lines, found only in spectra of solutions which have large polarographic limiting currents at -0.5 v., is the resonance for the intermediate. It arises from splitting of the B^{11} resonance by three equivalent protons and is in fair agreement with the predicted intensity ratio of $1:3:3:1$ for this splitting. The spin–spin coupling constant, J, is 82 c.p.s. for the quartet, the same as that for the hydroborate quintet, and its center of gravity is 13.9 p.p.m. upfield from the borate singlet.

The proton n.m.r. spectrum of the sample was identical with the spectrum of a basic $NaBH_4$ solution.[9] Thus, we conclude that the screening of the protons on the BH_4^- ion is unaffected by conversion to the $-BH_3$ entity.

The presence of the $-BH_3$ group in the base-stabilized, partially hydrolyzed $NaBH_4$ solution has also been indicated by: (1) electrolyzing the solution at a mercury anode at a constant potential, (2) measuring the H_2 given off in a lengthy hydrolysis of the solution, (3) determining its reducing power toward iodate ion. The details of these experiments will be reported. The results are consistent with the postulation of a $-BH_3$-containing entity in the mixture, which might be aquated borine,[10] $H_3B:OH_2$, or trihydrohydroxyborate ion,[11] BH_3OH^-. The latter formulation is favored by the analogy between the effect of ionic strength on the rates of reaction of the intermediate and the BH_4^- ion. Thus, for the reaction between BH_4^- and HCO_3^-, the rate was little changed by change in ionic strength, whereas for the reaction between BH_4^- and NH_4^+ the rate decreased with increasing ionic strength. The rates of reaction of the intermediate with the same two general acids show an identical dependence on ionic strength. Although the ionic strengths in the kinetic work (0.2, 0.5, 1.0) were too high to allow the straightforward application of the Brønsted salt effect equation,[12] the similar change in the rates of reaction of the two species may permit the choice of the negatively charged species, BH_3OH^-, as the more probable formula of the intermediate.

(9) In agreement with results of Mesmer and Jolly, ref. 3.

(10) Species postulated by Davis, et al., ref. 1.

(11) J. Goubeau and H. Kallfass, Z. anorg. allgem. Chem., **299**, 160 (1959).

(12) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1961, p. 150 et seq.

(13) Allied Chemical Foundation Fellow, 1963–1964.

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Electron Spin Resonance of Alkyl Nitrenes

Sir:

We have obtained the first direct physical evidence for primary, secondary and tertiary alkyl nitrenes, $R-N:$. Such species have been postulated as intermediates in the decomposition of alkyl azides.[1] The electron spin resonances (e.s.r.) of several aromatic nitrenes have been reported.[2,3] These were shown to

(1) D. H. R. Barton and L. R. Morgan, Jr., J. Chem. Soc., 622 (1962). One of us (C. S.) has made numerous attempts to repeat this work without success. In no case was it found possible to achieve a nitrene insertion reaction even though several different commercially available quartz-enclosed medium pressure mercury lamps were used and the procedures described by Barton and Morgan were followed as well as variations on these procedures.

be ground-state triplets with significant delocalization occurring into an adjacent aromatic system.

The samples were prepared by dissolving the azide precursor[4] in hexafluorobenzene or perfluorodimethylcyclobutane and irradiating with an HBO-200 mercury lamp at $4°K$. Observations of the spectrum were made by means of a Varian V-4500 spectrometer (9.3 kMc.) with 100 kc. modulation. At $4°K$ the spectra persisted for hours after irradiation indicating a ground-state triplet or a thermally accessible triplet lying not more than a few cm.$^{-1}$ above the ground state. The only significant absorption observed with these materials was near 8000 gauss. The shapes of the absorptions indicated that we were observing those molecules in the randomly oriented nitrenes for which the external magnetic field was approximately perpendicular to the $C-N$ bond, the z-axis.[5]

