in Table I; IR (KBr) 3060 (w), 1625 (s), 1600 (s), 1500 (s), 1480 (m), 1450 (s), 1230 (s), 1190 (m), 1070 (m), 1000 (s), 900 (s), 760 (s) cm^{-1}.

3-(2-Furyl)indazole (7). 4 (370 mg, 1.75 mmol) was pyrolyzed at 400 °C by slow sublimation from a sample flask held at 61 °C (10^{-4} torr). A volatile product condensed on the cold finger. A less volatile product condensed in the uncooled zone between the oven and the cold finger. The less volatile product was recrystallized from CCl_4 to give 128 mg (40%) of 7: colorless needles, mp 165–166 °C; NMR, see Table I; IR (KBr) 3200–2800 (br), 1610 (m), 1450 (m), 1325 (s), 1230 (s), 1000 (s), 980 (s), 880 (s), 760 (s), 715 (s) cm^{-1}; mass spectrum, m/e 184 (M^+, 100), 155 (36), 91 (11), 77 (7). Anal. Calcd for $C_{11}H_8N_2$: C, 71.73; H, 4.38; N, 15.21. Found: C, 71.65; H, 4.26; N, 15.20.

The more volatile product (18%) was identified as **10** as below.

Benzofulvene-8-carboxaldehyde (10). A pyrolysis of 1.0 g (4.7 mmol) of 4 at 720 °C (10^{-3} torr) gave a yellow product on the cold finger. This was freed from polymer (150 mg) by filtering a CH_2Cl_2 solution through Al_2O_3 (activity grade III). Subsequent removal of the solvent and sublimation at 85 °C (0.05 torr) furnished 470 mg (64%) of **10**: mp 88 °C (lit.[4] 90 °C); NMR ($CDCl_3$) δ 6.76 (dd, J = 8 and 1 Hz, 1 H), 7.03–7.76 (m, 6 H), 10.40 (d, J = 8 Hz, 1 H; CHO)[4] (this spectrum is ascribed to the E isomer (**10**); small doublets at δ 6.33 and 10.83 ($J \simeq 8$ Hz) may be due to the Z isomer (**10′**) (E/Z = 9:1)); IR (KBr) 3040 (w), 1660 (s), 1600 (w), 1450 (m), 1120 (m), 870 (m), 800 (m), 750 (s), 720 (m) cm^{-1}; mass spectrum, m/e 156 (M^+, 98), 155 (27), 128 (100), 127 (38).

Benzofulvene-8-carboxaldehyde Tosylhydrazone (12). A solution of 800 mg (5.12 mmol) of **10** and 960 mg (5.16 mmol) of tosylhydrazine in absolute methanol was stirred for 8 h; on concentration in vacuo, 998 mg (60%) of the tosylhydrazone (**12**) crystallized: mp 125 °C; NMR ($CDCl_3$) δ 2.40 (s, 3 H), 6.66 (d, J = 5 Hz, 1 H), 6.84–8.11 (complex, 11 H), 8.90 (br, 1 H, NH); IR (KBr) 3200 (m), 1590 (m), 1445 (s), 1355 (s), 1315 (s), 1160 (s), 1050 (s), 895 (s), 810 (s), 745 (s), 720 (m), 655 (s) cm^{-1}; mass spectrum (field desorption), m/e 324 (M^+, 100), 169 (26), 139 (93).

1-(2-Diazoethylidene)indene (14). Absolute methanol was added dropwise to a suspension of **12** (0.6 g, 1.8 mmol) in 70 mL of absolute ether until dissolution was complete. A suspension of sodium hydride (44 mg, 1.8 mmol) in ether was then added slowly to the magnetically stirred solution, which was kept under N_2 and in the dark. Rapid H_2 evolution took place and the tosylhydrazone sodium salt (**13**) precipitated after a few minutes. After the solution was stirred for 2 h, the salt was filtered under N_2, washed with ether, and dried under high vacuum in the dark. The yield was 620 mg. This salt was not examined further, but heated at 50–60 °C (10^{-3}–10^{-4} torr) in a flask attached to a cold trap cooled in liquid N_2. The orange-red solid which condensed in the trap was identified as 1-(2-diazoethylidene)indene (**14**) by comparison with a sample prepared by the method of Severin:[6] IR (CCl_4) 3030 (w), 2940 (w), 2050 (vs), 1585 (s); IR (KBr) 2050 (vs), 1570 (s), 1420 (m), 1380 (s), 1285 (m), 1240 (s), 975 (m), 765 (m), 735 (s), 700 (s) cm^{-1}; NMR (CCl_4) δ 5.3 (d, J = 10 Hz, 1 H, CH=N_2), 6.5 (d, $J \simeq 5$ Hz, 1 H, H-3), 6.75 (d, $J \simeq 5$ Hz, 1 H, H-2), 6.85 (d, J = 10 Hz, 1 H, H-8), 7.0–7.4 (m, 4 H); this spectrum is ascribed to the E isomer (**14**). A small doublet at δ 5.67 ($J \simeq$ 10 Hz) may be due to the CH=N_2 group of the Z isomer ($E/Z \simeq$ 8:1).

