

others.<sup>2</sup> An explanation based on steric obstruction would predict a ratio  $\text{CH}_3\text{T}/\text{CF}_3\text{T}$  smaller than that of  $\text{CH}_3\text{T}/\text{C}(\text{CH}_3)_3\text{T}$  from neopentane; and one based on bond strength would predict that  $\text{CH}_3\text{T}/\text{CF}_3\text{T}$  be unity since the strengths of the  $\text{CH}_3\text{-T}$  and  $\text{CF}_3\text{-T}$  bonds are virtually equal. The experiments showed a ratio  $\text{CH}_3\text{T}/\text{CF}_3\text{T}$  in excess of twenty, confirming the present model.

Competition for capture of the hot atom is thus controlled by the same factor in attack on both C-C and C-X bonds: The availability of a strong bonding orbital within the time of collision, where this is governed by the inertia of the substituents on the central atoms. This principle should be completely general for hot atom reactions but has no counterpart in thermal processes.

STERLING CHEMISTRY LABORATORY  
YALE UNIVERSITY  
NEW HAVEN, CONNECTICUT

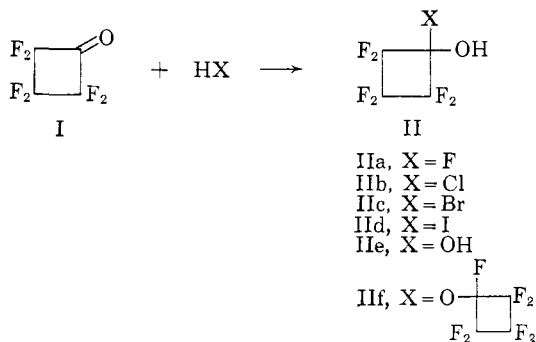
ROBERT ODUM  
RICHARD WOLFGANG

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### $\alpha$ -HALOALCOHOLS

Sir:

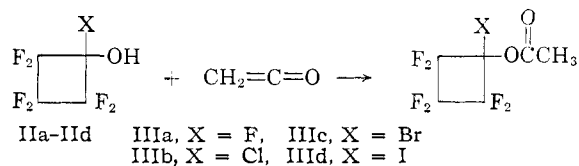
We wish to report the first preparation and *isolation* of certain  $\alpha$ -haloalcohols in pure form, and to describe some studies of hydrogen bonding in these systems. Hexafluorocyclobutanone (I), an



extraordinarily reactive ketone,<sup>1a</sup> reacts rapidly at low temperatures with hydrogen halides<sup>1b</sup> to give the distillable  $\alpha$ -haloalcohols IIa-IIId in high yields. Thus, equimolar quantities of I and hydrogen fluoride were condensed in an evacuated Monel vessel at  $-195^\circ$ . After allowing the mixture to warm to  $+20^\circ$ , distillation in a nitrogen atmosphere through a thoroughly dry glass column gave a 75% yield of heptafluorocyclobutanol (IIa), b.p.  $57\text{--}58^\circ$  (some dec.); b.p.  $6^\circ$  (85 mm.); Found: C, 24.6, 24.6; H, 0.7, 0.7; infrared O-H stretching absorption at  $3550$  and  $3450\text{ cm}^{-1}$  (shoulder);  $\text{H}^1$  n.m.r., singlet at  $5.52\tau$  (internal reference). IIa reacts vigorously and quantitatively with water to liberate HF and form hexafluorocyclobutanone hydrate (IIe),<sup>1</sup> also accessible *via* the addition of water to I. When two equivalents of I were combined with one equivalent of hydrogen fluoride as described above, an 80% yield of the hemiketal IIc, b.p.  $-21^\circ$  (0.05 mm.), was obtained. *Anal.* Found: C, 25.7; H, 0.5; F, 65.6; infrared O-H stretching absorption at  $3570$  (sharp) and  $3340\text{ cm}^{-1}$

(1) (a) D. C. England, *J. Am. Chem. Soc.*, **83**, 2205 (1961). (b) S. Andreades and D. C. England, Abstracts, 140th Meeting of the American Chemical Society, September, 1961, p. 14-M.

(shoulder). Reaction of IIa with ketene occurs exothermically to give 24% of heptafluorocyclobutyl acetate (IIIa), b.p.  $99\text{--}101^\circ$ . *Anal.* Found: C, 30.1; H, 1.4; F, 55.2.



In a similar manner, the alcohols IIb-IIId were prepared by the addition of the appropriate hydrogen halide to I in 73-90% yields and these alcohols were converted to the corresponding acetate IIIb-IIIId in 38-81% yields. Consistent elemental analyses, infrared,  $\text{F}^{19}$  and  $\text{H}^1$  n.m.r. spectra were obtained for all of the products described.<sup>2</sup>

In the absence of moisture, all of the alcohols were reasonably stable on storage except IId which slowly liberated iodine. At elevated temperatures, the equilibrium becomes unfavorable and the alcohols revert to some extent to ketone and hydrogen halide. This is a particular problem with IIa in glass apparatus since prolonged heating will consume HF (shifting the equilibrium to the left) and reaction of HF with glass produces water which also attacks the alcohol.

