84.39; H, 11.59.

3α-Hydroxy-4α,5-methanocholestane.—Using the procedure described for the 3β isomer, 910 mg (2.35 mmoles) of 3α-hydroxy-4-cholestene, 646 mg (2.35 mmoles) of zinc–copper couple, and 2.2 g (8.23 mmoles) of methylene iodide in 20 ml of ether were allowed to react; the crude product was immediately chromatographed on 47 g of alumina (activity III). Hexane–benzene (1:1) eluted 169 mg (18%) of Δ⁴-cholestene-3-one,[12] and benzene eluted 613 mg (65%) of crystalline 3α-hydroxy-4α,5-methanocholestane which was recrystallized from acetone: mp 105–106°; $[\alpha]^{22}D$ +88° (*c* 0.96); ν_{max} 3670, 3490 cm^{-1}; nmr τ 9.99 (quartet, *J* = 4.5 and 4.5 cps).

Anal. Calcd for $C_{28}H_{48}O$ (mol wt, 400.66): C, 83.93; H, 12.08. Found: C, 84.00; H, 11.98.

4α,5-Methano-3-cholestanone (5).—Following the procedure described for the oxidation of the 3β isomer, from 172 mg (0.43 mmole) of the 3α alcohol and 0.12 ml (10% excess) of 2.67 *M* Jones reagent there was obtained 155 mg (90%) of ketone **5** after recrystallization from aqueous acetone: mp 136–137°; $[\alpha]^{22}D$ +12° (*c* 1.14); ν_{max} 1670 cm^{-1}; λ_{max}^{EtOH} 204 mμ (ε 7300), 275 mμ (ε 58); λ_{max}^{hexane} 194 mμ (ε 8400); ORD (negative Cotton effect) [φ] −5140° (300 mμ), [φ] +11,300° (258 mμ); nmr τ 9.22 (singlet, C_{18}), 8.84 (singlet, C_{19}).

Anal. Calcd for $C_{28}H_{46}O$ (mol wt, 398.65): C, 84.35; H, 11.63. Found: C, 84.47; H, 11.48.

Dimeric Ether 4a.—To a solution of 116 mg (0.29 mmole) of 3β-hyroxy-4β,5-methanocholestane in 0.2 ml of methylene chloride at 0° there was added 7.4 mg (0.03 mmole) of iodine, and the solution was allowed to stand overnight at 0°. Hexane was added, and the resulting solution was washed twice with sodium thiosulfate solution and twice with water, and dried. The solvent was removed under reduced pressure, and the residual oil was chromatographed on 5.8 g of alumina (activity III). Hexane eluted 31 mg of an unidentified oil and 73 mg (64%) of crystalline dimer **4a** which was recrystallized from hexane–acetone (plates): mp 189.5–190.0°; $[\alpha]^{22}D$ −37° (*c* 0.68); ν_{max} 1090 cm^{-1}, ϵ_{200} 1000; nmr τ 9.91, 5.8.

Anal. Calcd for $C_{56}H_{94}O$: C, 85.86; H, 12.10; mol wt, 783.37. Found: C, 85.89; H, 11.90; mol wt, 781 (osmometer).

3β-Hydroxy-4β,5-methano-10-methyldecalin (2b).—The Simmons–Smith reaction was run on the mixture of isomeric alcohols obtained directly from the lithium aluminum hydride reduction of 3-keto-10-methyl-Δ⁴-octalin, in the usual manner except that the reaction was allowed to proceed for 16 hr. The desired **2b** was obtained by preparative glpc using a column with 30% Carbowax and 10% potassium hydroxide. The nmr spectrum showed an absorption at τ 9.98 (1 H, quartet, *J* = 4.5 and 4.5 cps) and at 9.38 (2 H, multiplet).

Dimeric Ether 4b.—Following the procedure given above for dimeric ether **4a**, 124 mg (0.69 mmole) of **2b** and 18 mg (0.07 mmole) of iodine in 0.8 ml of methylene chloride yielded, after chromatography, 55 mg of an unsaturated oil and 45 mg (38%) of crystalline dimer **4b**: mp 131.5–132.5°; $\nu_{max}^{CCl_4}$ 1055, 1020 cm^{-1}; nmr τ 9.93 (2 H, quartet, *J* = 4.0 and 4.0 cps), 5.93 (2 H, broad).

Anal. Calcd for $C_{24}H_{38}O$ (342.54): C, 84.15; H, 11.18. Found: C, 84.20; H, 11.02.