The spectra may be described in terms of the two parameters, D and E, which are proportional to the averages of $1/r^3 - 3z^2/r^5$ and $(y^2 - x^2)/r^5$ for the two unpaired electrons.[6] The values obtained, assuming $g = 2.0023$, were n-propylnitrene, $D = 1.607$ cm.$^{-1}$, $|E| = 0.0034$ cm.$^{-1}$; 2-octyl, 1.616, 0.0019; cyclohexyl, 1.599, <0.002; cyclopentyl, 1.575, <0.002; α-carbethoxybenzyl, 1.659, <0.002; and t-butyl, 1.625, <0.002. Since E is a measure of the difference in the unpaired electron distribution along the x- and y-axes, the small values are compatible with an approximately cylindrical distribution about the $C-N$ bond expected for these nitrenes. Symmetry would require that t-butylnitrene have $E = 0$ if there were no distortions due to the matrix.

The assignment of the spectra to nitrenes receive support from a comparison with the D of N–H. Dixon deduced a value of 1.86 cm.$^{-1}$ from the ultraviolet spectrum observed on flash photolysis of HNCO.[7] Theoretical values of D for N–H are 1.8[8] or 1.9 cm.$^{-1}$.[9] The somewhat smaller values of the substituted compounds mentioned above are compatible with some spin delocalization into the adjacent groups. Such delocalization is known to occur with substituted methyl radicals.[10] The less concentrated spin would reduce the dominant contribution to D, the interaction of the unpaired electrons on the nitrogen atom.

Additional support for the nitrene assignment is based on a comparison with an alkyl methylene. Both triplets have the unpaired electrons primarily in two p-orbitals on the same atom. D should be proportional to Z^3 where Z is the effective nuclear charge for the 2 p-orbital.[9] Then

$$D_{RCH} = (Z_C/Z_N)^3 D_{RN} = (3.25/3.9)^3 \cdot 1.6 \sim 0.9 \text{ cm.}^{-1}$$

(2) G. Smolinsky, E. Wasserman, and W. A. Yager, J. Am. Chem. Soc., **84**, 3213 (1962).

(3) G. Smolinsky, L. C. Snyder, and E. Wasserman, Rev. Mod. Phys., **35**, 576 (1963).

(4) The azides were prepared by reaction of sodium azide with the corresponding halide (usually the bromide) in boiling aqueous methanol solutions. All the alkyl azides thus prepared exhibited infrared absorption in the region 2100 cm.$^{-1}$ characteristic of the N_3 group [E. Lieber, C. N. Rao, T. S. Chao, and C. W. W. Hoffman, Anal. Chem., **29**, 9161 (1957)].

(5) E. Wasserman, L. C. Snyder, and W. A. Yager, J. Chem. Phys., to be published.

(6) M. Gouterman and W. Moffitt, ibid., **30**, 1107 (1959); J. H. Van der Waals and M. S. de Groot, Mol. Phys., **2**, 333 (1959).

(7) R. N. Dixon, Can. J. Phys., **37**, 1171, (1959).

(8) J. Higuchi, private communication.

(9) As may be deduced from H. Sternlicht, J. Chem. Phys., **38**, 2316 (1963). An interchange of the y- and z-axes is necessary.

(10) R. W. Fessenden and R. H. Schuler, ibid., **39**, 2147 (1963).

The observed values for several perfluoroalkylmethylenes are $D \sim 0.72$ and $E \sim 0.021$ cm.$^{-1}$ indicating an angle of 150–160° at the divalent carbon atom.[11] Comparison should be made with the corresponding linear structure which would have $D \sim 0.75$ cm.$^{-1}$,[12] in fair agreement with Z^3 dependence.

An interaction between the unpaired electrons, similar in magnitude to those observed in the alkyl nitrenes, was determined for methylsulfonylnitrene which has $D = 1.581$ cm.$^{-1}$, $E = 0.0036$ cm.$^{-1}$. In contrast, the values for phenylnitrene ($D = 0.99$ cm.$^{-1}$, $E < 0.002$ cm.$^{-1}$) indicate significant delocalization of one unpaired electron into the aromatic system.

