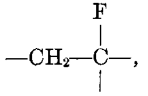
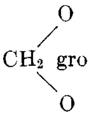
continuously increased from 3–10% acetone in Skellysolve B over 8 l. The first eluates contained negligible amounts of material. When the solvent consisted of approximately 6% acetone–Skellysolve B, gummy fractions totalling 227 mg. were eluted. Chromatography on paper[19] indicated that these fractions contained cortisone B.M.D. and the fluoro ether described below along with a variety of more polar materials presumably arising from degradation of the fluoroether. The first gummy fractions were followed by oils (380 mg.) which were crystallized from acetone–Skellysolve B affording 234 mg., m.p. 147° dec. A sample was recrystallized from the same solvents for analysis, m.p. 149.5–151° (dec.); $[\alpha]_D$ +104°; ν_{max} 1708, 1670, 1615, 1280, 1227, 1205, 1180, 1150, 1123, 1110, 1012, 1006, 993, 970 cm.$^{-1}$. N.m.r. spectroscopy indicated the presence of $-OCH_2F$,  $-CH_2-\overset{F}{\underset{|}{\overset{|}{C}}}-$, and  $CH_2\langle^{O}_{O}$ groups as well as the angular methyl groups.

Anal. Calcd. for $C_{23}H_{30}F_2O_5$: C, 65.08; H, 7.12; F, 8.95. Found: C, 65.19; H, 7.06; F, 9.09.

Hydrolysis of the Fluoro Ether from Cortisone B.M.D.—A solution of 11 mg. of the fluoro ether described above, m.p. 149.5–151°, in 8 ml. of 60% formic acid which had been previously purged with nitrogen was heated for 16 min. on the steam bath while bubbling nitrogen through the solution. The solution was cautiously poured into excess 10% potassium bicarbonate and extracted with three portions of methylene chloride. The extracts were dried (sodium sulfate) and concentrated to dryness leaving 9 mg. residue. This residue was dissolved in 5 ml. of methanol (previously purged with nitrogen), treated with 2 ml. of aqueous 1% potassium bicarbonate (previously purged with nitrogen), and stirred under nitrogen for 48 hr. After the potassium bicarbonate had been neutralized with acetic acid, the solution was concentrated to dryness under reduced pressure and the organic material isolated by extraction with methylene chloride and a small volume of acetone. The extracts held 8 mg. of gummy residue. Attempts at crystallization were not successful but paper chromatographic analysis[19] indicated that the major constituent of this residue moved with cortisone in two different systems (formamide stationary phase developed with 1:1 benzene–chloroform and the Bush B_5[20]).

Acknowledgment.—The authors are grateful to M. A. Rebenstorf and D. T. Kloosterman for running the sulfur tetrafluoride fluorinations and J. L. Johnson and W. A. Struck and associates for spectral and analytical determinations.

[19] The authors are grateful for Mr. L. M. Reineke of these laboratories for the paper chromatographic analyses.

[20] L. M. Reineke, *Anal. Chem.*, **28**, 1853 (1956).

The Radical Addition of Hydrogen Bromide to Hexafluoropropene

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In an earlier publication,[1] we have shown that free radical additions of thiols to trifluoroethylene and to hexafluoropropene are bidirectional. In view of these results and the fact that hydrogen bromide adds to trifluoroethylene to give both possible adducts,[2] the report[3] that radical addition of hydrogen bromide to hexafluoropropene gives only the single isomer, CF_3CFHCF_2Br, seemed questionable. We have now determined unequivocally that *both* isomers are formed in the X-ray- and ultraviolet-initiated reactions of hydrogen bromide with hexafluoropropene.

$$CF_3CF{=}CF_2 + HBr \longrightarrow \underset{\text{I}}{CF_3CFHCF_2Br} + \underset{\text{II}}{CF_3CFBrCF_2H}$$

The reactions were carried out at room temperature using equimolar amounts of reactants, and the products were analyzed by gas chromatography and nuclear magnetic resonance spectroscopy. The adducts, I and II, were found in a ratio of 58:42 for the X-ray-initiated reaction and 62:38 for the ultraviolet-initiated reaction, when determined by proton n.m.r. analysis. Gas chromatographic analysis of the products from the X-ray reaction showed a ratio of 57:43 for the two isomers, in excellent agreement with the values calculated from the n.m.r. spectrum.

In the absence of irradiation, no reaction occurs between hydrogen bromide and hexafluoropropene under the conditions used here.

