believe that the azide complex has a trigonal-planar geometry.[6]

Addition of $CS_2$ to a chloroform solution of $((C_6H_5)_3P)_2CuN_3$ in a 1:1 mole ratio results in a clear yellow solution which, upon photolysis,[7] very rapidly evolves nitrogen, deposits colloidal sulfur, and leaves a colorless solution from which crystalline material was isolated. This crystalline material was shown to be $((C_6H_5)_3P)_2CuNCS$ on the basis of elemental analysis and its physical properties, which are identical with those of an authentic sample of $((C_6H_5)_3P)_2CuNCS$.[8] *Anal.* Calcd for $((C_6H_5)_3P)_2CuNCS$: C, 68.8; H, 4.65; N, 2.16; P, 9.60; S, 4.95. Found: C, 68.3; H, 4.53; N, 2.0; P, 8.88; S, 5.22. The C–N stretching frequency of the thiocyanate is at 2090 cm$^{-1}$,[9] mp 210–213°. We can therefore write the following over-all reaction

$$((C_6H_5)_3P)_2CuN_3 + CS_2 \xrightarrow{h\nu} ((C_5H_5)_3P)_2CuNCS + S + N_2 \quad (1)$$

Since this is the first example of a photolytical conversion of a bonded azide to a bonded thiocyanate, we have decided to investigate this reaction in detail.

Prior to the photolysis we were able to isolate yellow crystalline material of the $CS_2$ adduct. On the basis of elemental and mass spectral analysis and a molecular weight determination in benzene, the compound is formulated as $((C_6H_5)_3PCuN_3 \cdot CS_2)_2$ (I). *Anal.* Calcd for $(C_6H_5)_3PCuN_3 \cdot CS_2$: C, 51.4; H, 3.38; N, 9.47; P, 7.0. Found: C, 50.94; H, 3.47; N, 9.20; P, 6.35. The molecular weight calculated for $((C_6H_5)_3PCuN_3 \cdot CS_2)_2$ was 887; found, 896. The loss of $(C_6H_5)_3P$ upon the formation of the yellow adduct was further verified by the isolation of triphenylphosphine from the filtrate of the $CS_2$ adduct. We also note that the complex $((C_6H_5)_3P)_2CuNCS$ can be obtained from I only if $(C_6H_5)_3P$ is added prior to the photolysis. In the absence of $(C_6H_5)_3P$ the products which are obtained from the photolysis of I are different, and these will be reported at a later date.

Of particular interest is the structure of the yellow $CS_2$ adduct.[10] The formation of I can be followed by the disappearance of the N–N stretching band of the azide and the appearance of a sharp band at 1235 cm$^{-1}$ which can be associated with a thiocarbonyl group. It is therefore reasonable to suggest that the addition occurs at the azide moiety, possibly by a 1,3-dipolar cycloaddition. Although several possible structures could be formulated for I, we feel that we do not have compelling evidence for any particular one. We have, therefore, undertaken the study of the crystal and molecular structure of I by X-ray diffraction techniques.

Preliminary results indicate that the metal atom and the other donor atoms in azide complexes have marked effects on the photochemical behavior of the coordinated azides. In order to study these effects in detail we have prepared a series of azido complexes of Cu(I), Ag(I), Au(I), Ni(II), Pd(II), and Pt(II) with a variety of mono- and bidentate ligands containing phosphorus donor atoms, and we are currently studying the photochemical reactions of these species. The results of this study will be presented at a later date.

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**Ronald F. Ziolo, Zvi Dori**
*Department of Chemistry, Temple University*
*Philadelphia, Pennsylvania 19122*

*Received July 23, 1968*

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(6) Crystal structure analysis of this complex is currently in progress.

(7) Photolysis was performed with a Hanovia Type L 450-W medium-pressure mercury lamp.

(8) $((C_6H_5)_3P)_2CuNCS$ was prepared by the addition of a methanolic solution of NaNCS to a chloroform solution containing cuprous chloride and an excess of $(C_6H_5)_3P$. The complex was recrystallized from a chloroform–ether solution.

(9) Although it is generally agreed that the N–C stretching frequency for an N-bonded NCS occurs below 2100 cm$^{-1}$ (see, for example, A. Sabatini and I. Bertini, *Inorg. Chem.*, **4**, 1665 (1965)), we do not rule out the possibility of an S-bonded thiocyanate in this complex.

(10) The adduct can be stored in the dark and under a nitrogen atmosphere for a long period of time with no apparent decomposition.