Pyrolysis of 1-(2-diazoethylidene)indene was carried out either by decomposition of the tosylhydrazone salt **13** at 50–60 °C or by sublimation of the pure diazo compound **14** at 20–50 °C unless otherwise indicated. The vapors were led directly into the pyrolysis tube at the desired temperature. In both cases, the yields of the pyrolysis products described below were generally poor (15–20%) due to partial decomposition of **14** in the sublimation flask with the formation of a crust, which prevented the major part of **14** from volatilizing.

(a) At 300 °C the pyrolysate was orange and shown by NMR to consist of unchanged **14**.

(b) At 400 °C a colorless pyrolysis product formed on the cold finger. This was vacuum transferred at room temperature and identified as spiro[cyclopropene-1,1′-indene] (**16**) by comparison of the NMR spectrum with that of an authentic sample.[6]

(c) At 600 °C a white crystalline material formed, mp ~0 °C, which was vacuum transferred at 0–25 °C (10^{-2} torr): NMR (CCl_4) δ 3.97 (d, $J \simeq$ 1.5 Hz, 2 H), 6.62 (m (three peaks), 2 H), 7.16 (narrow m, 4 H), identical with the spectra previously reported[7] for 1*H*-cyclopent[*cd*]indene (**18**).

(d) When the 600 °C pyrolysis was carried out by using very rapid sample introduction (decomposition of **13** at 90–100 °C), **18** was still the main product as shown by NMR, but the orange color and a weak absorption at 2050 cm^{-1} in the IR indicated that a trace of the diazo compound (**14**) survived even this temperature, thereby testifying to the mildness of the procedure.

(e) At 800 °C the pyrolysate was yellow: IR (KBr, −196 °C) 1935 (vs) cm^{-1} (C=C=CH_2); NMR ($CDCl_3$) as reported under c for **18**, together with a new peak at δ 5.43 (C=C=CH_2) due to **19**.[9] The ratio **18**:**19** ~ 2:1 was determined by integration. **18** could be removed from **19** by distillation at 0–25 °C (0.1–0.001 torr); only very little of the allene distilled under these conditions as shown by NMR and IR analyses. The distillation residue was a yellow-brown oil which, according to the IR spectrum, contained no allene function.

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Registry No. 4, 60637-07-2; 7, 3878-19-1; 10, 73017-90-0; 10′, 73017-91-1; 12, 73017-92-2; 13, 73017-93-3; (*E*)-14, 73017-94-4; (*Z*)-14, 73017-95-5; 16, 31337-05-0; 18, 209-69-8; 19, 73017-96-6.

Reactions of 1,1-Diarylethylenes and 1,1-Diarylimines with CF_3OF

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1,1-Diphenylethylene (**1**) reacts with CF_3OF to give products **2**–**6** in a cationic process. 9-Ethylidenefluorene reacts with CF_3OF to yield **8** and **10**. Amitriptyline (**12**) furnished a difluoro adduct (**13**) in low yield. Benzophenone oxime (**14**) gave a Beckmann rearrangement product on reaction with CF_3OF. Fluorenone anil (**15**) produced mainly fluorenone from reaction with CF_3OF. Diazepam (**16**) gave a 1:1 adduct (**18**) with CF_3OF. The adduct **18** reacted further to give an oxidation product (**17**).

Diarylethylenes have received considerable attention in synthetic and mechanistic organofluorine chemistry. 1,1-Diphenylethylene (**1**) has been subjected to fluorination under a variety of conditions and has provided some in-

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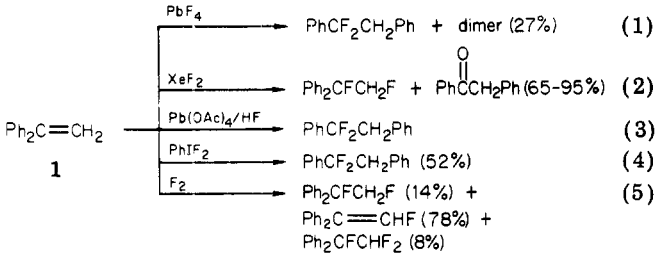
teresting and curious results. Bornstein et al. observed both dimeric and rearrangement products on fluorination of 1 with lead tetrafluoride (eq 1).[2] Zupan and Pollak found both rearranged and nonrearranged products when XeF_2 was used as the fluorinating agent (eq 2).[3] Tanner and van Bostelen found only rearrangement when fluorination was carried out with $Pb(OAc)_4/HF$ (eq 3).[4] Carpenter,[5] Zupan and Gregorcic,[6] and Patrick[7] have observed only rearrangement when $PhIF_2$ was used for fluorination (eq 4). Merritt, using elemental F_2 at low temperatures, observed products from fluorine addition, but rearranged products were absent (eq 5).[8] Mechanistically, reactions 1-3 have been interpreted as free radical or electron transfer in nature, and all have shown rearrangement.[2-4] Reaction 4 has been interpreted as an electrophilic process.[5-7] Reaction 5, the only reaction without rearrangement, has been interpreted as an ionic process.[8]

