Detection of Radicals and Radical Pairs in Photo-irradiated 2,4,6-Triisopropyl-4'-methoxycarbonylbenzophenone in the Solid State

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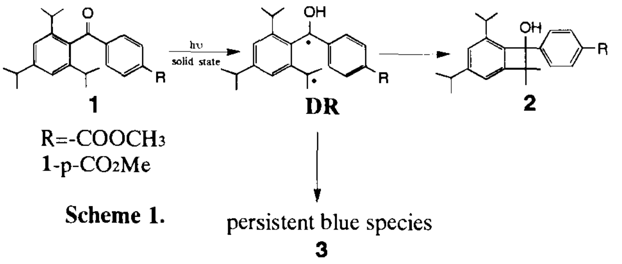
Polycrystalline 2,4,6-triisopropyl-4'-methoxycarbonylbenzophenone was photo-irradiated *in vacuo* and the colored solid obtained exhibited intense ESR signals which are attributable to mono-radical and radical pair species. These are intermediates after the hydrogen abstraction by photo-excited carbonyl from isopropyl group.

Almost a decade ago solid-state photocyclization reactions of 2,4,6-triisopropyl-4'-R-benzophenones **1** into the corresponding benzocyclobutenols **2** were reported to take place in quantitative yield.[1] These reactions in solutions had been investigated in great details, leading to a reaction mechanism of photochemical transformations *via* diradical intermediate DR (Scheme 1).[2]



Scheme 1.

In these experiments unusual substituent effect was disclosed, especially for the solid-state reactions, i.e. 2,4,6-triisopropyl-4'-methoxycarbonylbenzophenone (R=-$COOCH_3$, **1**-p-CO_2Me) exhibited substantially no conversion to benzocyclobutenol with a quantum yield $\Phi \sim 0.001$ and only a little formation in benzene solution with $\Phi = 0.13$. In addition, it was found that crystals of **1**-p-CO_2Me photo-irradiated *in vacuo* or in Argon were persistently blue and the color faded upon exposure to air.[3] These findings imply that the blue intermediates are stable radicals, which are to be evidenced by ESR observations in this letter.[4] Thus, in the case of **1**-p-CO_2Me, it can be understood by presuming a by-path reaction as in Scheme 1 that there is little possibility of the cyclization conversion from DR (**1**→DR→**2**).

Formation of the blue species by photolysis can be distinguished by the diffuse reflectance spectra shown in Figure 1.[5] A broad absorption band at λ_{max}=624 nm, which increased roughly linearly depending on the irradiation time, is a cause of the color change and is considerably suppressed by the presence of air, implying that the blue species are radicals.

ESR spectra of polycrystalline **1**-p-CO_2Me irradiated *in vacuo* for 2 h (Figure 2)[6] comprise a sharp intense absorption at g=2.00287 and several feeble side-peaks probably due to triplet spin state (S=1). The central peak increases proportionally to the irradiation time. When it becomes dominant one can easily detect side-peaks with high amplification. In this occasion, a half-field resonance at 164.5 mT, shown in Figure 2, can be observed with far higher amplification and magnetic field modulation. This absorption indicates a double quantum transition ($\Delta m_s = \pm 2$) and undoubtedly evidences the existence of a triplet state (S=1). Based on the polycrystalline analysis of S=1,[7] zero-field splitting parameters D and E are evaluated; $|D|$=5.5 mT and $|E|$=0.53 mT. These data explain three pairs of absorption corresponding to the three principal axes. The separations are $2|D|$, $|D+3E|$, and

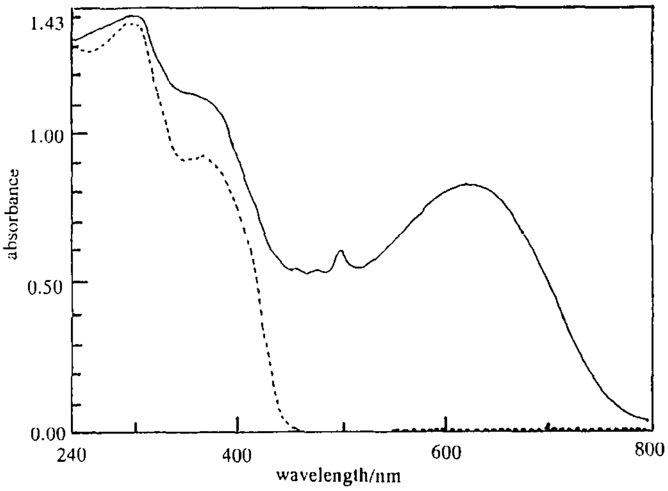


Figure 1. Diffuse reflectance spectra of the photo-irradiated **1**-p-CO_2Me for 6 h. The dotted and solid lines were observed before and after the irradiation, respectively.[5]