## Gas-Phase Acidities of Alcohols. Effects of Alkyl Groups

*Sir:*

As part of our continuing studies of gas-phase acidities,[1] we wish to report the relative acidities of a series of simple aliphatic alcohols. This is the first direct measurement of these acidities,[2] and it provides a unique demonstration of the effect of alkyl groups in stabilizing charge. Making use of ion cyclotron resonance (ICR) spectroscopy and pulsed double-resonance studies, we have been able to detect reactions of type 1 and determine the sign of $\Delta H°$.[3] Assuming $\Delta S° = 0$, this provides a measure of relative acidities for reactions of type 1.

$$ROH + R'O^- \rightleftharpoons RO^- + R'OH \quad (1)$$

The following order of relative acidities has been found: neopentyl alcohol > *t*-butyl > isopropyl > ethyl > methyl > water; and *t*-butyl ≈ *n*-pentyl ≈ *n*-butyl > *n*-propyl > ethyl.

Formally, the energetics of acid ionization can be considered as the sum of three thermodynamic processes: bond dissociation energy (to a radical and a hydrogen atom), ionization potential of the hydrogen atom (to a proton), and electron affinity of the radical (to an anion).[4] Since in all of the simple aliphatic

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(1) J. I. Brauman and L. K. Blair, *J. Amer. Chem. Soc.*, **90**, 5636 (1968).

(2) V. L. von Trepka, *Z. Naturforsch.*, **18a**, 1122 (1963); D. Vogt and H. Neuert, *Z. Physik*, **199**, 82 (1967). These authors have observed the reactions of hydroxide ion with alcohols in the gas phase.

(3) All alcohols (except 1-butanol) were of reagent grade and were used without further purification. Degassed alcohol mixtures (1:1 gas phase, room temperature) were prepared on a vacuum line. The alcohol mixture was allowed to mix with a comparable amount of water vapor in the unheated manifold of the ICR spectrometer. For these mixtures, the ionization efficiency curves of all the alkoxide ions (as well as that of benzyl anion in the case of toluene) had a maximum ion intensity at 6.2 eV (uncor), identical with that for $OH^-$. Neither alkoxide nor benzyl anion could be observed unless water was present. However, this has created no difficulties in ordering these acidities, since water is the least acidic compound studied. The principal negative ion formed on electron impact with $H_2O$ has been shown to be $H^-$ (dissociative attachment, peak maximum 6.5 eV), and the principal negative ion–molecule reaction is the proton transfer from $H_2O$ to $H^-$. See R. N. Compton and L. G. Christophorou, *Phys. Rev.*, **154**, 110 (1967), and references cited therein. Within the pressure range chosen for our studies, $H^-$ could not be observed, possibly because of a fast reaction with water and/or alcohol.

Reactions were studied in the pressure range 1.0–2.5 × $10^{-5}$ torr using the pulsed double-resonance technique. See ref 1 for pertinent literature citations and a generalized description of the experiment and techniques used in studying gas-phase acidities. Transfer of only the hydroxylic proton was demonstrated with appropriate deuterium-labeled compounds.

alcohols the RO–H bond strength is *ca.* 104 ± 1 kcal/mol,[5] the stabilizing effect of the alkyl group manifests itself in the electron affinity of the alkoxy radical. The stabilization observed is consistent with a model in which the alkyl groups, being polarizable, stabilize the charge by an induced dipole.[7] It is to be expected that methyl or methylene groups will be more effective than hydrogen in stabilizing both positive and negative charges and that such stabilization will be of more importance in the gas phase than in solution. The effect of alkyl groups in charge stabilization has been discussed extensively by Schubert.[8] Our observations are consistent with his picture.

The results obtained here are reversed from the "normal" inductive order observed in solution.[9] Thus, in contrast to the solution behavior, *t*-butoxide in the gas phase is less basic than methoxide. This relatively enhanced basicity of *t*-butoxide in solution may be due, in part, to less effective hydrogen bonding and considerable shielding of the negative charge from the bulk solvent by the alkyl groups. Naturally, the bulk properties of the solvent are of great importance, and acidities in *t*-butyl alcohol solvent are not directly comparable with those in methanol. In general, intrinsic acidities may well be expected to differ drastically from solution acidities in which specific solvation, dispersion forces, and steric effects can be large and determining factors.[10] Consequently, solution p*K*'s are complex functions of the medium as well as a reflection of intrinsic acidity.

To explore further the effect of alkyl groups on charges, we have, by ICR and pulsed double-resonance studies, confirmed the results of Munson[11] on the relative basicities of aliphatic amines. The basicities are $Me_3N > Me_2NH > MeNH_2 > NH_3$. Thus, in the gas phase, the "normal" order holds, uncomplicated by solvation and steric effects. In solution, the "intrinsic" basicities are obscured, probably by steric hindrance to solvation. In the gas phase, we assume that the polarizability is an important factor.