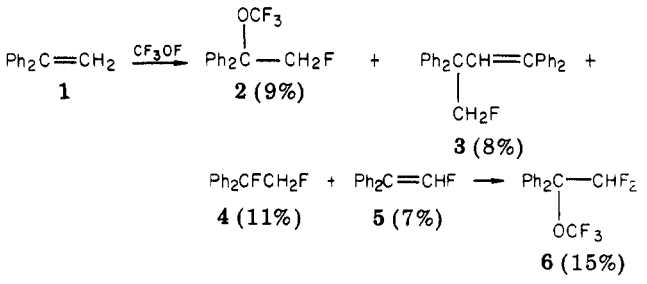


Barton, Hesse, and co-workers have studied many reactions of CF_3OF (fluoroxytrifluoromethane) with a variety of substrates.[9] In their studies with stilbenes or diphenylacetylene as substrates, they observed smooth syn addition of CF_3OF and F_2 occurring by electrophilic processes.[10,11]

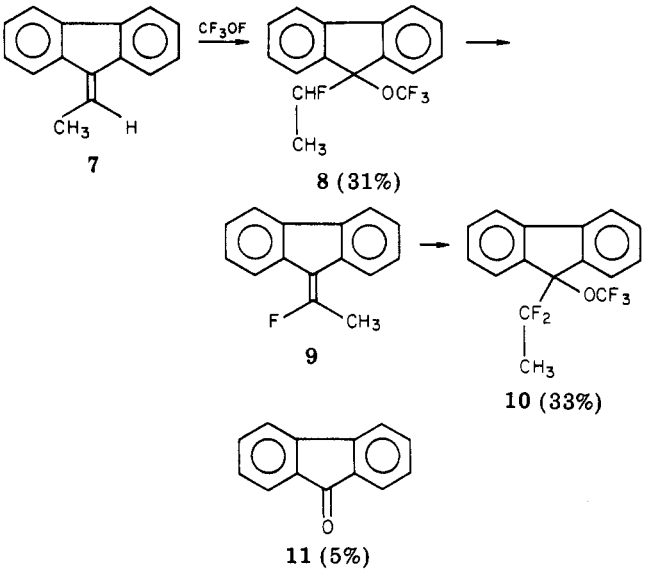
In our continuing interest in CF_3OF chemistry, we investigated the reaction between several 1,1-diarylethylenes and CF_3OF.[12] Our expectations were that the product types and regioselectivity based on substrate structure, coupled with the reported CF_3OF chemistry, would give good insight to the mechanism of CF_3OF reactions. Part I of this paper reports the results of our study.

The reactions of imines with fluorinating agents have received only limited attention. Merritt found some fairly complicated reactions between imines and F_2 at low temperatures.[13] Leroy and co-workers later observed a reaction process similar to that of Merritt's, using CF_3OF.[14]

Scheme I

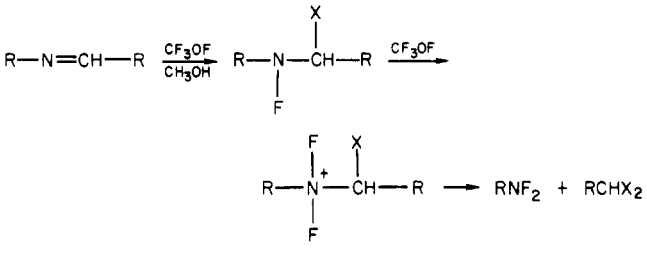


Scheme II



In more extensive studies, Barton, Hesse, and co-workers observed electrophilic reactions between CF_3OF and certain imines, and they developed the reaction into an elegant procedure for the preparation of *N,N*-difluoroamines.[15,16]

Because of our results from the studies of 1,1-diarylethylenes with CF_3OF and because of the relatively few studies of imines with CF_3OF, we felt that a study of the reactions of 1,1-diarylimines with CF_3OF could provide some useful mechanistic and synthetic information. Our results are reported in part II of this paper.



R = aliphatic or aromatic
X = OCH_3, F, OCF_3

I. 1,1-Diarylethylenes. Results

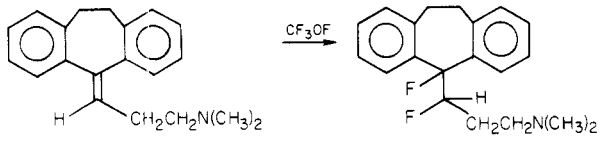
The reaction of 1,1-diphenylethylene (1) with CF_3OF in Freon-11 solution at −78 °C produced the substances shown in Scheme I. The yields are reported for isolated

