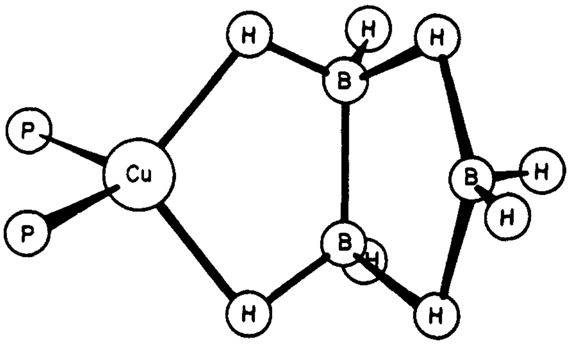
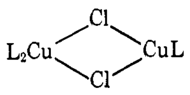
the ion was not bound. All other salts[11] of the L_2AgX class investigated to date showed binding of the anion. The strength of the anion binding apparently varies significantly within this group. This was reflected in variations of the coupling constants and the chemical shifts. The cyanide, halide, thiocyanate, and isocyanate groups had very low coupling constants (278–383 Hz), and at room temperature these complexes showed essentially no conductance in dichloromethane. The other anions within this group, most of which are conjugate bases of strong acids, had substantially larger coupling constants, 390–470 Hz, and exhibited a detectable although very low conductance in dichloromethane at 25° (1–2 mhos). The ^{19}F nmr data for the anion in the $S_2PF_2^-$ derivative clearly showed binding of this anion.[10] For all complexes in the $\mathbf{L_2AgX}$ group with bound anion there was no evidence of dimerization by bridging through the anion functionality, although this possibility cannot be rigorously excluded.

Copper(I) salts interact with tri-*p*-tolylphosphine to give primarily tetrahedral species, but in contrast to silver, most anions compete far more effectively than L for the coordination sphere. For example, $L_2CuB_3H_8$, even in the presence of a large excess of phosphine, exists solely as the pseudotetrahedral complex with $B_3H_8^-$ functioning as a bidentate ligand. The ^{31}P spectrum at −110° is an AB pattern fully consistent with the solid-state structure[12] established for $[(C_2H_5)_3P]_2CuB_3H_8$.

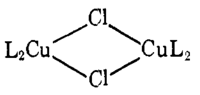


A similar AB pattern was found for $L_2CuB_{10}H_{13}$. The $S_2PF_2^-$ ion, although not effective as a bidentate ligand in the copper system, proved to be sufficiently well bound to prevent the formation of an L_4Cu^+ ion. Discrete $L_3CuS_2PF_2$ and $L_2CuS_2PF_2$ molecules were detected, and the ^{19}F nmr showed that the anion was bound at low temperatures in both of these complexes. The trisphosphino complex, however, underwent dissociation at room temperature to give solely $L_2CuS_2PF_2$ and L.[13]

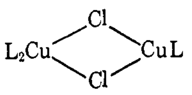
One of the most complex systems encountered was phosphinocopper(I) chloride. Here the phosphine cannot displace chloride ion; there was no evidence for the formation of $L_4Cu^+Cl^-$. L_3CuCl was a pseudotetrahedral species. The dimeric complex (A) showed two lines of relative intensity 2:1 in the ^{31}P spectrum, consistent with the established solid-state structure.[14]



A



B



C

The saturated dimer (B) was the major species present in solution at ∼−100°. Above this, two kinds of dissociation occurred so that at about −70 to −80° there was present in addition to the saturated dimer (C), L_3CuCl and a small amount of monomeric L_2CuCl. The bromide and iodide underwent a similar dissociation; however, *monomeric* L_2CuBr was present in higher concentrations and little monomeric or dimeric L_2CuI were discernible. Tetrakisphosphinocopper cations were detected in PF_6^- and NO_3^- systems; corroboration of this formulation was gained from an ^{19}F nmr study of the PF_6^- salt and from conductivity studies at low temperatures. The only tricoordinate species, $\mathbf{L_3Cu^+X^-}$, detected was the PF_6^- derivative, where again ^{19}F and conductivity data substantiated this formulation. In contrast, the nitrate ion in L_3CuNO_3 was bound.

For gold, complexes of the form $\mathbf{L_2Au^+}$, $\mathbf{L_3Au^+}$, and possibly $\mathbf{L_4Au^+}$ were identified from ^{31}P chemical shifts[15] and conductivity data. Unlike the copper and silver systems, there was no evidence of anion binding except for **LAuX** complexes. In solution, L_2AuCl partially disproportionates

$$2L_2Au^+Cl^- \rightleftharpoons L_3Au^+Cl^- + LAuCl$$

The K_{eq} value at −80° was $\sim 10^{-1}$.

