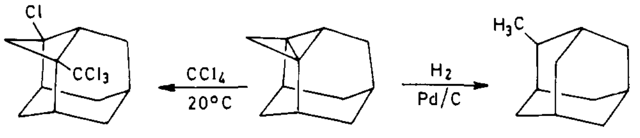
product sublimed into a trap cooled by liquid nitrogen and was found to be more than 95% pure by ^{13}C NMR.

The structure proof for **1** is based on the mass spectrum[11a] (m/e 146 (M^+)), the IR spectrum[11a] (ν 3040 cm^{-1}), the ^{1}H NMR spectrum ((C_6D_6) δ 2.36–1.06 (multiplet and two distinctive doublets at δ 2.12 and 1.08, J = 4 Hz[11b])), and the ^{13}C NMR spectrum ((C_6D_6) δ 64.4 (d, J = 166 Hz, 1 C; C-5), 50.1 (t, J = 129 Hz, 1 C; C-10 or C-6), 40.9 (dd, J = 151 and 169 Hz, 1 C; C-3), 44.0 (d, J = 138 Hz, 2 C; C-1, C-9), 34.2 (t, J = 128 Hz, 2 C; C-8, C-11), 30.8 (t, J = 129 Hz, 1 C; C-6 or C-10), 26.6 (d, J = 133 Hz, 1 C; C-7), and 24.2 (s, 2 C; C-2, C-4)). The C-H coupling constants of the ^{13}C NMR dd signal at δ 40.9 are typical of the methylene carbon in the bicyclobutane system.[13] In the ^{13}C NMR spectrum of 2,4-methano-*3,3-d_2*-2,4-dehydroadamantane (**1a**)[12] this signal is absent, which strongly supports the structure proof for **1**.

The chemistry of **1** is in accord with the structure of small-ring propellanes. At room temperature **1** decomposed slowly even in benzene solution under a nitrogen atmosphere. It reacted rapidly with oxygen and instantly with moisture, methanol, and bromine to give complex mixtures of products.[14] With carbon tetrachloride **1** reacted instantaneously at room temperature yielding 100% single product ($\geqslant$98% pure by GLC), the spectral data[15] of which indicated that it was 2-chloro-4-trichloromethyl-2,4-methanoadamantane (**4**). Compound **4** was thermally stable [bp 110 °C (0.01 mm)] and inert to bromine (at 20 °C for 24 h). Hydrogenolysis of **1** with Pd/C in benzene solution at 20 °C and 1 atm produced 2-methyladamantane (**5**) as the major product ($\geqslant$90%).[17] Interestingly, the central bond in **1** appears not to be cleaved in the first step, since this would lead to the stable 2,4-methanoadamantane.[18]



4 **1** **5**

The carbene center in 4-methylene-2-adamantylidene (**2**) is not "ideally" situated[19] for the intramolecular cycloaddition to the olefinic bond. The angle between the axes of the carbene center p orbital and the olefinic bond p orbitals is ~60°. The arrangements of the carbene center and the γ-CH bonds in **2** and 2-adamantylidene are essentially equal, and the latter inserts readily into the γ-CH bonds.[20] Nevertheless, **2** yields exclusively the intramolecular cycloaddition product, **1**.

Acknowledgments. This work was supported by the Research Council of the Republic of Croatia (SIZ II). We thank Dr. Z. Meić for recording the ^{13}C NMR spectra.

