by the hydrolysis of dichlorogermanium tetraphenylporphin, 300 mg, 0.42 mmol), acetic acid (238 mg, 4.0 mmol), and benzene (25 ml) was refluxed 1 hr. The resulting red solution was taken to dryness under vacuum and the red solid obtained washed with pentane. This product (334 mg) was recrystallized from benzene. *Anal.* Calcd for $C_{48}H_{34}N_4O_4Ge$: C, 71.76; H, 4.27; Ge, 9.04; OAc, 14.70. Found: C, 71.62; H, 4.25; Ge, 8.88; OAc, 14.65.

The nmr spectrum of this acetate in $CDCl_3$ showed a singlet at τ 11.08 together with the usual ligand multiplets (and two small impurity singlets, one attributable to hydrolytically formed free acetic acid and the other, of equal methyl intensity, attributable to hydrolytically formed monoacetoxy derivative). The position of the acetoxy singlet in the compound corresponds to a shift of 3.17 ppm from the analogous singlet of dilute acetic acid in $CDCl_3$.

Examples of the application of the reagents to alcohols (*e.g.*, *cis*-4-*tert*-butylcyclohexanol) and to phenols (*e.g.*, the highly hindered phenol 2,6-diisopropylphenol) have been worked out and will be reported later. An advantage of these reagents kindly pointed out by one of the referees is that, because of their diamagnetic nature, these reagents cannot lead to the paramagnetic broadening effects which sometimes become significant with the rare earth reagents.

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Electron Spin Resonance Spectra from Ultraviolet Irradiation in an Adamantane Matrix. The Primary Process for Aliphatic Amines

Sir:

In recent letters, Wood, *et al.*,[1,2] have reported a method for the preparation and esr study of free radicals in adamantane. The technique offers advantages over low-temperature isolation methods in that the samples are easy to prepare, the spectra are isotropic, and the radicals may have appreciable lifetimes at ambient temperature. The compounds studied were aliphatic amines. Radical species were formed by exposure to **X**-rays[1] and by dual irradiation, exposure to **X**-rays followed by exposure to uv.[2] Attempts to obtain spectra by exposure to uv only were unsuccessful.[2] This observation may lead to the conclusion that the method has severely limited usefulness for the study of photochemical processes in the uv region. We wish to report a simple extension of the technique which makes uv studies practical and results with some aliphatic amines.

The results obtained by the dual-radiation method indicate that failure to observe free radicals by uv irradiation alone was due to an intensity effect, since uv irradiation of free radicals, **X**-ray produced, induced formation of secondary radicals. Presumably, the initial radicals had much greater absorptivity than the parent compound. In the method used, adamantane was crystallized from solution, thereby trapping some of the solvent. The resulting small white crystals would be expected to scatter the incident uv light. To obviate this problem, we have made cylindrical pellets, 1.1 cm in diameter, of the crystallized adamantane at a pressure of 10.0 × 10^3 bars. The pellets present a milky translucent appearance. Esr spectra of uv-irradiated inclusions were readily obtained with the compounds studied, amines and chloro olefins.

For the compounds which both Wood, Lloyd, and Pratt,[2] and we have studied, analogous results were obtained. Using a mercury resonance arc housed in quartz, predominantly a source of a mixture of 185- and 254-nm light, the spectrum shown in Figure 1A was obtained from *n*-butylamine at ambient temperature. From the results with primary amines containing three or more carbon atoms, Wood, *et al.*,[2] suggest the reaction sequence

$$(R_1)(R_2)HC{-}NH_2 \xrightarrow{\text{X-ray}} \underset{\text{I}}{R_1R_2\dot{C}{-}NH_2} \xrightarrow{h\nu} \underset{\text{II}}{R_1R_2C{=}N\cdot}$$

where R_1 is an alkyl radical and R_2 is an alkyl radical or H. The computer fit, Figure 1B, was made using the reported coupling constants.[3] As the amines are virtually transparent at wavelengths greater than 240 nm, I may be attributed to absorption at 185 nm, while II may come from absorption of uv radiation by I. Subsequent irradiation with light from a high-pressure mercury arc gave the spectrum shown in Figure 1C. The central portion, radical I, has diminished, while the wings, radical II, have increased in intensity. Since radical II decays more rapidly than radical I, without this second radiation the central portion would have remained virtually unchanged while the wings would have diminished in intensity by some 15% in the elapsed time. Similar results were obtained with *n*-propylamine.

