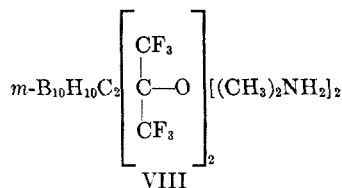


On the other hand, ammonia, hydrazine, and aliphatic amines reacted to give salt-like compounds such as the following.



Experimental Section

***m*-Carboranyl-1,7-bis(dimethylcarbinol) (I).**—*m*-Carborane (14.4 g 0.10 mole), was converted to its dilithio derivative as previously reported.⁶ The washed material was slurried in 200 ml of diethyl ether, cooled to 0°, and stirred rapidly while acetone (12.8 g, 0.22 mole) was added dropwise over a period of 45 min. Stirring was continued for 1 additional hr at 0–5°; the mixture was then hydrolyzed by slow addition of dilute hydrochloric acid. The ether layer was separated and dried over anhydrous MgSO₄, and the ether was evaporated to give 23 g of white, solid residue. This was recrystallized from benzene to give 8 g of white crystals (mp 122–123°).

*Anal.*⁷ Calcd for B₁₀C₈H₂₄O₂: B, 41.5; C, 36.9; H, 9.3. Found: B, 41.7; C, 36.9; H, 9.9.

***m*-Carboranyl-1,7-bis(methyltrifluoromethylcarbinol) (II).**—The dilithio salt of *m*-carborane (10 g, 0.069 mole) was prepared as described above and then slurried in diethyl ether. Trifluoroacetone (17.1 g, 0.1526 mole) was slowly added to the slurry, keeping the reaction temperature at 0° by cooling. After addition, the mixture was stirred for 1 hr at 5–10°, then hydrolyzed, and the ether layer was dried and the solvent was evaporated to give 18 g of yellow liquid residue. This was distilled under vacuum (1–2 mm) to give 4.9 g of a light yellow oil (bp 120–124°), which slowly solidified on standing.

Anal. Calcd for B₁₀C₈H₁₈F₆O₂: B, 29.3; C, 26.1; H, 4.9; F, 31.0. Found: B, 29.4; C, 26.2; H, 5.2; F, 31.0.

***m*-Carboranyl-1,7-bis(ditrifluoromethylcarbinol) (III).**—The dilithio salt of *m*-carborane (10 g, 0.069 mole) was prepared as above and slurried in diethyl ether. Hexafluoroacetone was passed into the stirred mixture through a dip tube until reaction appeared to be complete (1.5 hr at 0–5°). The mixture was then hydrolyzed, and the ether layer was dried and then evaporated to give 32.0 g of light yellow liquid residue; this crystallized after a few hours of standing. Recrystallization from petroleum ether (bp 30–60°) gave 5.8 g of white crystals (mp 80–81°).

Anal. Calcd for B₁₀C₈H₁₂F₁₂O₂: B, 22.7; C, 20.2; H, 2.5; F, 47.9. Found: B, 22.5; C, 20.2; H, 2.7; F, 47.7.

***m*-Carboranyl-1,7-bis(chlorodifluoromethyltrifluoromethylcarbinol) (IV).**—This preparation was the same as described for III, using pentafluoromonochloroacetone instead of hexafluoroacetone. Hydrolysis and evaporation of the dried ether layer from the reaction gave 31.5 g of brown, oily residue. This was vacuum distilled (1–2 mm) to yield 13.0 g of light yellow liquid, bp 140–145°. This solidified after standing for several hours (mp 43–45°).

Anal. Calcd for B₁₀C₈H₁₂Cl₂F₁₀O₂: B, 21.2; C, 18.9; F, 37.4; H, 2.4. Found: B, 21.5; C, 18.9; F, 37.2; H, 2.7.

1,7-Bis(2'-isopropenyl)-*m*-carborane (V).—*m*-Carboranyl-1,7-bis(dimethylcarbinol) (I, 26.0 g, 0.10 mole) was dissolved in 500 ml of benzene. Aluminum chloride (13.3 g, 0.10 mole) was added and the mixture was stirred and heated at reflux for 16 hr. The cloudy mixture was filtered under nitrogen and the filtrate was evaporated under reduced pressure to give 23.6 g of liquid residue. This was distilled under vacuum (1 mm) to yield 10 g of liquid, bp 85–91°; this solidified in the receiver. Recrystallization from petroleum ether (bp 30–60°) gave 4.8 g of white crystals (mp 46–47°).

