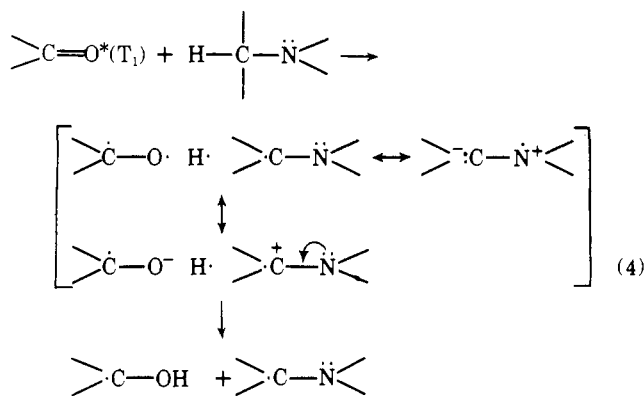


Inefficiency in reduction of ground-state ketone by radicals derived from tertiary amines may decrease quantum yields where N-H is absent. Evidence for this has been found in the products of coupling of ketyl and aminoalkyl radicals in photoreduction of fluorenone by triethylamine.¹⁴ Disproportionation 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

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.

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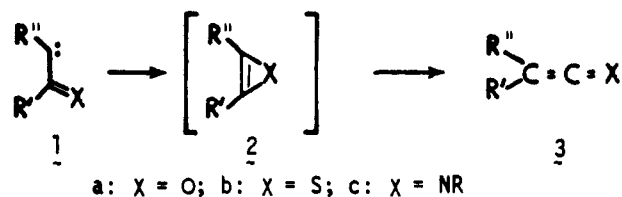
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Electron Spin Resonance of Iminocyclohexadienylidenes: Photoinduced Triplet Geometrical Isomerization

Sir:

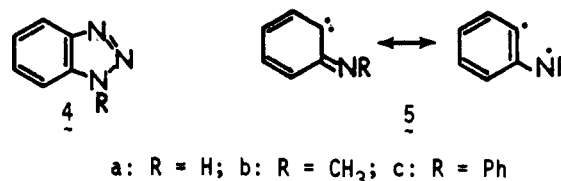
The intervention of ketocarbenes, thioketocarbenes, and iminocarbenes has been implicated in numerous photolytic and thermal reactions.¹⁻⁴ Their Wolff rearrangement to the ketene structure is a well-known reaction¹⁻⁴ and the possible intervention of antiaromatic $4n-\pi$ electron heterocycles **2a-c** 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 benzoylphenylmethylene⁷ and of carboxy and carbomethoxymethylene⁸ constitute, to date, the only direct evidence in the literature for the existence of ketocarbenes. Very recently we have reported⁹ the first ESR spectrum of a thioketocarbene, namely, that of thiobenzoylphenylmethylene.

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 calculations¹³ 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 = C₁₀H₂₁) 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.



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.