3β(?)-Hydroxy-17-acetoxy-Δ⁴-androstene (1c).—A solution of 5.11 g (15.45 mmoles) of 17-acetoxy-Δ⁴-androstene-3-one in 100 ml of dry ethanol was reduced with 292 mg of sodium borohydride and the reaction mixture, after the usual work-up, was chromatographed on alumina. Benzene eluted 3.0 g of crystalline material which was recrystallized twice from hexane–methanol: mp 125–135°, yield 2.04 g (40%), $[\alpha]D$ +39° (*c* 2.48). Tlc on silica gel showed this material to be mainly one compound (75%) and most likely it is the β isomer. This material was used for the subsequent reaction since further attempts to purify it failed.

3β(?)-Hydroxy-17-acetoxy-4β,5(?)-methanoandrostane (2c).—Following the standard procedure 2.0 g (6 mmoles) of the above enriched 3β(?)-hydroxy-17-acetoxy-Δ⁴-androstene, 3.28 g (50.5 mmoles) of zinc–copper couple, and 13.4 g (50 mmoles) of methylene iodide in 60 ml of anhydrous ether were allowed to react, and the crude product was immediately chromatographed on 100 g of alumina. Benzene eluted 400 mg of a cyclopropane derivative and this solid was recrystallized three times from aqueous methanol: mp 119–121°, yield 210 mg (10%), $[\alpha]D$ −29° (*c* 0.70).

Anal. Calcd for $C_{22}H_{34}O_3$ (mol wt, 346.49): C, 76.26; H, 9.89. Found: C, 76.14: H, 9.81.

4β,5(?)-Methano-17-actoxy-3-androstanone (3c).—Using the usual procedure, 161 mg (0.47 mmole) of the above 3β(?)-hydroxy-4β,5(?)-methano derivative was oxidized with 0.13 ml of 2.67 *M* Jones reagent. The crude product was chromatographed on alumina and hexane–benzene (1:1) eluted 50 mg (30%) of crystalline ketone which was recrystallized from acetone–hexane: mp 154.0–154.5°, $[\alpha]D$ +65°.

Anal. Calcd for $C_{22}H_{32}O_3$ (mol wt, 344.48): C, 76.70; H, 9.36. Found: C, 76.53; H, 9.08.

(12) In some runs the starting alcohol was obtained in place of this ketone.

Direct Fluorination of 1,1-Diphenylethylene[1,2]

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Previous work[1,3] has demonstrated the feasibility of the addition of elemental fluorine to rather sensitive olefins. The vicinal difluorides produced were predominately *cis* when the olefinic substrates were varied from Δ⁴-cholesten-3-one[3] to acenaphthylene.[1] The additions were relatively free of side products expected for an energetic free-radical process which, when coupled with apparent high stereospecificity of the adducts, tends to infer a general ionic scheme. In view of the high electronegativity of fluorine, an electrophilic process is to be expected.

The fluorination of 1,1-diphenylethylene has been examined with PbF_4[4] and electrochemically. These processes lead to rearranged products, *e.g.*, phenyl migration to yield 1,2-diphenyl-1,1-difluoroethane (I).

$$(C_6H_5)_2C{=}CH_2 \xrightarrow{PbF_4} \underset{\text{I}}{C_6H_5CF_2CH_2C_6H_5}$$

Quite convincing arguments are put forth by Bornstein,[4] *et al.*, to establish the process as being free radical in nature. It also appears that rearrangement *must* accompany addition as *no* 1,1-diphenyl-1,2-difluoroethanes could be found. It was then of interest to

(1) For part II, see R. F. Merritt and F. A. Johnson, *J. Org. Chem.*, **31**, 1859 (1966).

(2) This work was carried out under sponsorship of the U. S. Army Missile Command, Redstone Arsenal, Ala., under Contract No. DA-01-021 AMC-11536 (Z).

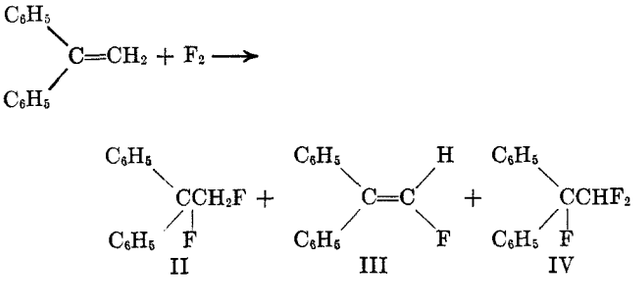
(3) R. F. Merritt and T. E. Stevens, *J. Am. Chem. Soc.*, **88**, 1822 (1966).