Anal. Calcd for B₁₀C₈H₂₀: B, 48.3; C, 42.8; H, 8.9. Found: B, 48.4; C, 42.8; H, 9.1.

Diacetate of *m*-Carboranyl-1,7-bis(dimethylcarbinol) (VI).—The diol I (3.0 g, 0.015 mole) was dissolved in 50 ml of ace-

tic anhydride. Three drops of concentrated sulfuric acid was added, and the mixture was stirred and warmed to 35° for 3 hr. After standing overnight at room temperature, the mixture was diluted with water and neutralized by slow addition of sodium bicarbonate. The mixture was then extracted with ether, the extract was dried, and the ether was evaporated to yield about 3 g of a yellow, crystalline solid. Recrystallization from petroleum ether (bp 30–60°) gave 1 g of white, crystalline product (mp 64.5–65.0°).

Anal. Calcd for B₁₀C₁₂H₂₈O₄: B, 31.4; C, 41.8; H, 8.2. Found: B, 31.5; C, 41.9; H, 8.4.

Dimethylammonium Salt of *m*-Carboranyl-1,7-bis(ditrifluoromethylcarbinol) (VIII).—Two grams (0.0042 mole) of diol III was dissolved in 25 ml of benzene, and 25 ml of petroleum ether (bp 30–60°) was added. Dimethylamine was then introduced through a glass dip tube until no further precipitate formed. The suspension was filtered, and the filter cake was washed with fresh petroleum ether and then dried under vacuum. The white solid weighed 2.2 g (mp 105–106°).

Anal. Calcd for B₁₀C₁₂H₂₆F₁₂N₂O₂: C, 25.4; H, 4.6; F, 40.3; N, 5.0. Found: C, 25.8; H, 4.7; F, 40.3; N, 4.9.

Acknowledgment.—The authors are grateful to Drs. N. S. Semenuk, H. A. Schroeder, and T. L. Heying for helpful discussions and wish to acknowledge the support of this work by the Office of Naval Research.

Preparation and Dimerization of 4,5-Methano-3-keto Steroids¹

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A continuing interest in modified steroids² led us to investigate the effect on the biological activity of the steroid system when the double bond of the 3-keto- Δ^4 grouping was replaced by a cyclopropane ring. Isomeric 4,5-methano-3-keto steroids were prepared stereospecifically³ by allowing either a 3 α - or a 3 β -hydroxy- Δ^4 steroid to react with the Simmons-Smith reagent⁴ (methylene iodide and zinc-copper couple) and the cyclopropane carbinols were, in turn, oxidized to the 3-keto compounds using the Jones reagent.⁵

The first material studied was 3 β -hydroxy- Δ^4 -cholestene (1a) and this compound reacted with the Simmons-Smith reagent to yield the desired 4 β ,5-methano derivative 2a, at a rate about one-fifth that of the simple cyclic alcohols.³ Upon oxidation 2a gave the ketone 3a in high yield. It was found that when the crude product from the Simmons-Smith reaction was allowed to stand, a dimer (4) was formed. This same material was obtained in 65% yield when a solution of the pure alcohol 2a in methylene chloride containing a trace of iodine was allowed to stand for 12 hr at 0°. Thus, it seems reasonable to assume that, when the crude product was allowed to stand without solvent, iodine, formed from

(1) This work was supported in part by Grant No. CY-04284, U. S. Public Health Service.

(2) For the previous paper in this series, see W. G. Dauben, G. A. Boswell, W. Templeton, and J. W. McFarland, *J. Am. Chem. Soc.*, **85**, 2302 (1963).

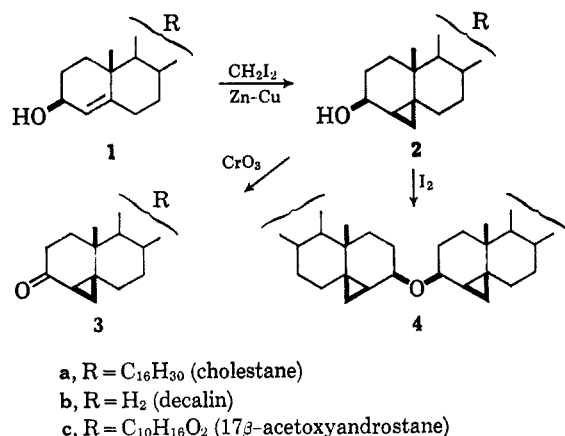
(3) W. G. Dauben and G. H. Berezin, *ibid.*, **85**, 468 (1963).