The effect of solvent change on the character of the solution complexes is now under intensive study and the dynamics of L and X exchange is being explored.

Acknowledgments. We are indebted to Mrs. Jean Read and Mr. Lou Walther for assistance in obtaining the 40.5-MHz ^{31}P spectra.

(11) CN^-, I^-, Br^-, Cl^-, SCN^-, OCN^-, $S_2PF_2^-$, $B_3H_8^-$, NO_3^-, and $OCOCF_3^-$.

(12) S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, 8, 2755 (1969).

(13) This was definitively established from the temperature dependence of the ^{31}P and ^{19}F nmr spectrum as well as the change in the anion J_{PF} values as a function of temperature.

(14) D. F. Lewis, S. J. Lippard, and P. S. Welcker, *J. Amer. Chem. Soc.*, 92, 3805 (1970), report the crystal structure of this unusual dimer based on the triphenylphosphine ligand.

(15) The ^{31}P resonance of a mixture of L_2Au^+ and L_3Au^+ salts consisted of the two resonances characteristic of these two cationic species.

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Electron Paramagnetic Resonance Study of Alkylimino Radicals Obtained by Photoinduced Decomposition of Aminoalkyl Radicals in Adamantane

Sir:

The observation of isotropic epr spectra of X-ray-induced free radicals trapped in an adamantane matrix

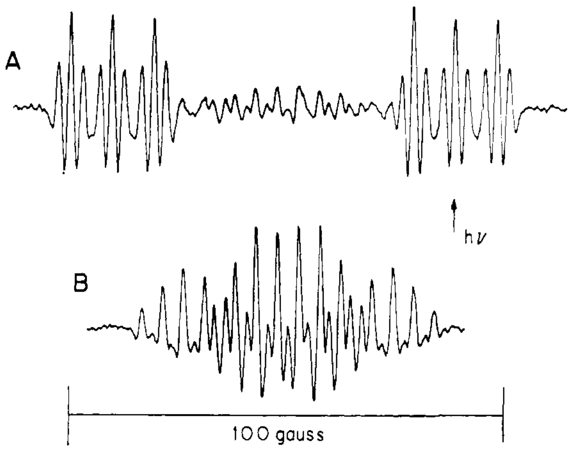


Figure 1. Second-derivative epr spectra of radicals from *n*-propylamine in adamantane: (A) after X-irradiation followed by ~2 sec of irradiation by Hg–Xe compact-arc lamp, (B) after X-irradiation only.

has recently been reported.[1,2] Since these radicals were present in an optically transparent medium, it appeared likely that optical experiments on them would prove fruitful. Preliminary experiments to test the feasibility of this approach have demonstrated that irradiation of the trapped free radicals with light gives rise to large and varied photochemical effects. We report here on one aspect of this investigation which demonstrates the versatility of this technique for the production of new classes of free radicals and the study of their photochemical behavior. In particular, the combined effect of X-ray and light irradiation on aliphatic amines in adamantane results in the production of alkylimino radicals of the type RR′C=N·, which are homologs of the methylene imino radical previously observed by Cochran, *et al.*[3]

The precursor aminoalkyl radicals are produced[1,2] by room-temperature X-irradiation of a solid pellet of zone-refined adamantane containing a small amount of deliberately added amine. The radicals are formally obtained by removal of a hydrogen atom α to the amine group; for example, X-irradiation of *n*-propylamine yields the radical CH_3-CH_2-$\dot{C}H$-NH_2.[1,2] Immediately following the recording of the epr spectrum of the precursor radical, the sample is irradiated *in situ* with light from a 1-kW compact-arc Hanovia Hg–Xe lamp, and a second, entirely different, spectrum is obtained. No epr signal is obtained if light irradiation is used without previous X-irradiation. With an *f*/1 quartz optical system, about 1–2 sec of irradiation at room temperature is required to effect complete conversion; the precursor radical partially reappears when the lamp is turned off with a $\tau_{1/2}$ of about 10 min. Wavelengths $\leq$5400 Å were found to be effective by use of a 0.25-m Bausch and Lomb monochromator.

Figure 1 shows the spectra obtained from *n*-propylamine. The striking feature of the photoinduced spectrum is the presence of a very large proton hyperfine splitting (hfs). As a second example, Figure 2 illustrates the spectra obtained from isopropylamine; here, the large proton doublet is absent in the photoinduced spectrum. Listed in Table I are the spectral parameters for these and other photoinduced free radicals obtained by a comparison of their experimental and computer-simulated spectra. Both the X-ray and photoinduced radicals exhibit isotropic spectra which demonstrate the relatively free rotation possible in adamantane.