(4) J. Bornstein, M. R. Borden, F. Nunes, and H. I. Tarlin, *ibid.*, **85**, 1609 (1963).

examine the same system utilizing elemental fluorine. A general free-radical process should be accompanied by rearrangement leading to similar products (including dimers) as observed by Bornstein.

Results and Discussion

1,1-Diphenylethylene could be smoothly fluorinated at −78° in CCl_3F with a single equivalent of elemental fluorine to produce a mixture of three products, 1,1-diphenyl-1,2-difluoroethane (II), 1,1-diphenyl-2-fluoroethylene (III), and 1,1-diphenyl-1,2,2-trifluoroethane (IV), as well as some unreacted starting material.



The vinylic fluoride III appeared as the major product (78% yield) accompanied by the unrearranged difluoride II (14% yield) and trifluoride IV (8%). As a routine work-up procedure, F^{19} nmr spectra were taken on crude reaction mixtures immediately after warming from −78°. No types of fluorine were apparent in these spectra which did not correlate with those of the three isolated products. No evidence was found for phenyl migration nor presence of dimers containing fluorine.

The difluoride can be unequivocally assigned as the unrearranged 1,1-diphenylethane by the fluorine and proton nmr. The fluorine atom on the methylene group appeared as a triplet (J = 48 cps) of doublets (J = 20 cps) at ϕ 226.3 and the tertiary fluorine atom as an apparent quartet (J = ~20 cps) at ϕ 156.6. The 48-cps value is indicative of geminal HF coupling[5] and therefore demands two equivalent geminal protons. The smaller value of 20 cps arises from the vicinal FF coupling. Both assignments were verified by standard homo- and heteronuclear decoupling experiments. The melting point of the adduct agreed with the unrearranged difluoride prepared by Bornstein.

The apparent quartet arises from nearly equivalent values of the vicinal HF and FF coupling constants. There are three isomeric possibilities of which two may be dismissed immediately. The compounds 1,1-diphenyl-2,2-difluoroethane and 1,2-diphenyl-1,1-difluoroethane would not fit the observed multiplicity and coupling constants and also would be expected to show a single group (F^{19}) chemical shift instead of two separate multiplets with the large observed (ϕ ~70) shift. The third isomer (*meso* and/or *dl*), 1,2-difluoro-1,2-diphenylethane, has been prepared from *cis* stilbene and exhibits the characteristic AA′XX′ spectra observed previously with the acenaphthylene–fluorine adduct,[1] and can be also excluded.

The monofluoride structure as written can be distinguished from the two isomeric possibilities of *cis* and *trans*-fluorostilbene by consideration of the magnitude of the HF coupling constant. The fluorostilbenes should exhibit a maximum J_{HF} of about 40 cps[5] for the *trans* isomer with the *cis* value being even smaller. The observed value of 83 cps is that expected[6] for the grouping $=C<^{F}_{H}$. The *cis*- and *trans*-fluorostilbenes were also prepared by HF elimination from the stilbene-fluorine adduct and were shown to have normal values of the *cis* and *trans* J_{HF} ($J_{HF\ cis}$ = 22 cps, $J_{HF\ trans}$ = 40 cps).

The trifluoride F^{19} spectrum of the CF_2H group consisted of a doublet (J_{HF} = 52 cps) of doublets (J_{FF} = 12 cps) at ϕ 129.9 and the tertiary fluorine atom as an apparent quartet at ϕ 158.4 in a ratio of 2:1, respectively. The isomeric possibility, 1,2-diphenyl-1,1-2-trifluoroethane would not show this large J_{HF} for *two* fluorine atoms and would have *quite* different multiplicity. The remaining isomer, 1,1-diphenyl-2,2,2-trifluoroethane would exhibit only a single F^{19} absorption band (doublet) typical of a trifluoromethyl group. In fact, the trifluoride IV may be readily prepared from the monofluoride (III) by fluorination and is presumed to have the same carbon backbone.

The presence of the trifluoride (IV) was disturbing in that it may have arisen from either II with hydrogen atom replacement or from III by direct addition. Attempts to fluorinate difluoride II under the same conditions were unsuccessful. Forcing the fluorination (−78°/P_{F_2} > 100 mm) caused indiscriminant substitution and cleavage. However, the fluoro olefin III was smoothly fluorinated to IV under the reaction conditions in almost quantitative yield. The olefin III is apparently the precursor of the trifluoride IV and must be present in the reaction media at −78°. The olefin III may arise from an HF elimination of adduct II. However, as III is present in the system at −78° it is unlikely that HF elimination had occurred under these conditions. In the author's experience, many sensitive materials which tend to dehydrofluorinate spontaneously may be stabilized indefinitely by storage at −78°.