(4) H. E. Simmons and R. D. Smith, *ibid.*, **81**, 4256 (1959); E. P. Blanchard and H. E. Simmons, *ibid.*, **86**, 1337 (1964); H. E. Simmons, E. P. Blanchard, and R. D. Smith, *ibid.*, **86**, 1347 (1964).

(5) A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemlin, *J. Chem. Soc.*, 2548 (1953).

(6) S. Papetti and T. L. Heying, *Inorg. Chem.*, **3**, 1448 (1964).

(7) All new carborane derivatives were also characterized by their infrared spectra, as well as by elemental analysis. Melting points were determined with a "Mel-Temp" apparatus and are uncorrected.



residual methylene iodide, initiated the dimerization. Care was therefore taken that the crude reaction mixture was chromatographed immediately after evaporation of the reaction solvent, and with this precaution the amount of dimerization could be reduced to 2%.

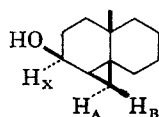
The crystalline dimer **4** had a molecular weight of 781, indicating the loss of one water from two molecules of alcohol to form an ether. In agreement with this suggestion was the presence of an ether absorption band at 1090 cm⁻¹ in the infrared spectrum and a band at τ 5.83 in the nmr spectrum. This latter spectrum showed no absorption for vinyl protons and this fact coupled with the very low end absorption in the ultraviolet established that the material was saturated. The presence of the cyclopropane rings were indicated by a broad, unresolved peak at τ 9.91; the integration was unreliable owing to the large number of protons present in the dimer.

In order to obtain a dimer of lower molecular weight which would give more useful spectral data, 3 β -hydroxy-4 β ,5-methano-10-methyldecalin (**2b**) was prepared⁶ and dimerized to crystalline **4b**.

The nmr spectrum of **2b** showed a high-field quartet at τ 9.98 due to absorption of one of the methylene hydrogens on the cyclopropane ring, and a diffuse multiplet at 9.38 for the other two hydrogens on the ring.⁷ The dimer **4b** retained the high-field quartet at τ 9.93 and the absorption was now equivalent to two hydrogens, indicating the presence of two cyclopropyl rings in the dimer. In addition, a new band at τ 5.93, equivalent to two hydrogens, was indicative of the presence of a disubstituted ether grouping. Again the infrared spectrum established the absence of a hydroxyl

(6) The 3 β -hydroxy- Δ^4 -10-methyloctalin could not be readily obtained in pure form and so the mixture of alcohols obtained from the hydride reduction of the related ketone was employed directly since the desired isomer is present in great excess; see H. B. Henbest and J. McEntee, *J. Chem. Soc.*, 4478 (1961).

(7) The cyclopropyl region of the nmr spectrum has now been fully analyzed by use of the experimental line positions and intensities with the aid of a computer program utilizing the equation of H. J. Bernstein, J. A. Pople, and W. G. Schneider [*Can. J. Chem.*, **35**, 65 (1957)] for an ABX system. The following assignments were made (W. G. Dauben and W. T. Wipke, in press).

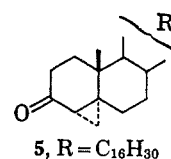


$$\tau_{H_B} = 9.98, \tau_{H_A} = 9.35$$

$$J_{AB} = 4.45 \text{ cps}, J_{AX} = 4.35 \text{ cps}, J_{BX} = 9.02 \text{ cps}$$

group. These spectral data support the structure assigned to the dimer. In these dimerizations, the ether must be formed by reaction of the cyclopropyl carbinol with the related cyclopropyl carbonyl carbonium ion. The simplicity of the high-field nmr absorption suggested that both groupings attached to the ether oxygen must be identical and, since one group must have the starting 3 β configuration, the 3 β -3 β stereochemistry was assigned to the ether.

