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THE MECHANISM OF PHOTOISOMERIZATION OF TETRABENZOYLETHYLENE

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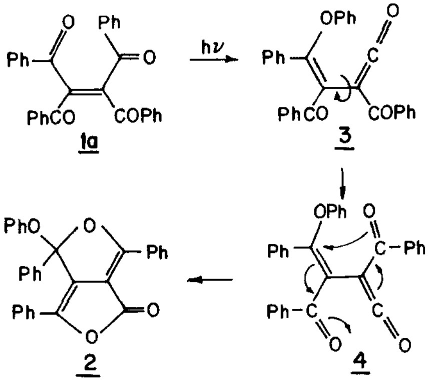
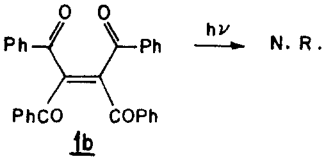
Abstract - Photoisomerization of the title compound proceeds via formation of a ketene and rotation about a single bond followed by intramolecular cyclization.

The photochemistry of tetrabenzoylethylene (1) was investigated during the period 1911 to 1948, mainly by von Halban and coworkers[1]. In 1978, 50 years after the first published work appeared, Cannon, White et al.[2] carried out an X-Ray crystallographic analysis and assigned the lactone-ether structure 2 to the photoproduct. Of particular interest was the observation that two polymorphic forms of 1 could be obtained. One crystal form (**1a**) produced 2 upon irradiation in the crystal while the other (**1b**) was photochemically inert; upon dissolution and irradiation in solution both **1a** and **1b** gave **2**. The major difference between the two forms was the conformation of a benzoyl group; in the photoreactive form, but not in the inert form, a phenyl group was in close proximity to the carbonyl oxygen of a cis-benzoyl group as illustrated in the structures below.

This requirement for photoreactivity suggested that the primary photochemical reaction of **1** might involve migration of a phenyl group to the proximate oxygen[3]. This would result in formation of the ketene **3** which could, by rotation about the central single bond, isomerize to conformer **4**. Cyclization of **4** to the observed product, **2**, could then proceed readily as indicated by the arrows.

Attempts to trap proposed **3** as the derived methyl ester by irradiations[4] of **1** in methanol solution at room temperature or -70° C only afforded **2**. Likewise, irradiation in hydrocarbon glasses at 77 K produced the characteristic UV-Vis spectrum of **2** without any evidence for an intermediate. It thus appeared that,





if the proposed mechanism is correct, rotation about the single bond and intramolecular cyclization of 3 are fast processes even at 77 K in hydrocarbon glasses and that only experiments at lower temperatures could provide experimental support for a ketene intermediate.

Accordingly, irradiation[4] of 1 was performed with a sample deposited in high vacuum on a window cooled to 10 K. This resulted in appearance of typical ketene absorption at 2110 (s), 1202 (m), and 748 (m) cm^{-1} in the infrared spectrum as shown in Figure 1. Similar behaviour was observed in an Argon matrix[5] at 10 K with very small shifts of absorption maxima (e.g. 2114 cm^{-1}). Warming resulted in disappearance of the ketene band with concomitant appearance of the expected absorption at 1740 cm^{-1} due to isomerization to 4 as shown in Figure 2; the rate of this thermal reaction became appreciable at about 120 K[6]. The relatively high temperature required for isomerization did not permit kinetic measurements. Recording of IR spectra in absorbance mode during free warming, showed a good correlation between disappearance of the ketene band at 2110 cm^{-1} and appearance of the unsaturated lactone carbonyl band of product at 1740 cm^{-1}.

Similar results were obtained when photolysis of 1 at 10 K was monitored in the UV-Vis region of the spectrum. Irradiation[4] resulted in a decrease in the intensity of the spectrum (λ_{max} 256 nm) without appearance of any new absorption in the visible. Warming resulted in appearance of the characteristic maxima of 2 at 401, 423, 448, and 482 nm in full agreement with the results obtained by infrared monitoring. It was not possible to obtain a good spectrum of the intermediate 3 because of the incomplete conversion discussed below.

