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 τ-value[10] near 5.5 p.p.m. at room temperature, extrapolation to infinite dilution in carbon tetrachloride gave these internally-referenced values: IIa, 5.72 τ, IIb, 6.30 τ; IIc, 6.42 τ. The dilution shifts to higher field are in the direction expected for alcohols when hydrogen bonds are being disrupted.[11] Moreover, shielding of the unassociated alcohol proton increases as the α-halogen is changed in the order: α-F $<$ α-Cl $<$ α-Br. Although caution must be exercized in the correlation of acidity with n.m.r. shielding parameters,[11b,11c] 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[12] 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**, 3164 (1959). Although the possibility of conformational hetereogeneity[13] 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
                 RECEIVED OCTOBER 21, 1961

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, $[(CH_3)_3C]_2N—O$.

Although some substituted nitroxides are known,[1,2,3,4] 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[5] 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 $C_{12}H_{27}NO$: 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 τ = 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 $C_8H_{18}NO$: 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 $\lambda_{max}^{n-hexane}$ 225 (shoulder) 238, 465 log ϵ, 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.$^{-1}$ which probably is due to the N–O bond.
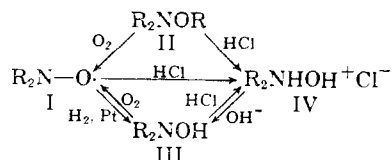
Spin assays of I by e.s.r. indicate one free spin per molecule with a determined value of 5.9 $\times$ 10^{23} free spins per mole. The g value is 2.0065 and the line width is 8.5 gauss. The observed magnetic moment 1.6 B.M. (theor., 1.73) also indicates the presence of one unpaired electron per molecule.

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.[6] 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 $C_8H_{19}NO$: 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).

III oxidizes rapidly in air to I and reacts with hydrogen chloride to form N,N-di-t-butylhydroxyl-ammonium chloride (IV) (Calcd. for $C_8H_{20}NOCl$: C, 52.88; H, 11.09; N, 7.71; Cl, 19.51. Found C, 52.58; H, 10.82; N, 7.75; Cl, 19.01; n.m.r. one peak at $\tau = 8.38$ for the two t-butyl groups and two broader peaks at $\tau = -1.37$ and -0.8). The intensity ratio of the peaks is 18:1:1, respectively, and the two low field peaks vanish in D_2O as expected for exchangeable hydrogens. IV also is formed by reaction of either I or II with anhydrous hydrogen chloride. This reaction of I is accompanied by the formation of t-nitrosobutane. Neutralization of IV with aqueous alkali reforms III. These transformations are summarized in the diagram.

$$R_2NOR$$
$$O_2 \diagup \quad \text{II} \quad \diagdown \text{HCl}$$
$$R_2N{-}O \xleftarrow{\text{HCl}} \xrightarrow{\text{HCl}} R_2NHOH^+Cl^-$$
$$\text{I} \quad \searrow O_2 \quad HCl \diagup \quad \text{IV}$$
$$H_2, Pt \searrow \diagup OH^-$$
$$R_2NOH$$
$$\text{III}$$

Further examination of this reaction and its products is being pursued and will be reported upon in the future. The authors wish to thank Dr. N. Elliot, Brookhaven National Laboratories, for magnetic susceptibility determinations, and Dr. J. H. Deonarine and his group, of these Laboratories, for microanalyses.

AMERICAN CYANAMID COMPANY   A. KENTARO HOFFMANN
CHEMICAL RESEARCH DEPARTMENT
CENTRAL RESEARCH DIVISION   AUDREY T. HENDERSON
STAMFORD, CONNECTICUT

HOMOGENEOUS HYDROGENATION CATALYZED BY BORANES

Sir:

Addition of molecular hydrogen to organic molecules with homogeneous catalysis has been reported for only a small fraction of the compounds which may be reduced by heterogeneous catalysis. Reduction of olefinic bonds has been observed frequently in the studies of hydroformylation. However, the utility of this method is limited since conditions have not been found which separate the reduction and hydroformylation reactions.[1]

More recently Halpern[2] and co-workers have reported the reduction of maleic acid catalyzed by a water soluble ruthenium(III). Walling and Bollyky[3] have reported the reduction of benzophenone and nitrobenzene in t-butyl alcohol catalyzed by potassium t-butoxide.
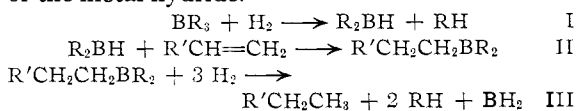
The facile addition reaction of boron hydrides to olefins has been developed by Brown[4] and co-workers. This has been shown to be a general reaction for olefinic bonds. The uncatalyzed hydrogenolysis of a number of carbon to metal bonds also has been reported.[5-8] In particular, Köster[7] has

(1) For a review and discussion, cf. M. Orchin, *Advances in Catalysis*, 5, 385 (1953).