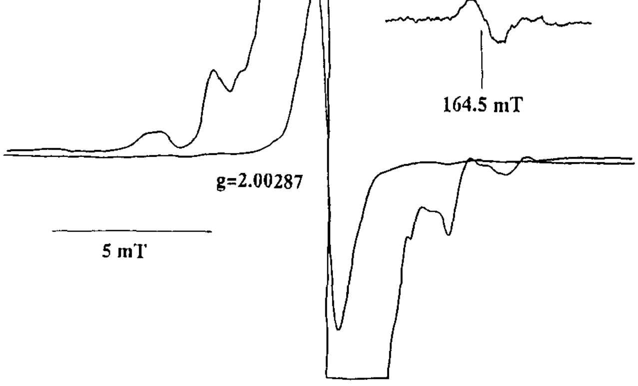
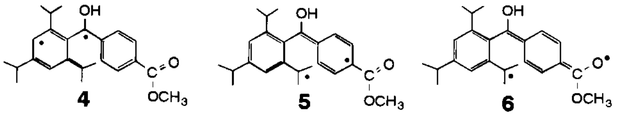


Figure 2. ESR spectra of the photo-irradiated **1**-p-CO_2Me for 10 h.[6] Field modulation of 0.2 mT was used.

$|D\text{-}3E|$. In addition to these comparatively intense triplet lines, some other weak peaks are discernible, suggesting the existence of different kinds of triplet entities. It is, however, difficult to draw reliable information about these from Figure 2.

The determined value of D enables one to estimate the distance of the two radical centers which form a triplet state.[7] A point-dipole approximation gave the distance r=0.77 nm. Assuming the intermediate DR structure, in which radical sites are on the carbon atoms of the isopropyl and the carbonyl groups, the intermolecular distance between the radicals is ca. 0.3 nm, giving a zero-field splitting parameter D of the order of 100 mT. This intramolecular pair (DR) can not account for the present observation. In polycrystalline samples this fine structure will spread over the field range of ±100 mT, resulting in extremely feeble spectral intensity. Accordingly, intermolecular radical pairs are also taken into account. Thus, we presume a by-path reaction *via* DR to the mono-radical species **3**, as is shown in Scheme 1. This scheme also explains the scanty product of photocyclization **2** for **1**-p-CO_2Me (R=-$COOCH_3$). The amount of the mono-radical species increases proportionally to the irradiation time. The DR intermediate can take some resonance structures as are shown in Scheme 2, indicating the positions of large unpaired electron density. The most plausible mechanism is supposed to be relevant to the resonance structure **6**, which will play a crucial role in hydrogen abstraction from the neighboring molecules in the crystal.



4 **5** **6**

Scheme 2.

Details of the mono-radical structures and the intermolecular interaction schemes would need further investigations, such as ENDOR (electron-nuclear double resonance) and single crystal experiments, which are now in progress.

References and Notes

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4 No substantial ESR signals were detected under the present experimental conditions for the other substituents such as R=-H, -CH_3, or -COOH.

5 Irradiations for reflectance spectroscopy were carried out under Ar with a 400 W high-pressure mercury lamp.

6 Irradiations for ESR spectroscopy were carried out *in vacuo* with a 450 W high-pressure mercury lamp. ESR measurements were made by using of a JEOL FE1XG type spectrometer with 100 kHz field modulation. Magnetic fields were calibrated using Mn^{2+} in MgO standard.

7 J. E. Wertz and J. R. Bolton, "Electron Spin Resonance, Elementary Theory and Applications", Chapman and Hall, New York, Chapter 10 (1986).