Preliminary results obtained with ethylamine, which was not included in the report of Wood, *et al.*,[2] are shown in Figure 2A. This system is more difficult to work with because of fast radical decay rates. The spectrum was not reproducible on the assumption of a mixture of I, $(CH_3)H\dot{C}{-}NH_2$, and II, $(CH_3)HC{=}N\cdot$. A better computer fit was obtained if III, $CH_3CH_2\dot{N}H$, was included, but even this was not completely successful.[4] Although additional work is required to completely elucidate the spectrum, evidence for ethylidenimino, II, is clear. The computer simulation, Figure 2B, of ethylidenimino was made using the following coupling constants: $a_\alpha{}^H$, 76.0; $a_\beta{}^H$, 3.1; a^N, 9.6 G. The fit is quite good in view of the interference from the other radicals present, the effect of which is expected to be most noticeable on the inner portions of the spectrum. The coupling constants are in reasonable agreement with values from INDO calculations:[5] $a_\alpha{}^H$, 60.0; a^N, 9.2; $a_\beta{}^{H(1)}$, 0.5; $a_\beta{}^{H(2)}$ =

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

(2) D. E. Wood, R. V. Lloyd, and D. W. Pratt, *J. Amer. Chem. Soc.*, **92**, 4115 (1970).

(3) For radical I, from ref 1: $a_\alpha{}^H = a_\beta{}^H$, 14.8; $a_N{}^H$, 5.0; a^N, 4.8 G. For radical II, from ref 2: $a_\alpha{}^H$ 79.5; $a_\beta{}^H$, 2.8; a^N, 9.5 G.

(4) (a) A range of probable coupling constants was used to attempt a computer fit. The values were: $a_\alpha{}^H = 32.0 \pm 4.0$; $a_\beta{}^H = 32.0 \pm 4.0$; $a^N = 15.0 \pm 3.0$ G. These values are based on those given by (b) W. C. Danen and T. T. Kensler, *J. Amer. Chem. Soc.*, **92**, 5235 (1970), for isotropic N coupling and for β-proton coupling in dimethyl- and diethylamino radicals, and by (c) S. G. Hadley and D. H. Volman, *ibid.*, **89**, 1053 (1967), for β-proton coupling in methyl- and dimethylamino radicals.

(5) P. Svejda and D. H. Volman, *J. Phys. Chem.*, **74**, 1872 (1970).

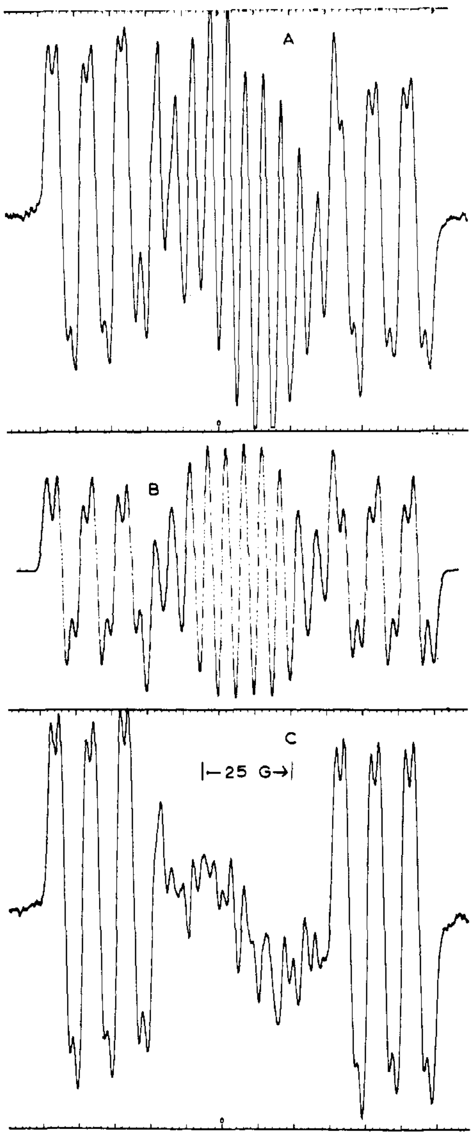

Figure 1. Esr spectra of uv-irradiated *n*-butylamine in an adamantane pellet: (A) mercury resonance lamp, 254 and 185 nm; (B) computer simulation of above; (C) same sample after exposure to high-pressure mercury arc radiation, λ >250 nm.