(1) (a) Taken in part from the M.S. Thesis of G.L.C., Southern Illinois University, 1979. (b) Taken in part from the M.S. Thesis of S.M.I., Southern Illinois University, 1979.
(2) J. Bornstein, M. R. Borden, F. Nunes, and H. L. Tarlin, *J. Am. Chem. Soc.*, **85**, 1609 (1963).
(3) M. Zupan and A. Pollak, *J. Chem. Soc., Chem. Commun.*, 845 (1973).
(4) D. D. Tanner and P. van Bostelen, *J. Am. Chem. Soc.*, **94**, 3187 (1972).
(5) W. Carpenter, *J. Org. Chem.*, **31**, 3688 (1966).
(6) A. Gregorcic and M. Zupan, *Bull. Chem. Soc. Jpn.*, **50**, 517 (1977).
(7) T. B. Patrick, W. H. Hall, and J. J. Scheibel, *J. Org. Chem.*, in preparation.
(8) R. F. Merritt, *J. Am. Chem. Soc.*, **88**, 3871 (1966).
(9) Reviewed by R. H. Hesse, *Isr. J. Chem.*, **17**, 60 (1978); D. H. R. Barton, *Pure Appl. Chem.*, **49**, 1241 (1977).
(10) D. H. R. Barton, R. H. Hesse, G. P. Jackman, L. Ogunkoya, and M. M. Pechet, *J. Chem. Soc., Perkin Trans. 1*, 739 (1974).
(11) D. H. R. Barton, L. J. Danks, A. K. Ganguly, R. H. Hesse, G. Tazia, and M. M. Pechet, *J. Chem. Soc., Perkin Trans. 1*, 101 (1976); *J. Chem. Soc., Chem. Commun.*, 227 (1969).
(12) T. B. Patrick and E. C. Hayward, *J. Org. Chem.*, **39**, 2120 (1974); T. B. Patrick, M. H. LeFaivre, and T. E. Koertge, *ibid.*, **41**, 3413 (1976); T. B. Patrick, G. L. Cantrell, and C. Y. Chang, *J. Am. Chem. Soc.*, **101**, 7434 (1979).
(13) R. F. Merritt and F. A. Johnson, *J. Org. Chem.*, **32**, 416 (1967).
(14) J. Leroy, F. Dudragne, J. C. Adenis, and C. Michaud, *Tetrahedron Lett.*, 2771 (1973).
(15) D. H. R. Barton, R. H. Hesse, M. M. Pechet, and H. T. Toh, *J. Chem. Soc., Perkin Trans. 1*, 732 (1974).
(16) D. H. R. Barton, R. H. Hesse, T. R. Klose, and M. M. Pechet, *J. Chem. Soc., Chem. Commun.*, 97 (1975).

pure compounds. Purification was accomplished after several difficult chromatographic separations. **2** and **6** were both extremely sensitive to moisture and were characterized as their respective alcohols. Complete regioselectivity was observed, and evidence was not obtained for the presence of the reverse addition products. **3** was proven to be a head-to-tail dimeric product by spectral analysis. Other orientations were not observed. The elimination product, 2-fluoro-1,1-diphenylethylene (**5**), was converted both in situ and in control experiments to **6**.

9-Ethylidenefluorene (**7**) reacted smoothly with CF_3OF at −78 °C in Freon-11 to produce the compounds in Scheme II. Regioselectivity was observed, as in the case of **1**. Fluoroalkene **9** was not isolated and is assumed, by analogy with Scheme I, to be the precursor to **10**. Fluorenone (**11**) may be the result of oxidation by CF_3OF or air of **7** or **9** The combined isolated yields of pure products represent a good material balance.

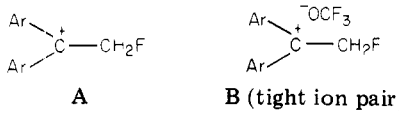
Amitriptyline (**12**) reacted very sluggishly with CF_3OF in methylene chloride solution at −20 °C to produce mainly a salt of the amine. Extended reaction of **12** with CF_3OF gave a complex mixture from which **13** was the only positively identified compound.[17]



12 **13**

Discussion

Previously reported studies on the reactions of CF_3OF and F_2 in dilute solutions at low temperatures have postulated ionic mechanisms.[8,9] The postulations have been based on stereochemical arguments, regioselectivity, syn addition, and reactivity. By analogy with accepted mechanisms, we discuss the reactions observed here with reference to pathways involving structures of the type A and B below. All structures are consistent with the known stereochemical results and electrophilic properties of CF_3OF reactions and are similar to those discussed by Hesse.[9]

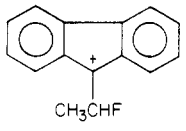


A **B (tight ion pair)**

The reaction of 1,1-diphenylethylene (**1**) may be viewed as a process in which the alkene behaves as a nucleophile toward CF_3OF, thereby producing cation A.[18,19] The reaction products are typical of carbocation reactions. Thus **2** arises from CF_3O^- combination with the cationic center, **3** arises from the cation reacting with **1**, **4** arises from reaction of A with F^- (formed from the documented decomposition of CF_3O^- to F^- and COF_2), and **5** results from deprotonation of A.

In the reaction of 2-fluoro-1,1-diphenylethylene (**5**) with CF_3OF, regioselectivity is observed but usual cationic products, especially the F_2 adduct, are missing. The reactivity of the alkene bond in **5** would be increased by fluorine p−π interactions.[20] Moreover, the fluorine should have a destabilizing influence on a cationic center.[21] Thus a path involving B, a tight ion pair, would satisfy both the energetics and the stereochemistry. Similar tight ion pairs have been suggested for CF_3OF reactions with stilbenes.[11]

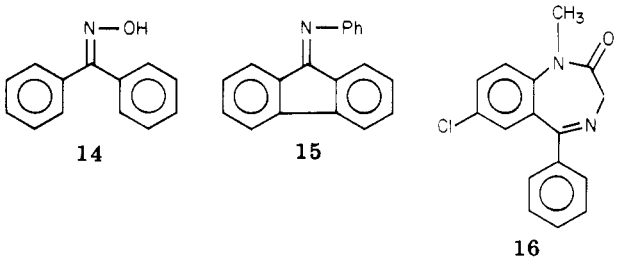
If 9-ethylidenefluorene (**7**) were to act as a nucleophile toward CF_3OF, then the antiaromatic system C would be formed.[22] Reaction paths which avoid this situation seem desirable. Alternative mechanisms, such as free-radical processes, must account for the observed regioselectivity. Further experimentation is required to resolve this problem.