Acknowledgments.—We are grateful to Mr. R. M. R. Cramer and Mrs. B. I. Feuer for their assistance.

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(12) J. Higuchi, *J. Chem. Phys.*, **39**, 1339 (1963). We employ the calculated change in D with change in angle to correct the observed value.

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Preparation of Biaxially Oriented Polycapramide by the Solid State Polycondensation of a Single Crystal of ε-Aminocaproic Acid[1]

Sir:

The possibility of preparing oriented polymer chains by polymerization in single monomer crystals was first demonstrated by the conversion of trioxane to polyoxymethylene.[2] Later it was shown that the polymer chains are oriented not only in the direction of the fiber axis but also in the plane perpendicular to it.[3] The relationship of the orientation of the polymer crystallites to the crystallographic directions of the parent monomer has been fully clarified.[4]

More recently, it has been shown that the heating of a single crystal of phthalanilic acid at temperatures 50° below its melting point leads to highly oriented crystallites of N-phenylphthalimide.[5] This example of topotaxy is remarkable in view of the fact that the water split off in the reaction has to diffuse out of the crystal. We have now shown that an analogous phenomenon is possible in a polycondensation. Single crystals of ε-aminocaproic acid (m.p. 204–205°) heated *in vacuo* for 16 hr. at 173° yielded highly oriented polycapramide as indicated by the X-ray diffraction photograph (rotation around b-axis of monomer) on Fig. 1. Weissenberg photographs proved that biaxial orientation was involved. The monomer crystal belongs to space group P2$_1$/c, $a = 8.56$ Å., $b = 5.90$ Å., $c = 15.13$ Å., and $\beta = 103.13°$,[6] while the polymer has space group

(1) Abstracted from the Ph.D. thesis to be submitted by N. Morosoff to the Graduate School of the Polytechnic Institute of Brooklyn in June, 1965. This work was supported by grants from the National Science Foundation and the U. S. Atomic Energy Commission.

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Figure 1.

P2$_1$, $a = 9.56$ Å., $b = 17.2$ Å., $c = 8.01$ Å., and $\beta = 67.5°$, with the polymer chains parallel to b.[7] Weissenberg photographs of partially converted monomer crystals showed that the following crystallographic planes of monomer and polymer are parallel to each other:　$11\bar{2}_{mon} \parallel 200_{pol}$;　$112_{mon} \parallel 202_{pol}$;　$004_{mon} \parallel 002_{pol}$.

These data indicate that the polymer chains grow parallel to the intersection of the 004 plane with the 110 or $1\bar{1}0$ plane of the monomer. The polymerization involves a contraction of 17% in the direction of the chain axis and an 18% reduction of volume; it is remarkable that this may be accomplished with retention of chain orientation.

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(8) On leave from the Institute of Macromolecular Chemistry, Czechoslovakian Academy of Sciences, Prague, Czechoslovakia.

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The Photochemical Reduction of Rare Earth Ions in Fused Halides[1]

Sir:

The reduction by X-rays[2] and γ-rays[3,4] of rare earth ions incorporated in crystalline halide hosts to lower oxidation states is well known. Recent studies at these laboratories[5] have shown that only the locally uncompensated rare earth ions are capable of being photoreduced, and, in addition, the divalent rare earths so produced are readily reoxidized by thermal and optical processes. The instability of the divalent state is due to interstitial halogen atoms which remain in the crystal after irradiation and which eventually recapture their electrons.

Irradiations of molten halides containing rare earths, which would eliminate most of the inherent difficulties associated with the solid-state irradiations, were therefore carried out. In preliminary studies, molten solutions of dried and brominated BaBr$_2$ with 0.2 mole %

(1) The research reported in this paper was sponsored by the Air Force Materials Laboratory, Research and Technology Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, under Contract No. AF33(657)-11221.

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