Group theory predicts four infrared-active fundamentals for $D_{4h}$ (square, planar) cyclobutadiene and seven for $D_{2h}$ (rectangular, planar) cyclobutadiene. It is interesting to note that group theory predicts four infrared-active fundamentals for any $D_{nh}$ c-$C_nH_n$ species.[18] Table I shows the four fundamentals for the known $D_{nh}$ c-$C_nH_n$ species. The simplicity of the cyclobutadiene infrared spectrum consisting of four fundamentals reinforced by the absence of additional bands even in unusually thick matrices leads us to the tentative conclusion that cyclobutadiene has $D_{4h}$ symmetry.

**Table I.** Infrared-Active Fundamental Modes for $D_{nh}$ c-$C_nH_n$ Molecules and Ions[a]

| Mode, | $C_nH_n$ | | | | | |
|---|---|---|---|---|---|---|
| | $C_3H_3^+$ | $C_4H_4$ | $C_5H_5^-$ | $C_6H_6$ | $C_7H_7^+$ | $C_8H_8^{2-}$ |
| Out-of-plane bend | 736 | 570 | 701 | 673 | 633 | 684 |
| In-plane bend | 908 | 650 | 1008 | 1037 | 992 | 880 |
| C-C stretch | 1276 | 1240 | 1442 | 1482 | 1477 | 1431 |
| C-H stretch | 3105 | (3040) | 3021 | 3064 | 3020 | 2994 |

[a] Data are from ref 18 except for $C_3H_3^+$ which is from R. Breslow, *Pure Appl. Chem.*, **28**, 111 (1971), and $C_4H_4$ from the present report.

Attempts to obtain the electronic spectra, electron spin resonance spectra, and laser Raman spectra of cyclobutadiene are in progress.

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(18) H. P. Fritz, *Advan. Organometal. Chem.*, **1**, 239 (1964).

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## Mercury Photosensitized Oxidation of Primary and Secondary Aliphatic Amines

*Sir:*

Our interest in the interaction between electronically excited reagents and nitrogen-containing systems has prompted us to investigate the mercury photosensitized chemistry of some aliphatic amines in the gas phase. We report here the results of some of our studies which show that (a) Hg $^3$P-photosensitized decomposition of primary and secondary aliphatic primary and secondary carbinamines results in oxidation to give the corresponding imines in high yield; (b) the reactions involve the intermediacy of hydrogen atoms and amine-derived radicals; and (c) in the case of isopropylamine, if not in general, hydrogen atoms formed in the primary process react selectively with amine to give $H_2$ and the corresponding $\alpha$-aminoalkyl radical.

Equations 1 and 2 and Table I show the results of mercury photosensitized decomposition of some representative primary and secondary aliphatic amines.

$$2R_1R_2CHNH_2 \xrightarrow[2537\ \text{Å}]{Hg} H_2 + NH_3 + R_1R_2C{=}NCHR_1R_2 \qquad (1)$$

Ia, $R_1 = H$; $R = C_2H_5$
b, $R_1 = R_2 = CH_3$

IIa, $R_1 = H$; $R_2 = C_2H_5$
b, $R_1 = R_2 = CH_3$

$$(R_1R_2CH)_2NH \xrightarrow[2537\ \text{Å}]{Hg} H_2 + R_1R_2C{=}NCHR_1R_2 \qquad (2)$$

IIIa, $R_1 = H$; $R_2 = C_2H_5$
b, $R_1 = R_2 = CH_3$
c, $R_1 = H$; $R_2 = i\text{-}C_3H_7$

IIa, $R_1 = H$; $R_2 = C_2H_5$
b, $R_1 = R_2 = CH_3$
c, $R_1 = H$; $R_2 = i\text{-}C_3H_7$

**Table I.** Imine Yields from Mercury Photosensitized Decomposition of Aliphatic Amines

| Amine | % conversion | Imine (% yield)[a] |
|---|---|---|
| *n*-Propylamine (Ia) | 45 | IIa (66) |
| Isopropylamine (Ib) | 29 | IIb (84) |
| Di-*n*-propylamine (IIIa) | 54 | IIa (58) |
| Diisopropylamine (IIIb) | 77 | IIb (49) |
| Diisobutylamine (IIIc) | 36 | IIc (73) |

[a] Based on starting material consumed.