C

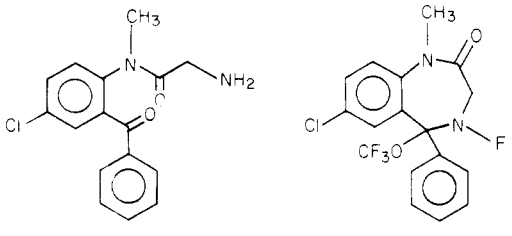
II. 1,1-Diarylimines. Results and Discussion

The substrates chosen for study are shown below.



14 **15** **16**

Benzophenone oxime (**14**) reacted rather sluggishly with CF_3OF to produce benzanilide in 70% yield, a reaction analogous to the Beckmann rearrangement.[23] Fluorenone anil (**15**) produced fluorenone (48%) and aniline. Our reaction conditions would not have permitted isolated of the unstable *N,N*-difluoroaniline. Diazepam (**16**) gave a 16% yield of the amine **17**. We did not observe a *N,N*-difluoroamino product, however. Reaction of **16** with CF_3OF at −70 °C produced **18** which was detected by ^{19}F and ^{13}C NMR spectroscopy.



17 **18**

The reactions of **15** and **16** with CF_3OF can occur by nucleophilic attack of the imino or hydroxyl functions on CF_3OF. Ultimately the C=N bond is broken, likely by

(17) J. E. Airey, Ph.D. Dissertation, University of London, 1973, has found that **12** reacts with CF_3OF in trifluoroacetic anhydride solution to produce about equal amounts of 10,11-dihydro-*N,N*-dimethyl-5*H*-dibenzo[*a,d*]cyclohepten-5-hydroxy-γ-fluoropropylamine and γ-fluoro-10,11-dihydro-*N,N*-dimethyl-5*H*-dibenzo[*a,d*]cyclohepten-$\Delta^{5(8)}$-propylamine. We thank Dr. Airey for this information.

(18) D. M. Sterling and J. B. Levy have observed that styrenes react with CF_3OF to give high yields of monophenyl products similar to those observed in Scheme I of this paper. Also, their results of a Hammett study of the reaction show that the styrenes behave as nucleophiles toward the CF_3OF with a ρ value of approximately −2. We thank Dr. D. M. Sterling for this information. Also see D. M. Sterling and J. B. Levy, Fourth Winter Fluorine Conference Abstracts, Jan 28–Feb 2, 1979, Daytona Beach, Fl, p 18.

(19) Y. Kobayashi, T. Toshida, and I. Kumadaki, *Tetrahedron Lett.*, 3865 (1979), have observed unusually good leaving group ability of CF_3O^- in trifluoromethyl trifluoromethylsulfonate.

(20) R. D. Chambers, "Fluorine in Organic Chemistry", Wiley, New York, 1973, p 142.

(21) G. A. Olah and Y. K. Mo, *Adv. Fluorine Chem.*, 7, 69 (1973).

(22) R. Breslow, *J. Am. Chem. Soc.*, **92**, 4139 (1970).

(23) L. G. Donaruma and W. Z. Heldt, *Org. React.*, 11, 1 (1960).

processes described by Barton, Hesse, et al.[15,16]

Experimental Section

Temperature readings are uncorrected. ^{1}H NMR spectra were recorded on a Perkin-Elmer R-24B (60-MHz) instrument with tetramethylsilane (δ 0.0) as an internal standard. ^{19}F NMR spectra were recorded at 56.4 MHz on a Varian T-60 with Freon-11 as an internal standard (ϕ 0.0). ϕ values are reported as positive upfield from Freon-11 and are uncorrected for concentration dependence. ^{13}C NMR spectra were recorded at 15 MHz on a JEOL FX-60Q spectrometer with tetramethylsilane (δ 0.0) as an internal standard. Infrared spectra were recorded on a Perkin-Elmer 710B spectrometer. TLC analyses were performed with Kodak precoated plates of silica gel (100 μm) with fluorescent indicator. Column chromatography was performed in Kimax columns containing Brinkman silica gel G (type 60).

General Reaction Procedure. A solution of the substrate, Freon-11, and chloroform or methylene chloride contained in a 50-mL round-bottomed flask was cooled to −78 °C. Nitrogen was bubbled through the solution for about 15 min, and CF_3OF (PCR, Inc.) was then passed into solution. Reaction progress was monitered by TLC, and the reaction was stopped when most of the substrate had been consumed. The mixture was then purged again with nitrogen at −78 °C to remove residual CF_3OF. The solvent was removed by rotary evaporation at low temperature. The reaction mixture was separated by medium-pressure chromatography on a 15 × 2.5 cm column containing 20 g of Brinkman silica gel G (type 60).[24] Fractions of 3-mL volume were collected automatically with a Gilson microfractionator. Each fraction was concentrated and analyzed.

Reactions with CF_3OF. I. 1,1-Diphenylethylene (1). A solution of **1** (Aldrich Chemical Co.) (0.62 g, 3.4 mmol) in 45 mL of Freon-11 was allowed to react at −78 °C with CF_3OF as described above. A total of 0.3 g (2.9 mmol) of CF_3OF was consumed. After chromatography the following compounds were isolated with hexane as eluant.