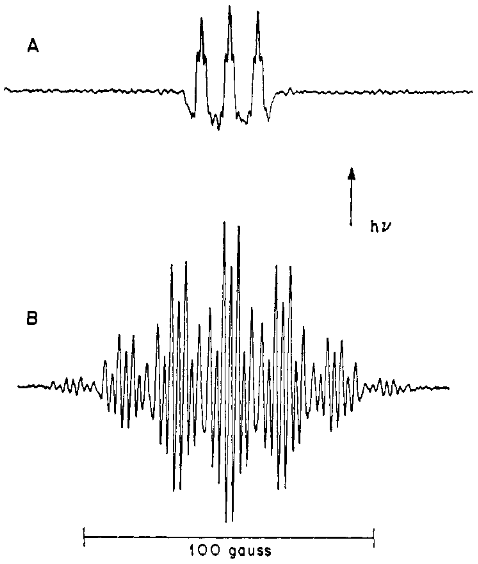


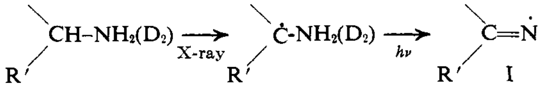
Figure 2. Second-derivative epr spectra of radicals from isopropylamine in adamantane: (A) after X-irradiation followed by continuous irradiation by Hg–Xe compact-arc lamp, (B) after X-irradiation only.

Table I. Epr Parameters of Radicals Obtained by Photoinduced Decomposition of Aminoalkyl Radicals in Adamantane at Room Temperature

Amine	Hyperfine splittings, G N	 H_α	 H_β	*g* value[a]
n-Propylamine	9.5	78.5	2.77 (2)	2.0030
n-Butylamine	9.5	79.5	2.84 (2)	2.0027
Neopentylamine	9.5	79.5		2.0027
Isopropylamine	9.7		1.33 (6)	2.0029
2-Aminopentane	9.6		1.25 (5)	
3-Aminopentane	9.5		1.25 (4)	2.0027

[a] Compared to DPPH = 2.0036. Data corrected to second order.

Replacement of the amine hydrogens in *n*-propylamine and isopropylamine with deuterium gave the expected RR′-$\dot{C}$-ND_2 radicals on X-irradiation. However, the subsequent photodecomposition of these radicals gave spectra identical with those obtained from the protonated amines. These results, together with the absence of the large proton splitting in the radicals derived from isopropylamine and the 2- and 3-aminopentanes, suggest the following reaction sequence



$$\begin{matrix}R\\ \ \ \diagdown\\ \ \ \ CH\text{-}NH_2(D_2)\\ \diagup\\ R'\end{matrix} \xrightarrow[\text{X-ray}]{} \begin{matrix}R\\ \ \ \diagdown\\ \ \ \ \dot{C}\text{-}NH_2(D_2)\\ \diagup\\ R'\end{matrix} \xrightarrow[h\nu]{} \begin{matrix}R\\ \ \ \diagdown\\ \ \ \ C{=}\dot{N}\\ \diagup\\ R'\end{matrix} \quad \text{I}$$

n-propyl, R = C_2H_5, R′ = H; isopropyl, R = R′ = CH_3

Additional experiments relating to the mechanism of conversion and its dependence on excitation intensity and wavelength are in progress.

The photoinduced radicals have small β-hydrogen coupling constants, a large α-hydrogen coupling con-

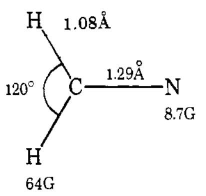
---

(1) D. E. Wood and R. V. Lloyd, *J. Chem. Phys.*, 52, 3840 (1970).

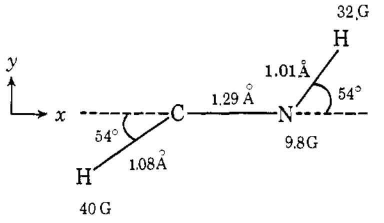
(2) D. E. Wood, *et al.*, *ibid.*, in press.

(3) E. L. Cochran, F. J. Adrian, and V. A. Bowers, *ibid.*, 36, 1938 (1962).

stant when R′ = H, and g values which are only slightly greater than the free-spin value of 2.0023. That these properties are consistent with the structure shown (I) is confirmed by an INDO calculation[4] on the model system II.



II



III

This indicates that most of the spin density (0.868) is in the p_y orbital on nitrogen and only a small fraction is in the carbon p orbitals, thus accounting for the small β-proton hfs. Satisfactory agreement of the calculated and observed α-proton and nitrogen hfs is also obtained (*cf.* structure II and Table I). The absence of appreciable spin density in the nitrogen p_x and p_z orbitals (0.001 and 0.047, respectively) shows that the nitrogen lone pair in II resides in a 2s orbital; therefore, no large g-value shift from free spin is expected.[5] Additional evidence in favor of structure I is the excellent agreement between our α-proton and nitrogen hfs and the values reported by Cochran, *et al.*,[3] for the H_2CN radical in argon.