It is, therefore, apparent that elemental fluorine does behave in a quite different manner than fluorine derived from either PbF_4, $C_6H_5IF_2$, or electrochemical fluorination.[4] The predominant mode of addition to other olefins[1,3] is *cis*, and no evidence has been found for a free-radical hydrogen abstraction of allylic or vinylic hydrogen atoms.

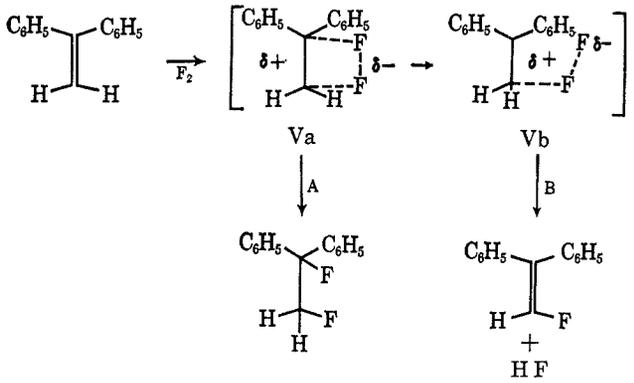
A satisfactory explanation (Scheme I) may lie in a molecular adduct (V) which may continue on to products through two competing routes shown as A and B.

A major contribution of complex Va *via* path A will favor direct *cis* addition and will predominate in cases where the incipient carbonium ion of Vb is not extensively stabilized. Examples such as steroidal olefins, indene,[3] and acenaphthylene[3] lead to adduct formation rather than elimination. Stilbene, examined briefly in this study, would form a carbonium ion of comparable stability to acenaphthylene and indene and it does produce the vicinal difluorides in yields of better than 95%.

(5) L. M. Jackman, Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry, Pergamon Press Inc., New York, N. Y., 1959.

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

SCHEME I



The 1,1-diphenylethylene presents a favorable case for stabilization of Vb and the proton elimination route (path B) is used almost to the exclusion of path A. Path B is also favored to the extent of 3 kcal/mole by average bond energy considerations. Such eliminations are observed in chlorinations and occur to the extent of 5–15% in nonpolar solvents in the chlorination of 1-phenylpropene.[7]

Direct low-temperature addition of elemental fluorine has been shown to be an ionic process and not the expected free-radical chain mechanism. The products to be expected are those arising *via* Va and b and are not completely unlike those found with the other halogens.

Experimental Section

Apparatus.—The static low-temperature fluorination apparatus has been previously described.[1] The fluorine was measured and manipulated with a standard remote fluorine system. Care must be taken to shield the reactor to protect the operator from inadvertent exotherms and/or fluorine leaks. All melting points are uncorrected.

Materials.—The fluorine was pure as received from Allied Chemical Corp. and was passed through an HF scrubber (NaF) before use. The 1,1-diphenylethylene was obtained from Aldrich Chemical Co. and purity established by nmr.

Fluorination of 1,1-Diphenylethylene.—The olefin (8.0 g, 44 mmoles) was dissolved in 400 ml of CCl_3F and this solution was slurried with 2.0 g of No. 4 A Molecular Sieve®.[8] The mixture was degassed and stirred at −78°. The fluorine (44 mmoles) was carefully admitted to the reactor at a rate such that the total pressure never exceeded 5 mm. The process required about 2.5 hr. The solvents were removed to yield 9.8 g of crude colorless oil. Of this crude product, 5.7 g was placed on a silicic acid (Bio-Rad 100–200 Mesh) column (20 × 200 mm) and eluted with a pentane–methylene chloride (60:1) solvent mixture. Three components were observed in F^{19} nmr and were eluted as follows.

Peak A.—1,1-Diphenyl-2-fluoroethylene (4.0 g 78% yield) appeared as a colorless liquid which decomposed upon distillation. The F^{19} spectrum has been discussed but the vinylic proton was a doublet J = 83 cps centered at δ 6.86. The remaining protons are aromatic (ratio 10:1) at δ 7.2. The infrared exhibited the following appropriate bands: 3.21 m, 6.12 m, 6.72 m, 6.98 m, 8.53 s, 9.20 s, 9.35 s, 9.75 m, 10.72 m, 11.0 m, 11.0 m, 12.01 w, 12.92 s, 13.10 s, 13.71 m, and 14.39 μ s.

Anal. Calcd for $C_{14}H_{11}F$: C, 84.82; H, 5.59; F, 9.58. Found: C, 84.25; H, 6.29; F, 9.40.