(2) J. Halpern, J. F. Harrod and B. R. James, *J. Am. Chem. Soc.*, 83, 753 (1961).

(3) C. Walling and L. Bollyky, *ibid.*, 83, 2968 (1961).

(4) H. C. Brown, *Tetrahedron*, 12, 117 (1961).

(5) H. Gilman, A. L. Jacoby and H. Ludeman, *J. Am. Chem. Soc.*, 60, 2336 (1938).

reported the hydrogenolysis of a trialkyl borane to give a dialkyl boron hydride and a saturated hydrocarbon. These observations indicated that boranes might be effective homogeneous catalysts for the hydrogenation of olefins.

We now report on this very effective method of reduction. Cyclohexene or caprylene containing 3.8 mole % tri-n-butylborane is quantitatively hydrogenated in three hours at 220° under 1000 lb./in.^{2} hydrogen pressure. The products were identified by gas chromatography and infrared spectroscopy. The reaction rate is highly temperature dependent (essentially no reaction below 200°) but is not markedly influenced by hydrogen pressures. The high temperature required has been identified with the hydrogenolysis of the carbon–boron bond. Very recently Köster[3] has published preliminary results on olefin reduction catalyzed by an amine–borane complex.

This reaction is particularly valuable when applied to the reduction of high polymers in solution. Such polymers are reduced only with great difficulty and under very special conditions, using heterogeneous catalysis. Usually only incomplete hydrogenation is realized. The borane catalyzed, reduction of cis-1,4-polybutadiene gave a crystalline polymer. The infrared spectra and melt characteristics were those of a high density polyethylene of moderate molecular weight. Polypiperylene and polyisoprene, prepared by Ziegler type catalysis, yielded identical spectra (essentially that of the random copolymer of ethylene and propylene). Emulsion polybutadiene and SBR also were reduced in a similar fashion to give complete saturation of the aliphatic double bonds.

The essential steps are: (1) the hydrogenolysis of the metal to carbon bond forming an alkyl metal hydride, and (2) the addition of the resulting hydride to an olefinic bond. Reaction III completes the sequence giving hydrocarbon and some form of the metal hydride.

$$BR_3 + H_2 \longrightarrow R_2BH + RH \qquad \text{I}$$
$$R_2BH + R'CH{=}CH_2 \longrightarrow R'CH_2CH_2BR_2 \qquad \text{II}$$
$$R'CH_2CH_2BR_2 + 3 H_2 \longrightarrow$$
$$R'CH_2CH_3 + 2 RH + BH_2 \qquad \text{III}$$

We also have evidence that the elimination reaction to give a dialkyl boron hydride and an olefin is also taking place, but this does not contribute to the over-all hydrogenation process.

(6) W. Ipatieff, G. Razuwajeff and I. F. Bogdanow, *Ber.*, 63, 335 1110 (1930).

(7) R. Köster, *Angew. Chem.*, 68, 383 (1956).

(8) R. Köster, B. Gunter and B. Paul, *Ann.*, 644, 1 (1961).

THE B. F. GOODRICH RESEARCH CENTER   E. J. DEWITT
BRECKSVILLE 41, OHIO   F. L. RAMP
L. E. TRAPASSO

HCL CATALYZED FREE RADICAL FORMATION OF ISOPROPYL CHLORIDE DURING THE RADIOLYSIS AND PHOTOLYSIS OF n-PROPYL CHLORIDE

Sir:

This communication reports evidence that the isomerization of n-C_3H_7Cl to i-C_3H_7Cl observed in both the Co^{60} radiolysis and the photolysis of degassed liquid n-C_3H_7Cl occurs by a hydrogen chlo-