(a) Unreacted **1,1-diphenylethylene** (0.22 g), fractions 3–5.

(b) 1,1-Difluoro-2-(trifluoromethoxy)-2,2-diphenylethane (6), fractions 5–7: ^{19}F NMR (Freon-11) ϕ 49.2 (3 F, OCF_3), 124.8 (d, CF_2). **6** was moisture sensitive and easily converted to the fully characterized alcohol 1,1-difluoro-2-hydroxy-2,2-diphenylethane, a tan solid: mp 140–142 °C; 75 mg (15%); ^{1}H NMR ($CDCl_3$) δ 7.2–7.66 (m, 10 H, aromatic), 6.18 (t, 1 H, CHF, J = 54 Hz), 2.79 (s, 1 H, OH); ^{19}F NMR ($CDCl_3$) ϕ 125.5 (d, 2 F, CHF_2, J = 54 Hz); ^{13}C NMR ($CDCl_3$) δ 206.7, 134.7, 133.5, 131.3, 126.5–130.0 (aromatic), 140.5 (t, CCF_2, J = 20 Hz), 116.9 (t, CF_2, J = 250 Hz); IR 3400 (OH), 975–1300 (CF) cm^{-1}; R_f 0.51 ($CHCl_3$). Anal. Calcd for $C_{15}H_{11}F_5$: C, 59.6; H, 3.64; F, 31.5. Found: C, 59.8; H, 3.44; F, 31.1.

(c) 2-Fluoro-1,1-diphenylethylene (5), fraction 8: 32 mg (7.3%); ^{1}H NMR ($CDCl_3$) δ 7.3 (s, 10 H, aromatic), 6.8 (d, 1 H, vinyl, J = 81 Hz); ^{19}F NMR ($CDCl_3$) ϕ 126.4 (d, CHF, J = 81 Hz); ^{13}C NMR ($CDCl_3$) δ 147.3 (d, CF J = 269 Hz), 129.1–130.8 (aromatic); IR (neat) 3100, 1100–1300 (CF) cm^{-1}; R_f 0.39 (hexane). Spectral data were identical with reported data.[8]

(d) 1,2-Difluoro-1,1-diphenylethane (4), fraction 9: 54 mg (11%); ^{1}H NMR ($CDCl_3$) δ 7.3 (s, 10 H, arom), 4.9 (dd, 2 H, CH_2F, J = 20 and 68 Hz); ^{19}F NMR ($CDCl_3$) ϕ 151.7 (d t, CF, J = 18 and 20 Hz), 218.9 (dt, CH_2F, J = 20 and 48 Hz); ^{13}C NMR ($CDCl_3$) δ 136.4 (dd, PhCF, J = 28 and 149 Hz), 126.5–131.0 (aromatic), 86.9 (dd, CH_2F, J = 28 and 183 Hz); IR (neat) 3080, 2975, 950–1350 (CF) cm^{-1}; R_f 0.32 (hexane). Spectral data were identical with reported data.[8]

The eluant system was changed to $CHCl_3$-hexane.

(e) 4-Fluoro-1,1,3,3-tetraphenyl-1-butene (3), fraction 1: 33 mg (8%); mp 106–109 °C; ^{1}H NMR ($CDCl_3$) δ 7.3 (s, 20 H, aromatic), 6.8–7.3 (m, 1 H, =CH), 4.7 (d, 2 H, CH_2F, J = 48 Hz); ^{19}F NMR ($CDCl_3$) ϕ 212.6 (t, CH_2F, J = 48 Hz); ^{13}C NMR ($CDCl_3$) δ 133.7 (d, PhCCF, J = 5 Hz); IR (KBr) 3000, 1040–1090 (C-F) cm^{-1}; mass spectrum (80 eV), m/e 378 amu (calcd 378), 359, 266, 122, 120; R_f 0.17 (hexane). Anal. Calcd for $C_{28}H_{23}F$: C, 88.9; H, 6.08; F, 5.02. Found: C, 90.0; H, 6.23; F, 4.96.

The eluant system was changed to $CHCl_3$–hexane (1:1).

(f) 2-Fluoro-1-(trifluoromethoxy)-1,1-diphenylethane (2), fractions 2 and 3: oil, 39 mg (9%); ^{19}F NMR ($CDCl_3$) ϕ 48.0 (s, OCF_3), 212.4 (t, CH_2F). **2** was converted to the alcohol and characterized fully: ^{1}H NMR ($CDCl_3$) δ 6.95–7.46 (m, 10 H, aromatic), 4.6 (d, 2 H, CH_2F, J = 48 Hz), 2.62 (s, 1 H, OH); ^{19}F NMR ($CDCl_3$) ϕ 216.0 (t, CH_2F, J = 48 Hz); ^{13}C NMR ($CDCl_3$) δ 130.5 (d, CCF, J = 14 Hz), 130.3 (aromatic center), 84.6 (d, CF, J = 183 Hz); IR (neat) 3600 (OH), 950–1260 (CF) cm^{-1}; R_f 0.53 ($CHCl_3$). Anal. Calcd for $C_{14}H_{13}OF$: C, 77.8; H, 6.02; F, 8.80. Found: C, 78.0; H, 5.88; F, 8.60.

