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THE PHOTOCHEMICAL GENERATION OF TRIPLET KETOCARBENES AND THEIR QUINTET STATE RADICAL PAIRS*

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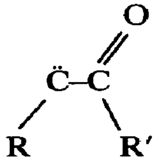
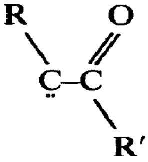
Ketocarbenes, formylmethylene and its derivatives $R\ddot{C}C(O)R$ have been postulated as reactive transients in the thermal and photochemical decomposition of α-diazoketones and α-diazoesters and in several other reactions. In spite of the frequent references to them in the literature, direct observations of ketocarbenes are sparse and the only one that had been reported prior to 1978 was triplet ground state benzoylphenylmethylene $\varphi\ddot{C}C(O)\varphi$ (1) by Trozzolo and Fahrenholtz [1]. These authors described the low temperature matrix isolation of compound 1 and its detection by electron spin resonance (ESR) spectroscopy from the photolysis of azibenzil $\varphi C(N_2)C(O)\varphi$ in glassy matrixes. Subsequently, Oncescu *et al.* [2] studied the photolysis of solid azibenzil at 77 K using ESR spectroscopy techniques and observed some additional absorptions.

In the past three years several new ketocarbenes have been reported. In 1978 Hutton and Roth [3] described the isolation and ESR characterization of carboxymethyl and carboxyethyl methylene and in both cases they were able to show the existence of two rotameric isomers



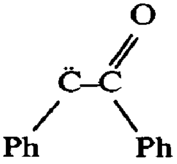
s-cis

and

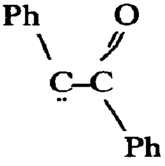


s-trans

In further developments, the present authors [4] have reported the preparation of several additional ketocarbenes and they have also carried out a re-examination of the low temperature ($T \leqq 77$ K) photolysis of azibenzil polycrystals with $\lambda \geqq 335$ nm light, which led to the isolation and identification of the *cis* and *trans* rotamers of 1:



s-cis-**1**



s-trans-**1**

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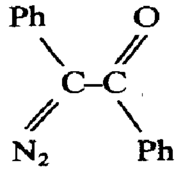
The intensity of the *trans* signal was found to be more than tenfold that of the *cis*, indicating that the precursor azibenzil molecule is present in the *trans* form



in the crystal and that the factor controlling the geometry of the product carbene is the geometry of the starting material. Indeed, a subsequent single-crystal X-ray diffraction study of azibenzil [5] showed that the azibenzil molecules have the *trans* geometry.

The primary step giving rise to *trans*-**1** is

$$trans\text{-azibenzil} + h\nu \rightarrow trans\text{-}\mathbf{1}(S_1) + N_2$$

followed by

$$trans\text{-}\mathbf{1}(S_1) \xrightarrow[\text{crossing}]{\text{intersystem}} trans\text{-}\mathbf{1}(T_0)$$

The exposure time dependence of the *trans*-**1**(T_0) signal intensity is linear at short irradiation times (Fig. 1), as required by this mechanism. Whether the small quantities of *cis*-**1**(T_0) produced are primary products or whether they arise from the secondary photosiomerization of the *trans*-**1**(T_0) could not be established. At elevated temperatures (150 - 190 K) both *cis*-**1** and *trans*-**1** decay with good first-order kinetics and rate constants given by

$$\log k(cis) = 14.6 - 14.7/2.3RT\ \mathrm{s}^{-1}$$

$$\log k(trans) = 10.4 - 9.9/2.3RT\ \mathrm{s}^{-1}$$

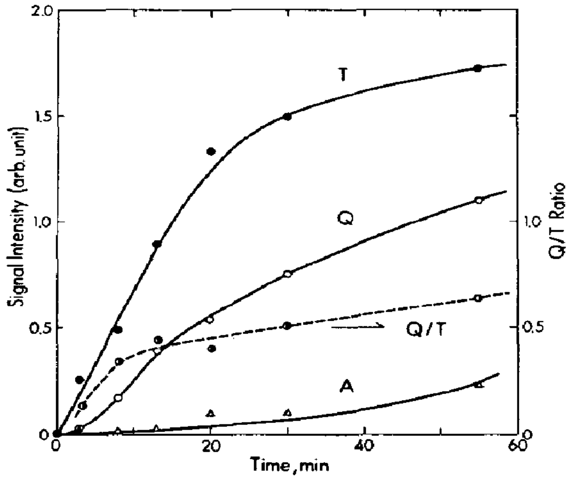


Fig. 1.