$a^{\beta H(8)}$, 9.9 G (H(1) is cis to the α H). The calculation confirms the large α-proton interaction and small β-proton interaction, as the β-proton coupling would be the same for all β protons in a freely rotating methyl group, and hence the calculation yields extremes.

Although fission of the α carbon–hydrogen bond has been postulated as a minor primary process in the uv photolysis of methylamine, the most important primary process in alkylamine photolysis has generally been considered to be fission of a bond to nitrogen.[6] Esr studies of the photolysis of primary, secondary, and tertiary methylamines frozen at 77°K have shown that alkylamino radicals are formed, and no evidence for fission of carbon–hydrogen bonds was obtained.[4c] Therefore, it is indeed surprising that in adamantane the radical found from uv irradiation of *n*-butylamine and *n*-propylamine is the same as that found from X-irradiation, the result of fission of the α C–H bond. The absence of alkylamino radicals does not necessarily mean that they are not formed in the primary process, as their lifetime at ambient temperature may be too short for observation. Also, although hydrogen-atom abstraction by free radicals from inclusion compounds in adamantane has not been reported and appears to be improbable, it cannot be absolutely ruled out as a mechanism for the formation of the alkylaminomethyl radical, I. This reservation precludes an unambiguous conclusion; however, it seems probable that radical I is formed in a primary photochemical process.

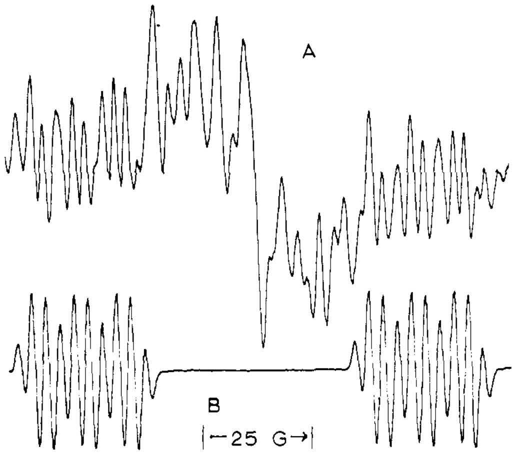

Figure 2. Esr spectra of uv-irradiated ethylamine in an adamantane pellet: (A) concurrent exposure to mercury resonance lamp and high-pressure mercury arc radiation; (B) computer simulation of ethylidenimino radical.

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(6) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 455.

Preparation and Crystallographic Characterization of a Hexameric Triphenylphosphinecopper Hydride Cluster[1]

Sir:

Copper(I) hydrido species[2] have recently attracted attention as stereoselective reducing agents in certain organometallic reactions.[3] Such species have also been implicated as intermediates in the thermal decomposition of copper(I)–alkyl complexes.[4] However, although Würtz prepared a "copper(I) hydride" over a century ago,[5] no truly stoichiometric hydridocopper species have yet been isolated.[3]

We now report the preparation and crystallographic

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(2) From the *in situ* reaction of copper(I) hydride with tri-*n*-butylphosphine in ether.

(3) G. M. Whitesides, J. San Filippo, Jr., E. R. Stredronsky, and C. P. Casey, *J. Amer. Chem. Soc.*, **91**, 6542 (1969).

(4) (a) G. M. Whitesides, E. R. Stredronsky, C. P. Casey, and J. San Filippo, Jr., *ibid.*, **92**, 1426 (1970); (b) K. Wada, M. Tamura, and J. Kochi, *ibid.*, **92**, 6656 (1970).

(5) A. Würtz, *Ann. Chim. Phys.*, [3] **11**, 250 (1844).