Finally, we have found that the acidity of toluene is approximately equal to that of ethanol. Since the bond strength in toluene[12] is *ca.* 19 kcal/mol lower than that in ethanol, the electron affinity of benzyl radical must also be *ca.* 19 kcal/mol lower than that of ethoxy radical. Thus, the increased electronegativity of oxygen enhances the intrinsic acidity of alcohols by its contribution to the electron affinity. Further work will clarify the importance of these effects in a wider range of compounds.

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[4] A. Streitwieser, Jr., and J. H. Hammons, *Progr. Phys. Org. Chem.*, 3, 41 (1965).

[5] S. W. Benson and R. Shaw in "Oxidation of Organic Compounds-I," Advances in Chemistry Series, No. 75, American Chemical Society, Washington, D. C., 1968. The bond dissociation energy of water is substantially higher.[6] Thus, it is difficult to draw direct comparisons between water and the simple alcohols.

[6] J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966); S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965).

[7] E. A. Moelwyn-Hughes, "Physical Chemistry," Pergamon Press, New York N. Y., 1957.

[8] W. M. Schubert, R. B. Murphy, and J. Robins, *Tetrahedron*, **17**, 199 (1962). It is particularly interesting to note the effect of neopentyl.

[9] The polar effect of alkyl groups in saturated systems has received considerable attention: F. W. Baker, R. C. Parish, and L. M. Stock, *J. Amer. Chem. Soc.*, **89**, 5677 (1967), and references cited therein; V. W. Laurie and J. S. Muenter, *ibid.*, **88**, 2883 (1966). In general the effect appears to be small.

[10] See C. D. Ritchie and R. E. Uschold, *ibid.*, **90**, 2821 (1968), for relevant comments.

[11] M. S. B. Munson, *ibid.*, **87**, 2332 (1965).

[12] R. Walsh, D. M. Golden, and S. W. Benson, *ibid.*, **88**, 650 (1966).

[13] A. P. Sloan Fellow.

[14] National Science Foundation Predoctoral Fellow, 1966–present.

**John I. Brauman,[13] Larry K. Blair[14]**
*Department of Chemistry, Stanford University*
*Stanford, California 94305*

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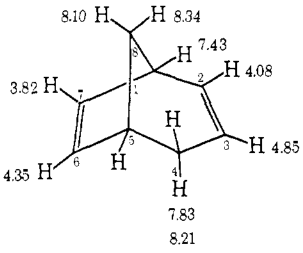
## The Bicyclo[3.2.2]nonatrienyl Anion. The Anionic Analog of the Norbornadienyl Cation[1]

*Sir:*

The successful generation and direct observation of the first homoaromatic carbanion[2,3] (II) prompted us to look for other anions which show evidence of similar electron delocalization. The importance of delocalization in, and the stability of, the norbornadienyl cation[4] suggested that the anionic analog of this cation, the bicyclo[3.2.2]nonatrienyl anion, would be interesting. Recently Goldstein[5] has used MO symmetry arguments to propose that this anion would have enhanced stability. We now wish to report the direct observation of the anion IV and evidence for its homoaromatic character.



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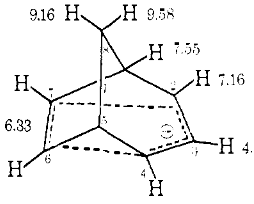

II

Stable solutions of the anion[6] IV are readily prepared by Na–K alloy cleavage of 4-methoxybicyclo[3.2.2]nonatriene-2,6,8 (III-OMe). This ether,[7] bp 31–32° (0.5 mm), was prepared by methylation[8] of the corre-

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[1] Research supported by the National Science Foundation.

[2] S. Winstein, M. Ogliaruso, M. Sakai, and J. M. Nicholson, *J. Am. Chem. Soc.*, **89**, 3656 (1967).

[3] (a) J. M. Brown, *Chem. Commun.*, 639 (1967); (b) J. M. Brown and J. L. Occolowitz, *J. Chem. Soc.*, *B*, 411 (1968).

[4] (a) S. Winstein and C. Ordronneau, *J. Am. Chem. Soc.*, **82**, 2084 (1960); (b) P. R. Story and M. Saunders, *ibid.*, **84**, 4876 (1962); (c) M. Brookhart, R. K. Lustgarten, and S. Winstein, *ibid.*, **89**, 6352 (1967).

[5] M. J. Goldstein, *ibid.*, **89**, 6357 (1967).

[6] Only slight signs of decomposition of the anion to yield the hydrocarbon III-H were detectable after 3 weeks at room temperature or 16 hr at 70° in DME.

[7] All new compounds gave satisfactory carbon and hydrogen analyses and/or mass spectra. Structures were assigned on the basis of the usual chemical and spectral criteria.

[8] U. E. Diner, F. Sweet, and R. K. Brown, *Can. J. Chem.*, **44**, 1591 (1966).