Ketones and hydrogen halides ordinarily do not give stable addition compounds.<sup>3,4</sup> Vorländer obtained some unstable ketone-hydrogen halide complexes<sup>3</sup> but the presence or absence of alcohol or ketone functions in these materials was not established. In general, 1,1-halohydrins cannot be isolated in pure form because of the rapid establishment of the addition-elimination equilibrium.<sup>5</sup> For example, 2-chloro-2-propanol cannot be isolated from an acetone-HCl mixture<sup>5</sup> although 1:1 and 1:2 acetone:HF nondescript complexes were reported in 1883.<sup>6</sup>

Previous attempts to prepare perfluorinated  $\alpha$ -fluoroalcohols have been unsuccessful,<sup>7,8</sup> although one example of an  $\alpha$ -fluoroalcohol, monofluoromethanol, has been reported.<sup>9</sup>

Neither ring strain factors nor fluorine substitution adjacent to the carbonyl function, *alone*, can account for the stability of these  $\alpha$ -haloalcohols relative to the ketones since neither  $\alpha$ -fluorocyclo-

(2) Difficulties were encountered in obtaining good analytical values for IId. These data will appear in a future publication.

(3) D. Vorländer, *Ann.*, **341**, 15 (1905).

(4) W. Hüchel, "Theoretical Principles of Organic Chemistry," Vol. I, Elsevier Publishing Co., New York, N. Y., 1955, p. 582.

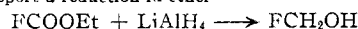
(5) D. J. Cram and G. S. Hammond, "Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 269.

(6) M. Loudolf, *Bull. Soc. Chim.*, **40**, 302 (1883).

(7) (a) J. Banus, H. J. Emeleus and R. N. Haszeldine, *J. Chem. Soc.*, 60 (1951). For example, attempts to prepare the primary  $\text{CF}_3\text{OH}$  from  $\text{CF}_3\text{I}$  produced fluorotrimethyl ether:  $\text{CF}_3\text{I} + \text{KOH} \rightarrow \text{CF}_3\text{H} + \text{KOI}$ . (b) R. N. Haszeldine and H. J. Emeleus, *Research*, **1**, 715 (1948). (c) R. N. Haszeldine and A. G. Sharpe, "Fluorine and Its Compounds," Methuen and Co., Ltd., London, 1951, p. 92. (d) W. H. Pearson in J. H. Simons, "Fluorine Chemistry," Vol. I, Academic Press, Inc., New York, N. Y., 1950, p. 483.

(8) A. M. Lovelace, D. A. Rausch and W. Postelnek, "Aliphatic Fluorine Compounds," Reinhold Publishing Corp., New York, N. Y., 1958, p. 137.

(9) Gy. Olah and A. Pavlati, *Acta. Chim. Acad. Sci.*, Hungary, **3**, 203 (1953), report a reduction in ether



butanol nor heptafluoro-2-propanol was isolated from equilibrium mixtures of cyclobutanone or hexafluoroacetone with hydrogen fluoride. Although both effects mentioned above must be important, such factors are irrelevant in the monofluoromethanol case.

The concentration dependence of the proton n.m.r. signals of IIa-IIc afforded an interesting comparison. Although in each case the pure liquid had a  $\tau$ -value<sup>10</sup> near 5.5 p.p.m. at room temperature, extrapolation to infinite dilution in carbon tetrachloride gave these internally-referenced values: IIa, 5.72  $\tau$ , IIb, 6.30  $\tau$ ; IIc, 6.42  $\tau$ . The dilution shifts to higher field are in the direction expected for alcohols when hydrogen bonds are being disrupted.<sup>11</sup> Moreover, shielding of the unassociated alcohol proton increases as the  $\alpha$ -halogen is changed in the order:  $\alpha$ -F <  $\alpha$ -Cl <  $\alpha$ -Br. Although caution must be exercised in the correlation of acidity with n.m.r. shielding parameters,<sup>11b,11c</sup> the observed trend is explicable in terms of the relative electronegativity of the halogen atoms. However, the relative magnitudes of the shifts seem to indicate the intermolecular hydrogen bond energies to the various covalently bound halogen atoms increase in the order F < Cl < Br. This interpretation is consistent with infrared data on IIa-IId and is in agreement with recent conclusions<sup>12</sup> based on infrared spectra of alcoholic alkyl halide solutions.

Details of this work including infrared and nuclear magnetic resonance spectra of these unusually modified alcohol functions will be described shortly.

(10) (a) G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958); (b) L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, London, 1959, p. 47.

(11) (a) 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, Chapter 15. (b) *Ibid.*, p. 175. (c) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960, Chapter 4.

(12) P. von R. Schleyer and R. West, *J. Am. Chem. Soc.*, **81**, 3184 (1959). Although the possibility of conformational heterogeneity<sup>13</sup> must be considered, the n.m.r. spectra do not seem explicable in these terms.

(13) R. Piccolini and S. Winstein, *Tetrahedron Letters*, No. 13, 4 (1959).