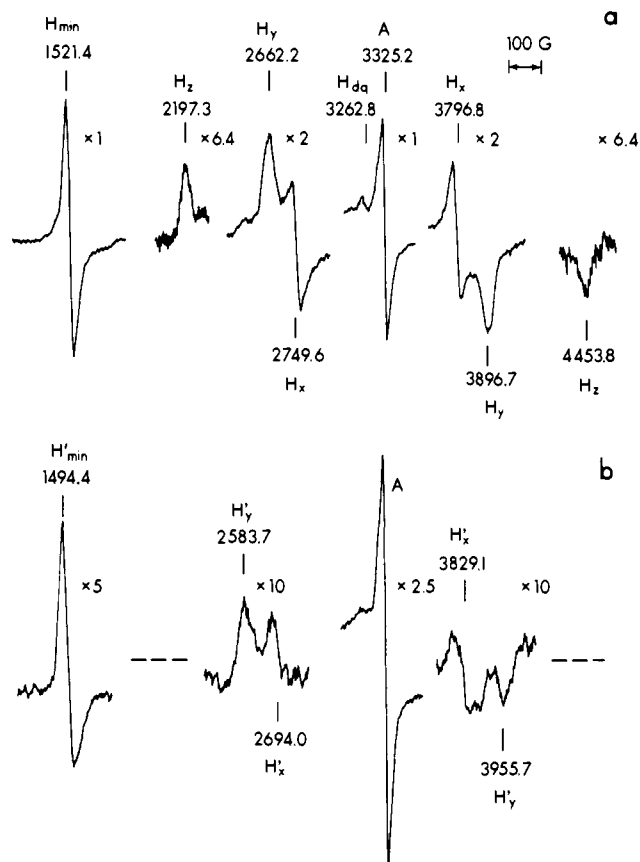


Figure 1. (a) ESR spectrum of triplet **5c** and doublet radical **A** generated in the Vycor-filtered light photolysis of *N*-phenylbenzotriazole (**4c**) powder at 77 K and recorded at 87 K. (b) ESR spectrum of triplet **5d** that remained after annealing the previous sample at 130 K for 5 min, recorded at 96 K. In both cases the klystron frequency was 9.318 GHz and the field values are given in gauss.

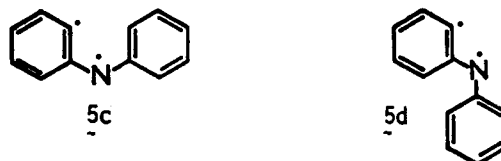
too weak to be observed, was obtained from the $\Delta m = 2$ transition using the minimum possible value of the resonance field (H_{min}) which corresponds to $D^* = D[1 + 3(E/D)^2]^{1/2}$.¹⁴ Since the value of $(E/D)^2$ can be estimated to be $<10^{-3}$, D^* can be used as a good approximation of D in this case. Also, for **5c**, a weak absorption (H_{dq} , Figure 1a) is observed at the magnetic field predicted by the values of D and E ¹⁵ for the double quantum transition; this assignment is supported by the fact that the signal intensity diminishes much more rapidly than the other signals when the microwave power is attenuated.

For comparison, the D values for **5a** were also calculated. The atomic π spin densities were obtained from an INDO calculation and the D value was estimated by using a method reported in the literature.¹⁶ The computed value for D was 0.16 cm^{-1} , in good agreement with experiment. The calculations also indicate that the appropriate representation of iminocyclohexadienylidenes is a 1,3-diradical structure ($\rho_{\text{carbene C}} = 0.25$; $\rho_{\text{N}} = 0.84$).

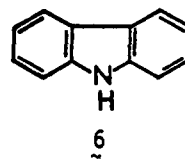
Prolonged irradiation of **4c** causes a distinctive shoulder to appear in the $\Delta m = 2$ transition of **5c**, indicating the presence of a new triplet species, **5d**. A better resolved spectrum of this new triplet (Figure 1b) was obtained by warming the sample to 130 K. Here the triplet spectrum **5c** fades irreversibly, but the **5d** signal intensity is unchanged, indicating that the conversion $\text{5c} \rightarrow \text{5d}$ is not thermally induced. Above 200 K the **5d** spectrum fades irreversibly. On photolysis **5c** and **5d** are readily interconvertible and reach a photostationary state. Moreover, photolysis of **4c** at 135 K, under which conditions **5c** is thermally unstable, led to the appearance of a single, very low intensity spectrum attributable to **5d**. We conclude that, al-

though some **5d** may be formed in the primary photolytical step, most of it is formed via secondary photolysis of **5c**.

The small differences between the zero field parameters D and E obtained for **5d** and **5c** (Table I) indicate that these species are rotameric conformers. This, in conjunction with the fact that **5c** is thermally less stable than **5d** and decays without yielding **5d**, would seem to suggest the assignments shown, which would be in line with the results of the solu-



tion-phase photolysis of **4c** where carbazole **6** is reported to be the sole product in $\sim 100\%$ yield.^{10c,d}



The decay of **5c** follows good first-order kinetics in the range of 104–124 K and, from the Arrhenius plot, consisting of seven points, $E_a = 5.2 \pm 0.5 \text{ kcal mol}^{-1}$ and $\log A \text{ (s}^{-1}\text{)} = 6.5 \pm 0.8$, probably corresponding to the activation energy for the triplet \rightarrow singlet intersystem crossing followed by rearrangement.

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