Following the general procedure described above, 3 α -hydroxy- Δ^4 -cholestene was converted into 4 α ,5-methanocholestan-3-one (**5**). In the 17 β -acetoxyandrostane-3-one series, the isomeric 3-hydroxy- Δ^4 derivatives could not be obtained pure and only a fraction highly enriched in one isomer, believed to be β , was used. The cyclopropyl derivative **2c** and the related ketone **3c** were prepared.



Experimental Section⁸

3 α - and 3 β -Hydroxy- Δ^4 -cholestenes.—A solution of 16.5 g (42.9 mmoles) of Δ^4 -cholesten-3-one in 150 ml of ether was reduced with lithium aluminum hydride and processed in the usual fashion.^{9,10} The crude reduction product was chromatographed on 830 g of alumina (activity III). Benzene eluted 2.24 g (13.5%) of the 3 α epimer as an oil which crystallized on standing at 0°, mp 81.0–82.5°. A mixture of benzene–ethyl acetate (19:1) eluted 13.48 g (81%) of crystalline 3 β epimer which was recrystallized from methanol, mp 131–132°, yield 12.1 g.

3 β -Hydroxy-4 β ,5-methanocholestan-3-one (2a).—To a magnetically stirred mixture of 687 mg (10.5 mmoles) of zinc–copper couple,^{3,11} 12 ml of dry ether, and a small crystal of iodine, there was added 2.34 g (8.75 mmoles) of methylene iodide. The mixture was warmed with an infrared lamp until the reaction started, and then allowed to react for 30 min in a water bath at 35°. A solution of 967 mg (2.5 mmoles) of 3 β -hydroxy- Δ^4 -cholestene in 7 ml of dry ether was added over a period of 20 min, and the mixture was stirred for 1 additional hr at 40°. The ice-cooled mixture was diluted with a saturated solution of ammonium chloride, the supernatant layer was decanted from the precipitate, and the precipitate was washed twice with ether. The combined ethereal extracts were washed with saturated sodium chloride solution and dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The residue was chromatographed immediately on 50 g of alumina (activity III). Hexane eluted a small amount of methylene iodide and 22 mg (2%) of dimer **4a**. Benzene eluted 622 mg (62%) of crystalline 3 β -hydroxy-4 β ,5-methanocholestan-3-one, which was recrystallized from acetone (fine white needles): mp 94–95° (second crystalline form as white powder, mp 81.0–81.5°); ν_{\max} 3600, 3460 cm⁻¹; $[\alpha]_D -10^\circ$ (*c* 0.92); nmr τ 9.98 (quartet, *J* = 4.0 and 4.5 cps).

Anal. Calcd for C₂₈H₄₈O (mol wt, 400.66); C, 83.93; H, 12.08. Found: C, 84.03; H, 12.02.

(8) All chromatography was conducted with Woelm neutral alumina. The infrared spectra were run in chloroform, and the nmr spectra were obtained in deuteriochloroform using TMS as an internal standard. Optical rotatory dispersion measurements were run in methanol and optical rotations were performed in chloroform. Ultraviolet spectra were measured with a Beckman DK-2A Far ultraviolet spectrometer. Melting points were taken in evacuated sealed capillaries and all analyses were performed by the Analytical Laboratory, College of Chemistry, University of California, Berkeley, Calif.

(9) Pl. A. Plattner, H. Heusser, and A. B. Kulkarni, *Helv. Chim. Acta*, **32**, 265 (1949).

(10) W. G. Dauben, R. A. Micheli, and J. F. Eastham, *J. Am. Chem. Soc.*, **74**, 3852 (1952).

(11) R. E. Shank and H. Shechter, *J. Org. Chem.*, **24**, 1825 (1959).

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.

4 β ,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°; $[\alpha]_D^{25} +71^\circ$ (*c* 1.05); ν_{\max} 1665 cm^{-1} ; $\lambda_{\max}^{\text{EtOH}}$ 200 $\text{m}\mu$ (ϵ 6400), 277 $\text{m}\mu$ (ϵ 45), $\lambda_{\max}^{\text{hexane}}$ 187 $\text{m}\mu$ (ϵ 8100); ORD (positive Cotton effect) $[\phi] +5590^\circ$ (304 $\text{m}\mu$), $[\phi] -6780^\circ$ (252 $\text{m}\mu$); nmr τ 9.22 (singlet, C₁₈), 8.82 (singlet, C₁₉).