CONTRIBUTION NO. 722 FROM  
CENTRAL RESEARCH DEPARTMENT S. ANDREADES  
EXPERIMENTAL STATION D. C. ENGLAND  
E. I. DU PONT DE NEMOURS AND COMPANY  
WILMINGTON, DELAWARE

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#### A NEW STABLE FREE RADICAL: DI-*t*-BUTYLNITROXIDE

Sir:

We wish to report the discovery of a new group of stable, aliphatic, nitrogen containing free radicals. These substances are the di-*t*-alkylnitroxides, an example of which is the liquid red di-*t*-butylnitroxide, I, [(CH<sub>3</sub>)<sub>2</sub>CH]N—O.

Although some substituted nitroxides are known,<sup>1,2,3,4</sup> none of these contain groups attached to nitrogen which are incapable of delocalizing the odd electron. Di-*t*-butylnitroxide, clearly discernible by its e.s.r. spectrum<sup>5</sup> is formed directly

(1) H. Wieland and F. Kögl, *Ber.*, **55**, 1798 (1922).

(2) F. H. Banfield and J. Kenyon, *J. Chem. Soc.*, 1612 (1926).

(3) H. Wieland and K. Roth, *Ber.*, **53**, 210 (1920).

(4) O. Piloty and B. Graf Schwerin, *ibid.*, **34**, 1870 (1901).

during a novel reaction of *t*-nitrobutane with one equivalent of metallic sodium in glyme at room temperature. After complete reaction of metal, evaporation of the solvent *in vacuo* affords a solid residue which on dissolution in water produces an immiscible organic layer comprised of I and tri-*t*-butylhydroxylamine (II). *Anal.* Calcd. for C<sub>12</sub>H<sub>27</sub>NO: C, 71.57; H, 13.52; N, 6.97; mol. wt., 201. Found: C, 71.52; H, 13.36; N, 7.58; mol. wt., 210 (vapor pressure thermistor); n.m.r., two single peaks corresponding to two types of *t*-butyl groups at  $\tau = 8.75$  and 8.83 in a ratio of 1:2, respectively. In addition, small amounts of *t*-nitrosobutane, *t*-butyl alcohol and recovered *t*-nitrobutane also were found. In a typical run involving some product loss during solvent evaporation, 25 g. (0.24 mole) of *t*-nitrobutane was reduced by 5.5 g. (0.24 mole) of sodium to give approximately 9 g. of crude product found by quantitative vapor phase chromatography (v.p.c.) to consist of 22% I and 70% II. On standing in air, II is oxidized slowly to I.

The remarkable stability of I is demonstrated by its isolation from the crude reaction mixture either by preparative v.p.c. through a two-meter column packed with silicone grease on Celite maintained at 118°, or by fractional distillation through a spinning band column. Di-*t*-butylnitroxide (I) (*Anal.* Calcd. for C<sub>8</sub>H<sub>18</sub>NO: C, 66.60; H, 12.58; N, 9.71; mol. wt., 144. Found: C, 66.77; H, 12.90; N, 9.74; mol. wt., 149 (cryoscopic in benzene); b.p. 74–75° (35 mm.); ultraviolet  $\lambda_{\max}^{n\text{-hexane}}$  225 (shoulder) 238, 465 log  $\epsilon$ , 3.30, 3.33, 0.95) is a red liquid moderately volatile in an oxygen (or nitrogen) stream at room temperature. Its infrared spectrum shows only *t*-butyl bands and a band at 1345 cm.<sup>-1</sup> which probably is due to the N-O bond.

Spin assays of I by e.s.r. indicate one free spin per molecule with a determined value of  $5.9 \times 10^{23}$  free spins per mole. The  $g$  value is 2.0065 and the line width is 8.5 gauss. The observed magnetic moment 1.6 B.M. (theor., 1.73) also indicates the presence of one unpaired electron per molecule.

Since the stability of I cannot be ascribed to electron delocalization over a conjugated system attached to nitrogen, an explanation of this stability must be sought in terms of a lowered ground state energy in I by the intrinsic stability of an N-O three electron bond, an explanation of which recently has been proposed by Linnett.<sup>6</sup> Additional stabilization of I may be due to the steric inhibition of N-N or N-O bond formation preventing the formation of dimer.

I, stable to oxygen, water and aqueous alkali inhibits the polymerization of styrene and undergoes one electron polarographic oxidation (+0.55 v.) and reduction (-1.63 v.) in acetonitrile. It readily absorbs one-half mole of hydrogen in the presence of platinum to form N,N-di-*t*-butylhydroxylamine (III) (*Anal.* Calcd. for C<sub>8</sub>H<sub>19</sub>NO: C, 66.16; H, 13.19; N, 9.67. Found: C, 66.53; H, 12.84; N, 9.85; m.p. 65–66° (sealed cap)).

(5) A. K. Hoffmann, W. G. Hodgson and W. H. Jura, *J. Am. Chem. Soc.*, **83**, 4675 (1961).

(6) J. W. Linnett, *ibid.*, **83**, 2643 (1961).