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(10) **3:** mp 135–138 °C; ^{13}C NMR (CCl_4) δ 209.7 (s), 152.5 (s), 104.9 (t), 57.9 (d), 45.6 (d), 41.7 (t), 38.8, 38.0, 37.7, 37.2, 27.5 (d); ^{1}H NMR ($CDCl_3$) δ 4.65 (dd, 2 H), 3.15 (br s, 1 H), 2.63 (br s, 2 H), 2.25–1.85 (m, 9 H); IR (KBr) ν 3075 (m), 2920 (s), 2855 (s), 1725 (s), 1652 (m), 1450 (m), 1225 (m), 1065 (m) cm^{-1}; MS m/e 162 (M^+, 59%), 134 (29), 119 (28), 105 (43), 93 (100), 92 (100), 91 (100).
(11) (a) MS m/e 146 (M^+, 65%), 131 (85), 118 (60), 105 (91), 104 (83), 92 (46), 91 (100); IR (KBr) ν 3040 (m), 2905 (s), 2850 (m), 1462 (m), 1450 (m), 1190 (m), 1070 (m), 1020 (m) cm^{-1}. (b) These doublets are absent in the ^{1}H NMR spectrum of 2,4-methano-*3,3-d_2*-2,4-dehydroadamantane (**1a**).[12]
(12) Compound **1a** was prepared by pyrolysis of the tosylhydrazone sodium salt of 4-methylene-d_2-2-adamantanone.
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(14) The study of the chemistry of **1** is in progress and will be published in a full paper.
(15) ^{13}C NMR (C_6D_6) δ 105.1 (s, 1 C), 62.4 (s, 1 C), 57.3 (s, 1 C), 51.4 (d, J = 145 Hz, 1 C), 43.0 (dd, J = 140 and 146 Hz, 1 C),[16] 39.2 (d, J = 138 Hz, 1 C), 35.8 (dd, —, 1 C), 34.0 (t, J = 128 Hz, 1 C), 31.3 (d, J = 135 Hz, 1 C), 31.0 (t, J = 126 Hz, 1 C), 27.2 (t, J = 126 Hz, 1 C), 24.9 (d, J = 135 Hz, 1 C); ^{1}H NMR (CCl_4) δ 3.05–1.25 (multiplet and two distinctive doublets[16] at δ 2.64 and 2.23, J = 9 Hz); IR (neat) ν 3010 (m),[16] 2920 (s), 2855 (m), 1465 (m), 1450 (m), 1157 (s), 920 (m), 890 (s), 783 (s), 760 (s) cm^{-1}; MS m/e 298 (M^+, 5%), 300 (6), 302 (3), 264 (100), 262 (100), 229 (45), 227 (70), 115 (50), 91 (79), 79 (73), 77 (83).
(16) This signal(s) is absent in the spectrum of 2-chloro-4-trichloromethyl-2,4-methano-*3,3-d_2*-adamantane (obtained from **1a**).
(17) The product was identified by comparing its ^{13}C NMR, ^{1}H NMR, IR, and mass spectra with those of an authentic sample of 2-methyladamantane.
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Received July 23, 1979

Primary Quantum Yields of Ketyl Radicals in Photoreduction by Amines. Abstraction of H from N

Sir:

We report here laser flash photolysis studies which show that the primary reaction of benzophenone triplet with common aliphatic amines in benzene solution gives benzophenone ketyl radical with quantum yield φ = 0.9–1.0. Thus, significant quenching and return to ground-state ketone do not occur in an initially formed exciplex, and a modification of the proposed mechanism for photoreduction by amines is required.[1]

Ketone-amine solutions in benzene in 1 × 1 cm Pyrex cells were degassed by freeze-thaw cycles, placed under 1 atm of argon, and subjected to pulsed-laser photolysis at 347 nm. Flash apparatus and procedures were as described.[2] Transient spectra over the range of 360–700 nm and decay kinetics with time resolution ~50 ns identified the initial and final flash intermediates as benzophenone triplet and ketyl radical, respectively.[3,4] Triplet and radical decay were followed at 530 nm, where the short-lived triplet absorbs more strongly than the long-lived radical (Figure 1). The time resolution of the measurement permits use of such high concentrations of amine that over 90% of the triplet, calculated from triplet lifetimes in absence and presence of donor, decayed via reaction with the amine.[5] The resulting pseudo-first-order rate constant, k_d, was linear in concentration of donor, and the primary reaction rate constant, k_{ir}, was obtained from the slope (eq 1).

$$k_d = k_d{}^0 + k_{ir}[\text{amine}] \qquad (1)$$

The yield of radical from triplet is proportional to the ratio, $r = \Delta D_R{}^\infty / \Delta D_T{}^0$, where $\Delta D_T{}^0$ is the initial increment in absorbance immediately following the flash and $\Delta D_R{}^\infty$ is the change in absorbance corresponding to total formation of radical after decay of triplet is complete (Figure 1). Since the lifetime of the neutral radical is very much greater than that of the triplet, $\Delta D_R{}^\infty$ is obtained by a short extrapolation of the initial portion of the radical decay curve back to zero time,[5] and the ratio r may be measured with good precision. To convert values of r into quantum yields, we take φ_{ketyl} = 2 for