An obvious alternative structure for radicals exhibiting a large proton hfs is III. This possibility is ruled out by (a) total energy considerations for several variations of III, including both *syn* and *anti* forms; (b) poor agreement between calculated and observed α-proton hfs; and (c) observation of small β-proton coupling constants. On this basis the structure I is preferred for all radicals listed in Table I.

It is apparent that the use of this unique matrix for photochemical studies on free radicals offers distinct advantages over conventional low-temperature matrix experiments;[6-8] namely, (a) the large temperature range over which the experiments may be performed,[1,2] (b) the straightforward analysis of the resulting isotropic epr spectra, and (c) the transparency of the matrix in wavelength regions of photochemical importance. Preliminary experiments have indicated that many other classes of free radicals in adamantane produced by X-irradiation yield results of similar photochemical interest. These results will be reported at a later date.

[4] J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Amer. Chem. Soc.*, **90**, 4201 (1968).

[5] A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance," Harper and Row, New York, N. Y., 1967.

[6] G. V. Pukhal'skaya, A. G. Kotov, and S. Ya. Pshezhetskii, *Dokl. Akad. Nauk SSSR*, **171**, 1380 (1966).

[7] S. G. Hadley and D. H. Volman, *J. Amer. Chem. Soc.*, **89**, 1053 (1967).

[8] D. Cordischi and R. Di Blasi, *Can. J. Chem.*, 47, 2601 (1969).

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Evidence against the Generality of the Ion-Pair Mechanism for Nucleophilic Substitution

Sir:

Recently, evidence has been reported[1-3] which suggests that certain nucleophilic displacements occur *via* attack of the nucleophile on a previously formed ion pair. Such evidence has been reported only for reactions in which the carbonium ion member of that pair would be stabilized by substituents. However, the proposal has been made[2] that *all* nucleophilic displacements from saturated carbon, including those involving primary and methyl substrates, occur *via* ion pairs, and that "Ion pairs have been established as substrates for nucleophilic attack; covalent, saturated carbon has not."[2]

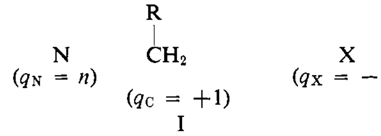
Studies in progress in these laboratories indicate that a full positive charge cannot be present on the central carbon of activated complexes for nucleophilic displacements on haloacetic acids; such a charge is required by an ion-pair mechanism. Covalent, saturated carbon therefore can and does act as a substrate for nucleophilic attack.

Consider a displacement in which nucleophile and leaving group are identical (*e.g.*, reaction 1, Table I). If the forward reaction passes through an ion pair prior to the rate-determining step, then the principle of detailed balance[4] requires that the reverse reaction pass through the same intermediate after its rate-determining step, and the symmetry of the reaction requires that such intermediates lie on both sides of the rate-determining transition state (eq 1). If direct

$$X^- + RX \rightleftarrows X^- + R^+X^- \underset{\text{step}}{\overset{\text{rate-determining}}{\rightleftarrows}} X^-R^+ + X^- \rightleftarrows XR + X^- \qquad (1)$$

attack on covalent, saturated carbon *never* occurs (as has been suggested),[2] then analogous arguments require that the rate-determining transition state also lie between ion-pair intermediates when the displacement is nonsymmetric. The activated complex would therefore resemble an ion triplet.

If the ion-pair mechanism were general, displacement by a nucleophile, N^{n+}, on a primary halide, RCH_2X, would thus proceed through a rate-determining transition state in which the central carbon of the activated complex, I, carried a charge, q_C, of one protonic unit



$$\underset{(q_N = n)}{N} \qquad \underset{(q_C = +1)}{\overset{R}{\overset{|}{CH_2}}} \qquad \underset{(q_X = -1)}{X}$$

I

and the charges, q_N and q_X, on N and X had values characteristic of free N^{n+} and X^-. If a fully covalent description of the transition state were correct, q_C would be zero and the sum, $q_N + q_X$, would be one

[1] (a) R. A. Sneen and J. W. Larsen, *J. Amer. Chem. Soc.*, **91**, 362 (1969); **88**, 2593 (1966); (b) H. Weiner and R. A. Sneen, *ibid.*, **87**, 287, 292 (1965).

[2] R. A. Sneen and J. W. Larsen, *ibid.*, **91**, 6031 (1969).

[3] W. J. Albery and B. H. Robinson, *Trans. Faraday Soc.*, **65**, 980, 1623 (1969).

[4] R. C. Tolman, "The Principles of Statistical Mechanics," Oxford University Press, London, 1938, p 165.