Experimental

X-Ray-initiated Addition of Hydrogen Bromide to Hexafluoropropene.—A mixture of 15 g. (0.1 mole) of hexafluoropropene and 8 g. (0.1 mole) of anhydrous hydrogen bromide in a 100-ml. stainless steel reaction vessel at 25–35° was irradiated with X-rays for 5 hr. at an average dose rate of approximately 30,000 rads/min. The reaction vessel was then cooled to −10° and the volatile material removed slowly. The liquid residue (16.5 g.) was distilled through a small spinning-band column to give 12 g. (52% yield) of 1:1 adduct boiling at 34°/760 mm.

Anal. Calcd. for C_3HBrF_6: Br, 34.63; F, 49.35. Found: Br, 34.82; F, 49.16.

The proton n.m.r. spectrum of this product indicated the presence of the isomers I and II in a ratio of 58:42. The spectrum of a portion of the crude reaction product gave a similar result indicating that no fractionation of isomers occurred during distillation.

Examination of a portion of the distilled product by gas chromatography (6-ft × 1/4 in. o.d. column packed with 20% ethyl ester of "KelF" acid No. 8114[4] on "Columnpak"[4]; helium flow rate, 62.5 ml./min.; temp., 0°) showed the presence of two principal constituents with elution times of 18.6 min. and 21.3 min. in the ratio of 43:57, together with some nine minor ones totaling about 2.5% of the sample. The principal constituents were separated for identification by preparative-scale gas chromatography.

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[1] John F. Harris, Jr., and F. W. Stacey, *J. Am. Chem. Soc.* **83**, 840 (1961).

[2] R. N. Haszeldine, *J. Chem. Soc.*, 2800 (1957), obtained 58% $BrCHFCHF_2$ and 42% $BrCF_2CH_2F$ in an ultraviolet-initiated reaction of hydrogen bromide with trifluoroethylene. With X-ray irradiation, we have obtained the same products in a nearly identical ratio of 57:43.

[3] R. N. Haszeldine, *ibid.*, 3559 *(1953)*.

[4] "KelF" acid no. 8114 was obtained from Minnesota Mining and Manufacturing Co. "Columnpak" was obtained from Fisher Scientific Co.

The A-60 proton n.m.r. spectrum of the 43% constituent consists of a triplet centered at $\delta = 5.7$ (I) $(CH_3)_4Si$ external = 0.0 with J = 53 c.p.s. The components of the triplet are further split to doublets (J = 5 c.p.s.), and at very high resolution, the further splitting of the doublets to quadruplets can be detected (J ≈ 1 c.p.s.). The pattern thus is wholly consistent with that predicted for the previously unreported 2-bromo-1,1,1,2,3,3-hexafluoropropane (II) ($n^{24}D$ 1.3059). The proton spectrum of the other isomer, 3-bromo-1,1,1,2,3,3-hexafluoropropane (I) ($n^{24}D$ 1.3032), consists of a doublet centered at $\delta = 4.7$ with J = 44 c.p.s. The doublet components further resolve to quartet–quadruplet combinations (J1 doublet = 10 c.p.s.; J2 doublet = 5.5 c.p.s.; J quad. = 5.5 c.p.s.) by virtue of the asymmetry of the central carbon atom.[5]

Ultraviolet-initiated Addition of Hydrogen Bromide to Hexafluoropropene.—A mixture of 11.5 g. (0.08 mole) of hexafluoropropene and 6.3 g. (0.08 mole) of anhydrous hydrogen bromide was sealed in a 50-ml. Pyrex Carius tube and irradiated with a G.E. C3-H85 lamp at a distance of *ca.* 6 inches for 6 days. The tube was cooled to −78° and opened. The liquid reaction product was distilled through a small spinning-band column to give 13.5 g. (76% yield) of 1:1 adduct mixture boiling at 34–35°/760 mm. The proton n.m.r. spectrum of this material showed that it consisted of a mixture of isomers I and II in a ratio of 62:38.

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[5] (a) P. M. Nair and J. D. Roberts, *J. Am. Chem. Soc.*, **79**, 4565 (1957). (b) J. J. Drysdale and W. D. Phillips, *ibid.*, **79**, 319 (1957).