Anal. Calcd for C₂₈H₄₆O (mol wt, 398.65): C, 84.35; H, 11.63. Found: C, 84.39; H, 11.59.

3 α -Hydroxy-4 α ,5-methanocholestanone.—Using the procedure described for the 3 β isomer, 910 mg (2.35 mmoles) of 3 α -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 Δ^4 -cholestene-3-one,¹² and benzene eluted 613 mg (65%) of crystalline 3 α -hydroxy-4 α ,5-methanocholestanone which was recrystallized from acetone: mp 105–106°; $[\alpha]_D^{25} +88^\circ$ (*c* 0.96); ν_{\max} 3670, 3490 cm^{-1} ; nmr τ 9.99 (quartet, *J* = 4.5 and 4.5 cps).

Anal. Calcd for C₂₈H₄₆O (mol wt, 400.66): C, 83.93; H, 12.08. Found: C, 84.00; H, 11.98.

4 α ,5-Methano-3-cholestanone (5).—Following the procedure described for the oxidation of the 3 β isomer, from 172 mg (0.43 mmole) of the 3 α 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°; $[\alpha]_D^{25} +12^\circ$ (*c* 1.14); ν_{\max} 1670 cm^{-1} ; $\lambda_{\max}^{\text{EtOH}}$ 204 $\text{m}\mu$ (ϵ 7300), 275 $\text{m}\mu$ (ϵ 58); $\lambda_{\max}^{\text{hexane}}$ 194 $\text{m}\mu$ (ϵ 8400); ORD (negative Cotton effect) $[\phi] -5140^\circ$ (300 $\text{m}\mu$), $[\phi] +11,300^\circ$ (258 $\text{m}\mu$); nmr τ 9.22 (singlet, C₁₈), 8.84 (singlet, C₁₉).

Anal. Calcd for C₂₈H₄₆O (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 3 β -hydroxy-4 β ,5-methanocholestanone 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°; $[\alpha]_D^{25} -37^\circ$ (*c* 0.68); ν_{\max} 1090 cm^{-1} , ϵ_{200} 1000; nmr τ 9.91, 5.8.

Anal. Calcd for C₅₆H₉₄O: C, 85.86; H, 12.10; mol wt, 783.37. Found: C, 85.89; H, 11.90; mol wt, 781 (osmometer).

3 β -Hydroxy-4 β ,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- Δ^4 -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°; $\nu_{\max}^{\text{CCl}_4}$ 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 C₂₄H₃₈O (342.54): C, 84.15; H, 11.18. Found: C, 84.20; H, 11.02.

3 β (?) -Hydroxy-17-acetoxy- Δ^4 -androstene (1c).—A solution of 5.11 g (15.45 mmoles) of 17-acetoxy- Δ^4 -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%), $[\alpha]_D +39^\circ$ (*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.

3 β (?) -Hydroxy-17-acetoxy-4 β ,5(?) -methanoandrostane (2c).—Following the standard procedure 2.0 g (6 mmoles) of the above enriched 3 β (?) -hydroxy-17-acetoxy- Δ^4 -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%), $[\alpha]_D -29^\circ$ (*c* 0.70).

Anal. Calcd for C₂₂H₃₄O₂ (mol wt, 346.49): C, 76.26; H, 9.89. Found: C, 76.14; H, 9.81.

4 β ,5(?) -Methano-17-acetoxy-3-androstanone (3c).—Using the usual procedure, 161 mg (0.47 mmole) of the above 3 β (?) -hydroxy-4 β ,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°, $[\alpha]_D +65^\circ$.

Anal. Calcd for C₂₂H₃₂O₂ (mol wt, 344.48): C, 76.70; H, 9.36. Found: C, 76.53; H, 9.08.

Direct Fluorination of 1,1-Diphenylethylene^{1,2}

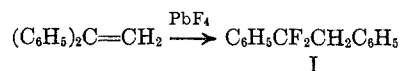
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Received June 13, 1966

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 Δ^4 -cholesten-3-one³ 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 PbF₄⁴ and electrochemically. These processes lead to rearranged products, *e.g.*, phenyl migration to yield 1,2-diphenyl-1,1-difluoroethane (I).



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).

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