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Table I. Pulsed Laser Flash Irradiation of 0.004 M Benzophenone-Donor Systems in C_6H_6

donor			% triplet	k_{ir},		quantum yield, %	
no.	compd	M	trapped	$M^{-1}\,s^{-1}$	$\Delta D_R{}^{\infty}/\Delta D_T{}^0$ [a]	ketyl	overall reductn
	$(C_6H_5)_2CHOH$	0.60	95	9×10^6	0.771	2.00	0.96[b]
I	t-C_4H_9OH	1.0	~0			~0	
II	t-$C_4H_9NH_2$	0.05	94	6.4×10^7	0.368	0.96	0.06
III	*sec*-$C_4H_9NH_2$	0.01	93	2.3×10^8	0.378	1.00	0.54
IV	c-$C_6H_{11}NH_2$	0.008	93	3.3×10^8	0.359	0.95	0.49
V	$(n$-$C_3H_7)_2NH$	0.001	93	3.4×10^9	0.336	0.89	0.34
VI	$(C_2H_5)_3N$	0.001	93	3.0×10^9	0.378	1.00	0.3[c]

[a] Average value. [b] Secondary actinometer.[6] [c] Possibly complicated by light-absorbing transients.

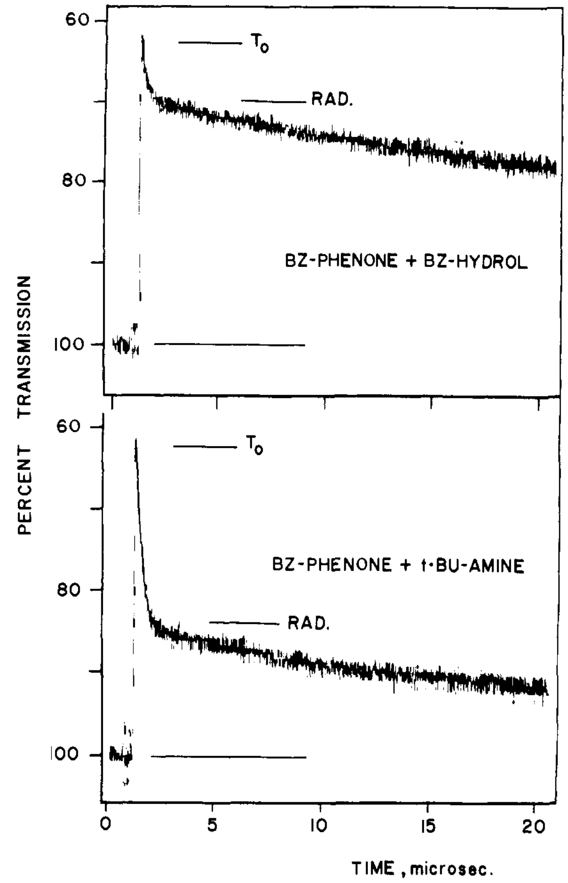


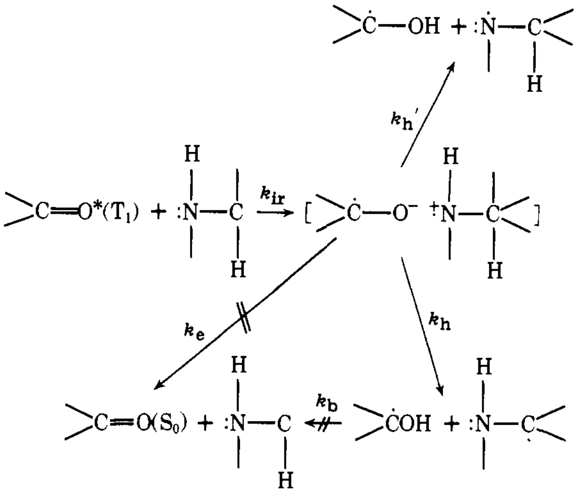
Figure 1. Flash oscillogram showing transmission at λ 530 nm, following laser flash at 347 nm. Transmissions are indicated corresponding to formation of the initial benzophenone triplet and total ketyl radical: cell path, 1 cm; room temperature; total sweep time, 20 μs; 4×10^{-3} M benzophenone containing 0.6 M benzhydrol ($\Delta D_R{}^{\infty}/\Delta D_T{}^0 = 0.768$) (upper curve) or 0.05 M *tert*-butylamine ($\Delta D_R{}^{\infty}/\Delta D_T{}^0 = 0.377$) (lower curve).

the case where all triplets are trapped by benzhydrol, since the quantum yield of benzophenone reduction in this case approaches unity.[6] Ketyl quantum yields for the other donors were obtained from their values of r relative to that for 0.6 M benzhydrol, after correction for untrapped triplet. Quantum yields for reduction of ketone were also determined from the decrease in absorption at 340 nm. The results are summarized in Table I.