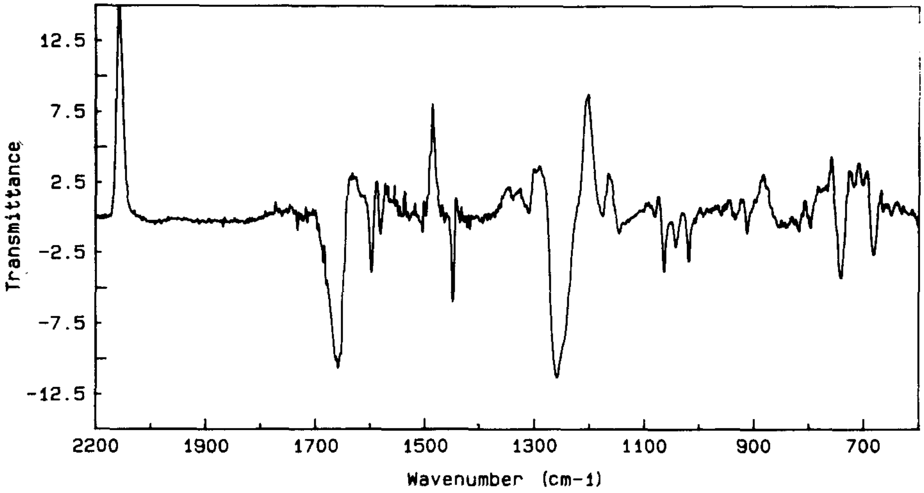


Fig. 1. Difference IR spectrum showing photolysis of 1 to 3 in Argon at 10K. Top part: bands due to 3 appearing; bottom part: bands of 1 disappearing.

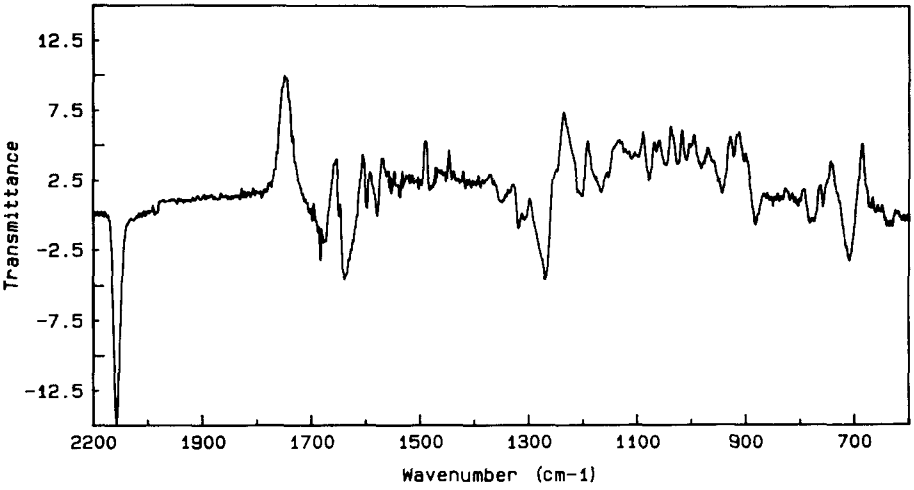


Fig. 2. Difference IR spectrum showing thermal isomerization of 3 to 4. Top part: bands of 4 appearing; bottom part: bands of 3 disappearing.

The observed spectroscopic changes suggested that only partial conversion **1** → **3** had occurred during photolysis. Formation of a mixture of **3** plus unreacted **1** in the irradiation could, in fact, be demonstrated by recooling to 10 K after isomerization of **2** to **4** was complete and then continuing the irradiation or by washing the material from the window and irradiating at room temperature. In both experiments, further reaction was observed. We attribute this behaviour to the formation of a mixture of reactive and unreactive conformers during the deposition and to subsequent conformational equilibrium at sufficiently higher temperatures.

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Dedicated to Professor Ernst Fischer, a longtime advocate of low temperature photochemistry, on the occasion of his 65th birthday.

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2. J.R. Cannon, V.A. Patrick, C.L. Raston, and A.H. White, Aust. J. Chem., **31**, 1265 (1978).

3. For analogy with the behaviour of cis-dibenzoylethylene see: G.W. Griffin and E.J. O'Connell, J. Am. Chem. Soc., **84**, 4148 (1962); H.E. Zimmerman, H.G.C. Durr, R.G. Lewis, and S. Bram, ibid, **84**, 4149 (1962); R. Barik, K. Bhattacharya, P.K. Das, and M.V. George, J. Org. Chem., **51**, 3420 (1986) and references therein.

4. Irradiations were performed at 366 nm using a 200 watt mercury vapor lamp (Osram HBO 200) and Corning or Schott filters. Irradiations at 77 K were performed in 1:1 methylcyclohexane-isohexane or 1:1 isopentane-isohexane mixtures. For experimental details of measurements at 10 K see W.W. Sander, Spectrochimica Acta, **43A** (1987), in press.

5. The warming experiments could not be performed in argon matrix due to evaporation of the argon with concomitant spoiling of the spectrum at temperatures much below those required to observe the isomerization of **3**.

6. The temperature required for formation of **2** from **3** in the deposition experiments was much higher than in the hydrocarbon glasses. This result presumably reflects differences in the rotational barrier in **3** in the different media.

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