Peak B.—1,1-Diphenyl-1,2-difluoroethane (0.8 g, 14.0% yield) was eluted as a colorless solid, mp 40–41.5°, lit.[4] mp 41.8–42.6°. The proton nmr spectrum showed the two nonaromatic protons as a doublet (J = 49 cps) of doublets (J = 20 cps) centered at δ 4.83.

Anal. Calcd for $C_{14}H_{12}F_2$: C, 77.04; H, 4.54; F, 17.41. Found: C, 76.94; H, 6.27; F, 17.85.

Peak C.—1,1-Diphenyl-1,2,2-trifluoroethane (0.5 g, 8% yield) was eluted as a colorless oil which rapidly eliminated HF upon standing. The proton nmr spectrum showed the single nonaromatic proton as a triplet (J_{HF} = 55 cps) of doublets (J_{HF} = cps) centered at δ 6.13. The aromatic protons (ratio 10:1) appear as a single peak at δ 7.31. The infrared spectrum contained the following bands: 3.21 w, 3.31 w, 6.72 m, 6.94 m, 7.30 m, 8.12 w, 8.60 w, 8.78 s, 9.20 s, 9.50 m, 9.70 m, 9.88 m, 10.0 w, 10.26 w, 10.62 m, 11.0 m, 12.55 m, 13.2 s, 13.85 s, and 14.35 μ s.

Anal. Calcd for $C_{14}H_{11}F_3$: C, 71.18; H, 4.69; F, 24.13. Found: C, 70.68; H, 4.96; F, 24.73.

Fluorination of 1,1-Diphenyl-2-fluoroethylene.—The fluoroolefin (2.3 g, 14 mmoles) was fluorinated in the same manner described above with 14 mmoles of fluorine. The crude mixture (2.6 g) was immediately purified by chromatography on silicic acid to provide a single component identical (infrared, nmr) with the 1,1-diphenyl-1,2,2-trifluoroethane formed in the 1,1-diphenylethylene fluorination.

Fluorination of *cis*-Stilbene.—The *cis*-stilbene (4.0 g, 22 mmoles) was fluorinated at −78° in the manner already described with 22 mmoles of fluorine. The solvent was removed to yield 4.7 g (yield 95%) of a mixture (5:1) of *meso*- and *dl*-1,2-difluoro-1,2-diphenylethanes.[9] The F^{19} and proton nmr spectra of both isomers were AA′XX′ cases very similar to that observed for the acenaphthylene adduct.[1]

The *meso* isomer could be separated by elution chromatography on silicic acid from the *dl* isomers as a crystalline solid, mp 99–100°.

Anal. Calcd for $C_{14}H_{12}F_2$: C, 77.04; H, 5.54; F, 17.41. Found: C, 76.64; H, 5.71; F, 17.62.

Acknowledgment.—The author is grateful to Mrs. Carolyn Haney for infrared and nmr spectra and to Mr. Morris Howard for technical assistance.

(7) R. C. Fahey, C. Schubert, *J. Am. Chem. Soc.*, **87**, 5172 (1965).

(8) ® Trademark of the Linde Co., utilized as an *in situ* HF scrubber.

(9) Further work on this system will be published shortly.

Indirect Methods of Preparation of Pure Monoalkylphenylacetonitriles[1]

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Preparation of a pure, simple α-alkylphenylacetonitrile by direct alkylation of phenylacetonitrile has not been very satisfactory because of accompanying dialkylation.[2,3] Thus, even though phenylacetonitrile was converted to its sodio salt by means of 1 equiv of sodium amide in liquid ammonia and 1 equiv of methyl iodide, *n*-butyl bromide, or benzyl chloride was then added, the resulting monoalkyl derivative was obtained contaminated with the dialkyl derivative and regenerated phenylacetonitrile.[2] Only 2–18% of these impurities was present when the alkylation was effected in toluene or by means of lithium amide in liquid ammonia,[2] but even these relatively small amounts are difficult to remove completely by ordinary distillation when the alkyl group introduced was *n*-butyl or lower.

We have now devised indirect methods (A and B) that have afforded vpc-pure α-methyl-, α-*n*-butyl-, and α-benzylphenylacetonitriles. Method A involved alkylation and decarboxylation starting with phenyl-

(1) Supported by the National Science Foundation.

(2) W. G. Kenyon, E. M. Haiser, and C. R. Hauser, *J. Org. Chem.*, **30**, 4135 (1965).

(3) A. C. Cope, H. L. Holmes, and H. O. House, *Org. Reactions*, **9**, 107 (1957).