Ketyl radical was not formed and triplet lifetime was not affected by *tert*-butyl alcohol (I), even at 1 M concentration. Ketyl was formed with $\varphi = 0.9$-1.0 from low concentrations of *tert*-butylamine (II), *sec*-butylamine (III), cyclohexylamine (IV), di-*n*-propylamine (V), and triethylamine (VI). Comparison of I and II indicates that H is not abstracted from $-CH_3$, but is abstracted efficiently from $-NH_2$. The data for triethylamine (VI) show that H is also abstracted rapidly and efficiently from α-C. Thus, in compounds III, IV, and V, which contain N-H and α-C-H, H may be abstracted from both positions. Quantum yields for overall reduction of benzophenone are lower than for formation of ketyl radical, most notably in reduction by *tert*-butylamine.

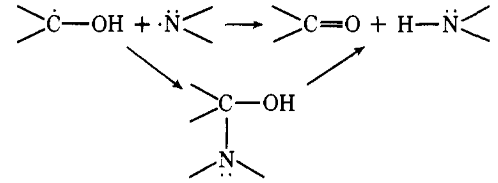
Values of k_{ir} are highest for the secondary and tertiary amines, and lower for primary amines.

It has been proposed[1] that photoreduction by amines proceeds via initial formation of a charge-transfer exciplex (eq 2).



(2)

This would account for the high rate constants, k_{ir}, and the effective photoreduction by amines of ketones which are not photoreduced by alcohols. Loss in quantum efficiency, compared with that in the less generally effective photoreduction by alcohols, was accounted for by postulating a quenching transition within the complex (eq 2), k_e, in competition with radical formation, k_h. Now, the primary formation of ketyl radical with $\varphi = 0.9$-1.0 from reaction with amines II-VI demonstrates that such charge-transfer quenching[7,8] does not occur substantially with the common amines in benzene. Subsequent back-reactions must be invoked to explain low photoreduction efficiencies. The low overall quantum yield for reduction of benzophenone by neat *tert*-butylamine, $\varphi \sim 0.1$,[9] indicates that starting materials are regenerated by disproportionation of ketyl and aminyl radicals, whether by direct hydrogen transfer or after combination (eq 3), as previously

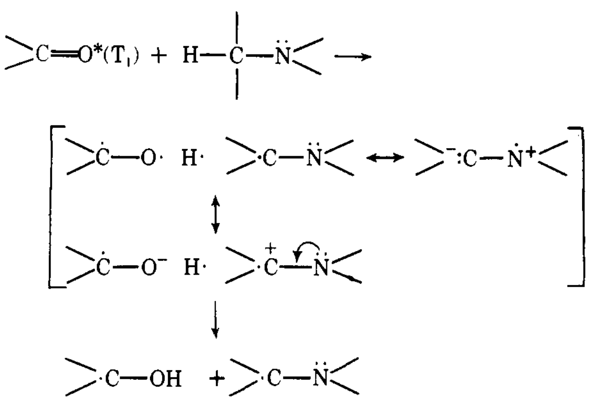


(3)

proposed for thiyl,[10] anilino,[11] and hydrazyl radicals.[12] Thus, formation of N-centered radicals from primary and secondary amines (eq 2), k_h', and their disproportionation (eq 3) may account for loss of quantum efficiency. Higher quantum yields in reduction by tertiary amines may reflect absence of N-H.[13]

Inefficiency in reduction of ground-state ketone by radicals derived from tertiary amines may decrease quantum yields where N-H is absent. Evidence for this has been found in the products of coupling of ketyl and aminoalkyl radicals in photoreduction of fluorenone by triethylamine.[14] Disproportionation of carbon-centered radicals was not observed (eq 2), k_b, but this merits further study.