Primary amines are oxidatively deaminated, and secondary amines are oxidized when subjected to these reaction conditions.[1]

When these reactions were carried out in the presence of *cis*-2-butene, the product mixtures at low conversion were found to contain *n*-butane, 1-butene, and the 3,4-dimethylhexanes in addition to the amine oxidation products. In these cases the initial rate of formation of hydrogen was substantially reduced even after correction for competition between amine and olefin for excited mercury atoms.[2] These results suggest that the above amine oxidations involve a two-step process in which hydrogen atoms and amine-derived radicals are intermediates. Radical disproportionation would then give products in the correct oxidation level. With secondary amines these are the final products; with primary amines initially formed unsubstituted imines undergo condensation with amine followed by loss of ammonia to give the observed products. These mechanistic features are summarized in Scheme I.

**Scheme I.** Mechanism of Hg $^3$P-Photosensitized Amine Oxidation

$$R_1R_2CHNHR_3 \xrightarrow[2537\ \text{Å}]{Hg} \underset{\text{A}}{R_1R_2\dot{C}NHR_3} \text{ or } \underset{\text{B}}{R_1R_2CH\dot{N}R_3} + H\cdot$$

$$H\cdot + R_1R_2CHNHR_3 \longrightarrow H_2 + \text{A or B}$$

$$2\text{A}, 2\text{B}, \text{A} + \text{B} \longrightarrow R_1R_2C{=}NR_3 + R_1R_2CHNHR_3$$

when $R_3 = H$

$$R_1R_2C{=}NH + R_1R_2CHNH_2 \longrightarrow R_1R_2C{=}NCHR_1R_2 + NH_3$$

At present it is not possible to unequivocally distinguish between the $\alpha$-aminoalkyl- or neutral amino radical structures (Scheme I, A and B, respectively) for the products of the reactions between Hg $^3$P atoms and aliphatic amines. On the other hand, we have deter-

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(1) Photolyses were performed at ambient temperatures in a 5-l. globe containing a drop of mercury and charged with reactants at pressures such that direct absorption by reactant was negligible. Mercury resonance radiation (2537 Å) was provided by a 50-W helical low-pressure resonance lamp contained in a Corning 7910 Vycor sleeve which protruded into the globe. Photolysates were worked up on a conventional vacuum line, and products were identified by comparison with authentic materials.

(2) A. A. Baum and L. A. Karnischky, *J. Amer. Chem. Soc.*, submitted for publication.

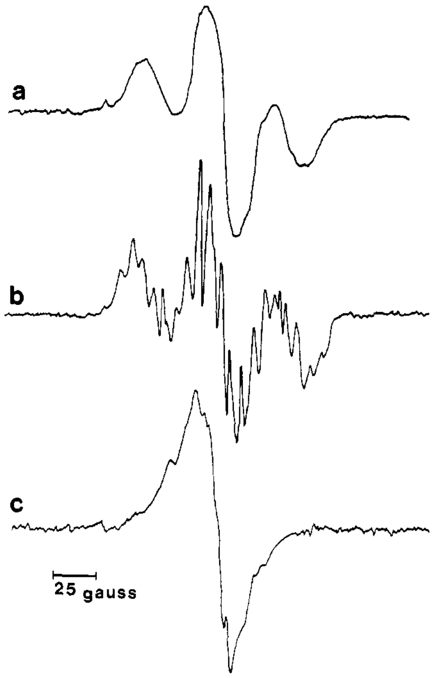
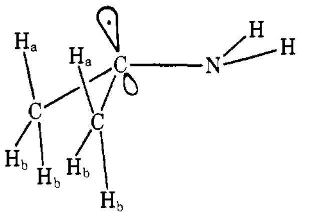


Figure 1. Esr spectrum of the product of the reaction between H· and (a) $(CH_3)_2CHNH_2$; (b) $(CH_3)_2CHND_2$; (c) $(CD_3)_2CDND_2$.