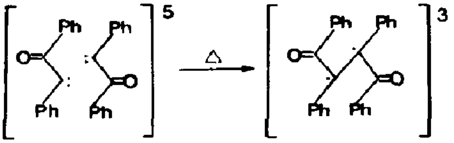
The magnitude of the pre-exponential factors suggests a fully allowed reaction for the decay of *cis*-**1** and a spin-forbidden path for *trans*-**1** which are probably

cis-**1**$(T_0) \rightarrow$ *trans*-**1**(T_0)

and

trans-**1**$(T_0) \rightarrow Ph_2C{=}C{=}O$

The ESR spectrum of polycrystalline azibenzil exhibited another complex set of absorptions consisting of eleven lines in the range 100 - 6400 G. Annealing studies showed this set to belong to a single carrier which decayed above 90 K with good first-order kinetics to yield a new triplet diradical species. Since a triplet species possesses not more than six $|\Delta m| = 1$ absorption lines the unknown carrier must have a multiplicity higher than triplet, and since a quartet state could not readily form from a triplet ketocarbene or convert unimolecularly to a triplet diradical the multiplicity of the carrier must be a quintet. A stable quintet species that can be thought of as arising from the photolysis of azibenzil cannot be a molecular species but must be a radical pair formed from the interaction of two nearest-neighbour triplet benzoylphenylmethylenes. This, on annealing, can then convert to a triplet by forming a single bond:



All the known kinetic features of the quintet appear to be consistent with this interpretation of the data. Thus, the time profile of the signal growth shows that the carrier is not a primary photoproduct and that its rate of growth is higher than first order in compound **1**. The peculiar signal growth which occurs after cessation of irradiation and which lasts for many minutes proves that production of the quintet occurs not in a photochemical reaction but in the dark between two triplet photochemical products. It is also important to note that quintet formation is absent, when the photolysis of azibenzil is carried out in glassy matrixes, because of the combined effects of dilution and random orientation.

The photolysis of polycrystalline azibenzil provided the first example for the existence of a stable, higher than triplet state, radical pair.

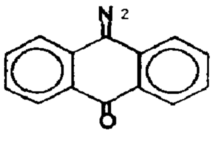
Similarly, the $\lambda \geqq 335$ nm photolysis of $CF_3C(N_2)C(O)CF_3$ yields the corresponding ketocarbenes, *cis*- and *trans*-$CF_3\ddot{C}C(O)CF_3$ (**2**) and a somewhat weaker absorption corresponding to their quintet state radical pair.

When the photolysis at 8 K was monitored by IR spectroscopy the final product proved to be bis(trifluoromethyl)ketene which appears to form via a stable intermediate, either compound **2** or the elusive oxirene

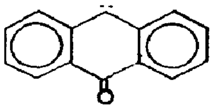
Unambiguous assignment of the spectrum of the intermediate has not yet been accomplished.

On the basis of the ESR spectra the more intense spectrum was assigned to the *s-cis* isomer of **2** and the less intense to the *s-trans*-**2**. From this it appears that the parent diazo compound has a *cis* geometry.

Photolysis of diazoanthrone



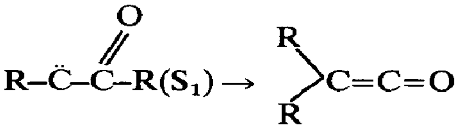
polycrystals afforded the carbene



(T_0)

and its quintet state radical pair.