The Synthesis of Dihydropyrimidines from Benzamidine and α,β-Unsaturated Ketones

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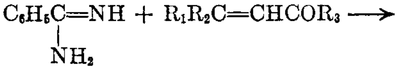
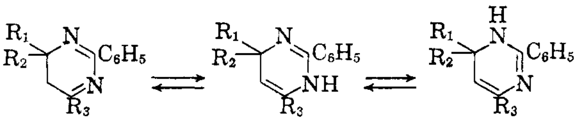
The reaction of amidines (*e.g.*, benzamidine, I) with α,β-unsaturated ketones is an attractive approach to the synthesis of dihydropyrimidines bearing an alkyl or aryl group at the 2-position. Traube and Schwarz[1] treated benzamidine (I) with mesityl oxide (IIa) in the absence of solvent and obtained a product, m.p. 91°, to which they assigned structure IIIa. Ruhemann[2] found that the reaction of benzamidine with 3-benzylidene-2,4-pentanedione at 100° results in the loss of an acetyl group with formation of a dihydromethyldiphenylpyrimidine, to which structure IV (R_1 = H, R_2 = C_6H_5, R_3 = CH_3) was assigned. Dodson and Seyler[3] used the reaction of benzamidine with various α-benzylidene ketones (II, R_1 = H, R_2 = C_6H_5) for the preparation of 6-substituted-2,4-diphenylpyrimidines; the presumed dihydropyrimidine intermediates, to which structure III (R_1 = H, R_2 = C_6H_5) was assigned, were not isolated.



$$C_6H_5\underset{\underset{\textstyle NH_2}{|}}{C}{=}NH + R_1R_2C{=}CHCOR_3 \longrightarrow$$

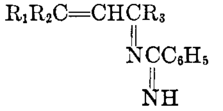
I

IIa. $R_1 = R_2 = R_3 = CH_3$
b. $R_1 = CH_3$, $R_2 = R_3 = C_6H_5$



III IV V

a. $R_1 = R_2 = R_3 = CH_3$
b. $R_1 = CH_3$, $R_2 = R_3 = C_6H_5$



$$R_1R_2C{=}CH\underset{\underset{\underset{\textstyle NH}{\|}}{NCC_6H_5}}{\overset{}{C}}R_3$$

VIa. $R_1 = R_2 = R_3 = CH_3$
b. $R_1 = CH_3$, $R_2 = R_3 = C_6H_5$

In our hands the reaction of benzamidine with mesityl oxide in ethanol or under Traube and Schwarz's conditions[1] yielded a compound melting several degrees higher than reported[1] and having an analysis consistent with the formula $C_{13}H_{16}N_2$. The infrared spectrum (carbon tetrachloride solution) has a band at 2.89 μ (N—H), which contradicts IIIa but is consistent with the tautomerized structures IVa and Va and the open-chain structure VIa. The proton nuclear magnetic resonance spectrum, taken in carbon tetrachloride solution with tetramethylsilane as internal standard, also rules out IIIa. Absorption occurs at 8.83 τ (*gem*-dimethyl), 8.23–8.25 τ (doublet, methyl), 5.60 τ (vinylic hydrogen), and 2.25–2.79 τ (multiplet, phenyl group) with approximate relative areas of 6:3:1:5. The absorption of the amino hydrogen, which is undoubtedly broad,[4] could not be detected with certainty. Structure VIa can be ruled out by comparing the τ-value of the *gem*-dimethyl groups with those of model compounds, as summarized in Table I. The *gem*-dimethyl grouping absorbs close to that of isopropylamine and at considerably higher τ than that of mesityl oxide, demonstrating that the two methyls are attached to a saturated carbon.

An analogous reaction occurs between benzamidine and dypnone (IIb); the elemental analysis, molecular weight, and infrared and n.m.r. spectra demonstrate that the product is IVb or Vb. The infrared spectrum has an N—H maximum at 2.91 μ, while n.m.r. peaks are present at 8.35 τ (methyl), 4.64 τ (vinylic hydrogen), and 2.00–3.00 τ (multiplet, phenyl) with approximate area ratios of 3:1:15. Structure VIb is ruled out by the data in Table I. The τ-value of the methyl protons of the reaction product is close to those of α-methylbenzylamine (a model for structure Vb) and N-benzylidene-α-methylbenzylamine (a model

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[1] W. Traube and R. Schwarz, *Ber.*, **32**, 3163 (1899).

[2] S. Ruhemann, *J. Chem. Soc.*, **83**, 1371 (1903).

[3] R. M. Dodson and J. K. Seyler, *J. Org. Chem.*, **16**, 461 (1951).

[4] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 270.