II. 9-Ethylidenefluorene (7).[25] A solution of **7** (0.46 g, 2.39 mmol) in 45 mL of Freon-11 was allowed to react at −78 °C with 0.3 g (2.9 mmol) of CF_3OF. Chromatography yielded the following (hexanes):

(a) 9-(1,1-Difluoroethyl)-9-(trifluoromethoxy)fluorene (10), fraction 4: 251 mg (33%); yellow oil; ^{1}H NMR (CCl_4) δ 7.1–7.8 (m, 8 H, aromatic), 1.21 (t, 3 H, CH_3, J = 18 Hz); ^{19}F NMR ($CDCl_3$) ϕ 49.3 (s, 3 F, OCF_3), 101.0 (q, 2 F, CF_2, J = 18 Hz); IR (oil) 1000–1400 (br, OCF_3) cm^{-1}; R_f 0.36 (hexane). Anal. Calcd for $C_{16}H_{11}OF_5$: C, 61.1; H, 3.50; F, 32.3. Found: C, 61.3; H, 3.33; F, 32.0.

(b) 9-(1-Fluoroethyl)-9-(trifluoromethoxy)fluorene (8), fraction 6: 215 mg (31%), oil; ^{1}H NMR (CCl_4)δ 7.07–7.86 (m, 8 H, aromatic), 5.1 (dq, 1 H, CHF, J = 7 and 47 Hz), 0.86 (dd, 3 H, CH_3, J = 3 and 23 Hz); ^{19}F NMR ($CDCl_3$) ϕ 50.0 (s, 3 F, OCF_3), 181.6 (dq, 1 F, CHF, J = 7 and 47 Hz); R_f 0.35 (hexane). **8** converted easily to the alcohol, 9-(2-fluoroethyl)-9-hydroxyfluorene, on exposure to moisture: ^{1}H NMR ($CDCl_3$) δ 7.0–7.7 (m, 10 H, aromatic), 4.97 (dq, 1 H, CHF, J = 6 and 40 Hz), 2.63 (s, 1 H, OH), 1.9 (dd, 3 H, CH_3, J = 6 and 24 Hz); ^{19}F NMR ($CDCl_3$) ϕ 181.6 (dq, CHF, J = 6 and 46 Hz); ^{13}C NMR ($CDCl_3$) δ 121.5–132.2 (aromatic), 95.6 (d, CF, J = 177 Hz), 15.7 (d, CH_3, J = 23 Hz); IR 3430 (OH), 750, 1140 (C–F) cm^{-1}; R_f 0.08 (hexane). Anal. Calcd for $C_{15}H_{13}FO$: C, 78.9; H, 5.70; F, 8.33. Found: C, 80.1; H, 5.91; F, 8.11.

(c) Fluorenone (11), $CHCl_3$ eluant, fraction 2: yellow crystals, 24 mg (5%); mp 80–82 °C, mixture melting point with authentic sample gave no depression; ^{1}H and ^{13}C NMR ($CDCl_3$) were identical with those of authentic material; R_f 0.07 (hexane).

III. Amitriptyline (12), 3-(10,11-Dihydro-5*H*-dibenzo-[a,d]cyclohepten-5-ylidene)-*N*,*N*-dimethylpropanamine.[26] A solution of **12** (0.62 g, 2.2 mmol) in 45 mL of methylene chloride was allowed to react at −50 °C with 0.6 g (5.8 mmol) of CF_3OF. ^{19}F NMR indicated the presence of a complicated mixture. A singlet at ϕ 129.6 disappeared on treatment with dilute NaOH solution, and 0.3 g of crude **12** was recovered. It is presumed that an ammonium salt was formed. Chromatography of the crude reaction mixture yielded several products. The major product was characterized as 3-(10,11-dihydro-5-fluoro-5*H*-dibenzo[*a*,-*d*]cyclohepten-5-yl)-3-fluoro-1-*N*,*N*-dimethylpropanamine (**13**): clear oil, 35 mg (5%); ^{1}H NMR ($CDCl_3$) δ 7.0–8.0 (m, 8 H, aromatic), 2.5–4.0 (m, 4 H, CH_2 of propanamine), 2.2 (s, 4 H, CH_2 of bridge), 2.1 (s, 6 H, CH_3); ^{19}F NMR ($CDCl_3$) ϕ 159.2 (dd, 1 F, CF, J = 11 and 26 Hz), 196.0–198.0 (m, 1 F, CHF); ^{13}C NMR ($CDCl_3$) δ 131.8 (dd, C5, J = 22 and 194 Hz), 124.7–131.8 (aromatic signals), 74.1 (dd, C3 of propanamine, J = 22 and 130 Hz), 48.8 (C10, C11), 58.0 (NCH_3), 46.0 (d, CH_2, J = 18 Hz), 41.2 (CH_2); IR (neat) 1460, 1120, 740 (C–F) cm^{-1}; R_f 0.23 (CH_2Cl_2). Anal. Calcd for $C_{20}H_{23}NF_2$: C, 76.2; H, 7.30; F, 12.1. Found: C, 76.4; H, 7.39; F, 12.5.

Another 25 mg of material showing fluorine (ϕ 160.2 (d, J = 29 Hz)) and hydroxyl (3150–3700 cm^{-1}) was obtained but was not characterized because of decomposition.