In all these cases the ground state of the carbene was a triplet, and intersystem crossing in the excited singlet state produced in the primary photolytic step to the T_0 state was quite efficient. This, however, is not always the case. For example, pure $PhSO_2C(N_2)SO_2Ph$ on photolysis at 8 K gives no detectable ESR absorption apart from a very weak doublet. However, when a benzophenone-doped sample of $PhSO_2C(N_2)SO_2Ph$ was irradiated under otherwise identical conditions, a well-developed triplet signal corresponding to the carbene $PhSO_2\ddot{C}SO_2Ph$ (**3**) appeared via the triplet-benzophenone-sensitized decomposition of compound **3**. Thus, in this case the excited singlet state of compound **3** produced in the direct photolysis decays via some route other than intersystem crossing to the ground state triplet. Indeed, we found that many α-diazoketones, while readily undergoing decomposition when irradiated with UV light at $T \leqq 77$ K, do not yield triplet carbenes, probably because intersystem crossing did not compete favorably with the Wolff rearrangement from the S_1 state:

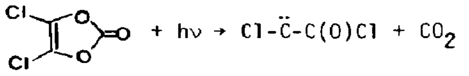


$$R{-}\ddot{C}{-}\overset{O}{\overset{/\!/}{C}}{-}R(S_1) \rightarrow \begin{matrix} R \\ & \!\!>C{=}C{=}O \\ R \end{matrix}$$

All those diazoketones which gave triplet carbenes also gave a doublet species with *g* values of approximately 2.003 showing no sign of fine structure. From the growth pattern of the *g* signal with time, illustrated by the example of azibenzil in Fig. 1, it is apparent that these doublets are secondary photolysis products arising probably from the photolysis of the ketocarbenes:

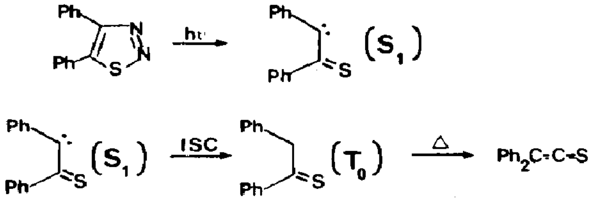
$$R{-}\ddot{C}{-}C(O){-}R(T_0) + h\nu \rightarrow R{-}\ddot{C}\cdot + R{-}\dot{C}{=}O$$

Lending credence to this postulate is the observation that in the gas phase room temperature flash photolysis of dichlorovinylene carbonate [6]



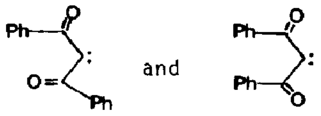
chloromethyne CCl can be readily detected by flash spectroscopy [7].

The isolation of a thioketocarbene has been achieved from a 1,2,3-thiadiazole precursor. The $\lambda \geqq 335$ nm photolysis of diphenyl-1,2,3-thiadiazole polycrystals at $T \leqq 77$ K yielded a triplet ESR spectrum which was assigned to the triplet ground state thiobenzoylphenylmethylene. This carbene is stable at 77 K but starts to decay at about 80 K with first-order kinetics and a rate coefficient given by $\log k = 9.1 - 5.4/2.3RT\ \mathrm{s}^{-1}$. On warming the irradiated sample to room temperature the ESR signals disappear and the colour of the sample changes from brown to violet. The IR spectrum in Nujol exhibits a distinctive absorption characteristic of thioketenes. Thus, the following reactions seem to take place:

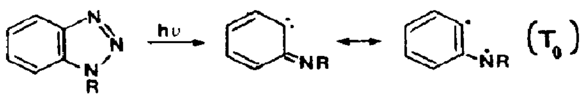


The parent compound 1,2,3-thiadiazole and several other derivatives were also photolysed but they gave only the doublet sulphur pattern and perhaps another doublet as ESR detectable products.

A diketocarbene, dibenzoylmethylene, was also isolated from the photolysis of polycrystalline dibenzoyldiazomethane. Photolysis yielded two triplet spectra which were assigned to the rotameric isomers



Several iminocarbenes have also been prepared. Photolysis of benzotriazole and its derivatives gave the iminocarbenes



where R ≡ H [4], CH_3 [4], Ph [4] and $C_{10}H_{21}$ [8]. The phenyl-substituted iminocarbene has been shown to exist in two rotameric conformers which are photolytically interconvertible.

The success rate of photolytically producing triplet carbenes could probably be significantly increased by the use of suitable triplet photosensitizers and under conditions favouring intersystem crossing of the initially formed singlet excited carbene to the triplet ground state.

Acknowledgment

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