mined that when atomic hydrogen and isopropylamine react in the gas phase, α-aminoisopropyl is the only (>90%) radical produced. Hydrogen atoms generated by electrodeless discharge of molecular hydrogen were allowed to mix with the vapors of isopropylamine in a flow system, and the resulting products were isolated in an argon matrix at 4°K. The esr spectrum of the radical product of this reaction is shown in Figure 1a.[3] A broad triplet ($A$ = 35 G) with an approximately 1:2:1 intensity distribution and centered at a position corresponding to $g = 2.002$ was observed. This result suggests that the radical formed has the odd electron strongly coupled to two hydrogens and is consistent with either radical A or B (Scheme I, $R_1 = R_2 = CH_3$, $R_3 = H$). A triplet pattern with this appearance could also arise from coupling to the $^{14}N$ nucleus ($I = 1$) if the outer components were broadened by an anisotropic hyperfine interaction. In order to distinguish between these alternatives, the reaction was repeated with isopropylamine-$N$-$d_2$[4] and isopropylamine-$d_9$.[5] Figure 1b shows the result when isopropylamine-$N$-$d_2$ was allowed to react with hydrogen atoms as above. The triplet nature of the spectrum persists, showing that hydrogen bound to nitrogen is not involved in the major hyperfine interaction. Additionally, each triplet component now consists of at least seven resolved lines. With isopropylamine-$d_9$ as the reactant, the spectrum (Figure 1c) consists of a single broad line showing that the 35 G splitting in Figures 1a and b is due to the methyl hydrogens. These results are best accommodated by structure IV for the radical product. Thus, at 4°K in argon, α-aminoisopropyl assumes a preferred conformation in which one hydrogen of each methyl group becomes eclipsed (or nearly so) with the orbital of the odd electron at the α carbon. These eclipsed hydrogens couple to the electron with $A^{H_a} = 35$ G; the smaller splittings observed in each triplet component (Figure 1b) are attributed to coupling with the remaining methyl protons ($A^{H_b} \leq 10$ G) and possibly the nitrogen nucleus.



IV

Wood has shown that the (bent) α-aminoisopropyl radical has an *isotropic* coupling constant of 18.27 G for protons bound to the *freely rotating* methyl groups.[6] For alkyl radicals, $A_\beta{}^H \approx B\cos^2\theta$, where $B$ is constant and $\theta$ is the dihedral angle between the $C_\beta$–$H_\beta$ bond and the orbital of the odd electron;[7] for freely rotating methyl groups $A_\beta{}^H \sim {}^1/_2B$. In the present case $\theta$ (for the $H_a$'s) is $\sim 0$, and the large triplet splitting is not surprising. Indeed, our observed value of 35 G provides additional support for structure IV.

In summary, mercury photosensitized oxidation of primary and secondary aliphatic amines to give imines proceeds by a free-radical mechanism in which both Hg $^3P$ atoms and H atoms function as hydrogen abstractors. To the extent that results obtained with isopropylamine are general, hydrogen atoms react with primary and secondary aliphatic carbinamines to give α-aminoalkyls. These data will be elaborated in our full paper.[2]

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[3] The liquid helium cryostat–X-band esr spectrometer system has been described previously: P. H. Kasai, E. B. Whipple, and W. Weltner, Jr. *J. Chem. Phys.*, **44**, 2581 (1966).

[4] H. J. Emeleus and H. V. A. Briscoe, *J. Chem. Soc.*, 127 (1937).

[5] Prepared by Na–Hg/$CH_3OD$ reduction of hexadeuterioacetone oxime.

[6] D. E. Wood and R. V. Lloyd, *J. Chem. Phys.*, **53**, 3932 (1970).

[7] See, for example, J. R. Morton, *Chem. Rev.*, **64**, 453 (1964).

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## Homonuclear Decoupling and Peak Elimination in Fourier Transform Nuclear Magnetic Resonance

*Sir:*

If a system is subjected to a periodic time-dependent perturbation $\mathcal{H}'(t)$ with period $T$ seconds, the spectrum in the limit $T \rightarrow 0$[1] consists of a central component together with a large number of side bands at the frequencies $\pm n/T$ Hz from the central ($n = 0$) component. The central component in the spectrum corresponds to the Hamiltonian $\mathcal{H}_0 + \overline{\mathcal{H}'}$, where $\mathcal{H}_0$ is the unperturbed Hamiltonian and $\overline{\mathcal{H}'}$ is the average of $\mathcal{H}'(t)$ over the period $T$.[2] In the Fourier mode, the dwell time used for recording the free induction decay can be shared between a perturbation $\mathcal{H}'$ and the receiver so that there is no direct interaction between the receiver and the perturbation. The dwell time is then the period $T$.

In this note we describe two applications of this technique in which the perturbation $\mathcal{H}'(t)$ is a contin-

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[1] The $T \rightarrow 0$ limit is approached if $T \ll$ typical relaxation times and $T \ll 1/[\mathcal{H}'(t)]$.

[2] For a detailed discussion, see U. Haeberlen and J. S. Waugh, *Phys. Rev.*, **175**, 453 (1968).