IV. Benzophenone Oxime (14). A solution of **14** (0.5 g, 2.5 mmol) in 40 mL of $CHCl_3$ was allowed to react at 0 °C with 0.5 g (4.8 mmol) of CF_3OF. The concentrated mixture gave yellow crystals which were recrystallized from chloroform to give pure benzanilide (0.35 g, 70%); melting point and mixture melting point with authentic material were 156–160 °C. ^{1}H NMR and IR spectra were identical with those of an authentic sample.

V. Fluorenone Anil (15).[27] A solution of **15** (0.5 g, 1.9 mmol) in 50 mL of $CHCl_3$ was allowed to react at 0 °C with 0.5 g (4.8

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mmol) of CF_3OF. The concentrated reaction mixture showed ^{19}F NMR signals at ϕ 70 and 146. Chromatography revealed the presence of a complex mixture from which fluorenone (0.16 g, 48%) was isolated; melting point and mixture melting point with authentic sample were 80–83 °C. ^1H NMR and IR spectra were identical with those of an authentic sample.

VI. Diazepam (16),[26] 7-Chloro-1-methyl-2*H*-1,4-benzodiazepin-2-one. A solution of **16** (0.5 g, 1.75 mmol) in 40 mL of acetone was allowed to react at −50 °C with 0.2 g (1.9 mmol) of CF_3OF. The concentrated reaction mixture gave 0.43 g of black crystals which after recrystallization from benzene–hexane gave **17** as tan crystals (0.3 g, 57%): mp 152–156 °C; ^1H NMR δ 6.9–7.6 (m, 8 H, aromatic), 4.6 (s, 2 H, NH_2), 3.4 (s, 2 H, CH_2), 1.6 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 134.0 (aromatic s), 244 (C=O), 49.0 (CH_2), 30 (CH_3); IR (KBr) 1640 and 1680 (C=O) cm^{-1}. Anal. Calcd for $C_{16}H_{15}N_2O_2Cl$: C, 63.6; H, 4.97; N, 9.27. Found: C, 63.5; H, 4.84; N, 9.50.

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Registry No. **1**, 530-48-3; **2**, 73037-93-1; **2** alcohol, 337-72-4; **3**, 73037-94-2; **4**, 379-83-9; **5**, 390-75-0; **6**, 73037-95-3; **6** alcohol, 337-53-1; **7**, 7151-64-6; **8**, 73037-96-4; **8** alcohol, 73037-97-5; **10**, 73037-98-6; **11**, 486-25-9; **12**, 50-48-6; **13**, 73037-99-7; **14**, 574-66-3; **15**, 10183-82-1; **16**, 439-14-5; **17**, 36020-94-7; **18**, 73048-41-6; CF_3OF, 373-91-1; benzanilide, 93-98-1.

Reactions of Superoxide with Peroxides

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The reactions of superoxide with *tert*-butyl hydroperoxide and 98% H_2O_2 have been studied in aprotic solvents. In benzene solvent, the proton-catalyzed disproportionation of superoxide followed by the base-catalyzed disproportionation of H_2O_2 appear to be the only reactions to occur. In acetonitrile, peroxy anions react with the solvent to form, ultimately, acetamide. Reactions of superoxide with diacyl peroxides are rather complex, but this reacting system produces intermediates capable of epoxidation of a number of olefins. Reactions of superoxide with acid chlorides and anhydrides in the presence of olefins also produce epoxides. Plausible mechanisms for these reactions are discussed.

The organic chemistry of superoxide ion, $O_2^{-}\cdot$ has been an area of intense interest in recent years. Examination of the biochemical[1,2] or the organic chemical[3,4] literature in this area, including a very recent excellent review,[5] shows that the reactions of superoxide with a large number of substrates proceed with the formation of a variety of peroxides, either as intermediates or as final products. Indeed, the initial experiments conducted in this work, aimed at elucidating the mechanism of nucleophilic attack by superoxide on a number of organic substrates, indicated that an understanding of the reactions between superoxide and various peroxidic species was crucial to the understanding of superoxide chemistry in general. The work reported here represents an attempt to elucidate the mechanisms of the direct reactions of superoxide with several peroxidic species.[6] For mechanistic reasons, the reactions of superoxide with protic peroxides will be discussed separately from the reactions with diacyl peroxides.

Results and Discussion

At the time of the initiation of this study, the most commonly written reaction in the literature[1-3,7] between superoxide and peroxides was the Haber–Weiss redox reaction (eq 1).

$$H_2O_2 + O_2^{-}\cdot \rightarrow O_2 + HO\cdot + HO^- \quad (1)$$

More recent studies,[8-13] including the present work, indicate that eq 1 is, at best, too slow to compete with more favorable processes. It now appears that the only reaction involving superoxide in the presence of protic peroxides in aprotic solvents is the proton-catalyzed disproportionation sequence (eq 2 and 3).

$$O_2^{-}\cdot + ROH \rightleftarrows HOO\cdot + RO^- \quad (2)$$

$$HOO\cdot + O_2^{-}\cdot \rightleftarrows O_2 + HOO^- \quad (3)$$

All of the data obtained in this work, which are summarized in Table I, can be explained by using only eq 2 and 3 plus subsequent reactions of RO^- or HOO^-, if any. R in eq 2 and 3 can be H, HO, *t*-BuO, or CH_3COO.

Addition of an excess of water to KO_2 suspended in 0.1 M 18-crown-6 ether in benzene causes an immediate re-

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