Direct abstraction of H from α-C, without benefit of an exciplex, would be facilitated by a polar contribution to the transition state and/or stabilization of the incipient radical by the n electrons of the adjacent N (eq 4) and may not be ruled out.[16] This would be similar to the process envisaged for direct abstraction from α-C of alcohols, more rapid because of greater stabilization by N than by O, and most rapid for tertiary amines. Such a process might differ little at the transition state from one proceeding via an exciplex.[17]


(4)

While loss of overall quantum efficiency no longer is evidence which may support a charge-transfer exciplex in the above reaction, the very high rates with tertiary and secondary amines still imply exciplex formation. The lower rate with primary amines may reflect higher ionization potentials.[17] Also abstraction of H from N, rendered acidic by charge transfer, would be greatly facilitated by such interaction.

The high radical yields observed here do not, of course, rule out direct quenching in the primary step in other cases. We will report unambiguous examples of such quenching later.

Acknowledgment. This work was supported by the National Science Foundation, CHE 75-09592 and 78-09333, and by the Department of Energy, EY-76-S-02-3117.

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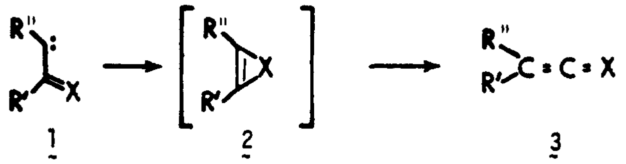
Received June 29, 1979

Electron Spin Resonance of Iminocyclohexadienylidenes: Photoinduced Triplet Geometrical Isomerization

Sir:

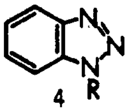
The intervention of ketocarbenes, thioketocarbenes, and iminocarbenes has been implicated in numerous photolytic and thermal reactions.[1-4] Their Wolff rearrangement to the ketene structure is a well-known reaction[1-4] and the possible intervention of antiaromatic 4n-π electron heterocycles **2a-c** in these rearrangements has attracted considerable attention.[3,5,6] This is in contrast to the paucity of reports on the direct observations of carbene species **1**. Thus, the ESR spectra of benzoylphenylmethylene[7] and of carbethoxy and carbomethoxymethylene[8] constitute, to date, the only direct evidence in the literature for the existence of ketocarbenes. Very recently we have reported[9] the first ESR spectrum of a thioketocarbene, namely, that of thiobenzoylphenylmethylene.


1 **2** **3**

a: X = O; **b**: X = S; **c**: X = NR

A similar situation exists for iminocarbenes **1c** which have been invoked in the photolysis and thermolysis of triazoles.[4,10,11] Although singlet state iminocarbenes have been suggested for the Wolff rearrangement,[12] other reactions observed[10,11] are better explained via triplet ground state iminocarbene intermediates and ab initio MO calculations[13] also predict a triplet ground state. The only direct observation of an iminocarbene spectrum is that briefly referred to in a review article by Claus et al.,[11] who assigned the ESR signal observed upon photolysis of *N*-decylbenzotriazole (**4**, R = $C_{10}H_{21}$) at 77 K to *N*-decyliminocyclohexadienylidene (**5**).

We report here new ESR spectra of iminocyclohexadienylidene and its *N*-methyl and *N*-phenyl derivatives, from the 77 K Vycor-filtered light photolysis of benzotriazole **4a** and *N*-methyl- (**4b**) and *N*-phenylbenzotriazole (**4c**) powder.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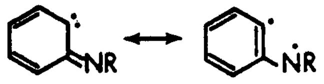
5

a: R = H; **b**: R = CH_3; **c**: R = Ph

Irradiation resulted in the appearance of strong and resolvable spectra, as illustrated in Figure 1a for the case of **4c**. Those from either **4a** or **4b** were similar but of lower intensity. The signals were assigned to the randomly oriented triplet states of **5a**, **5b**, and **5c** and to an unidentified doublet radical. All were stable for several hours at 77 K.

The values of the zero field parameters are listed in Table I; for **5a** and **5c** they were derived from the $\Delta m = 1$ transition. The D parameter for **5b**, for which the $\Delta m = 1$ transition was

Table I. Zero Field Parameters[a]

assigned structure	D, cm^{-1}	E, cm^{-1}
5a	0.1704	0.0025
5b	0.146[b]	
5 (R = $C_{10}H_{21}$)[c]	0.13	0.0040
5c	0.1054	0.0029
5d	0.1150	0.0037

[a] $g = 2.0010$ was used as the best fit of these data. [b] D^* obtained from H_{min}; see text. [c] From ref 11.

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