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# PHOTOCHEMICAL REARRANGEMENTS OF A BENZOYLNAPHTHOBARRELENE-LIKE SYSTEM †

KURT SCHAFFNER and MARTIN DEMUTH

*Max-Planck-Institut für Strahlenchemie, D-4330 Mülheim an der Ruhr (F.R.G.)*

In this paper a study of the photochemistry of a benzoylnaphthobarrelene-like system is summarized; this summary is abstracted from a paper by Demuth *et al.* [1]. The ketone **12a** (Fig. 1) rearranges in a photochemical di-$\pi$-methane-type process to the isotopomeric products **14a** - **14c**. The hydroxy analogue **21a** undergoes a similarly regioselective rearrangement to **23a** - **23c**. The composition of the product mixtures varies with temperature but is largely insensitive to the nature of the solvent and to the mode of excitation (*i.e.* direct excitation at vari-

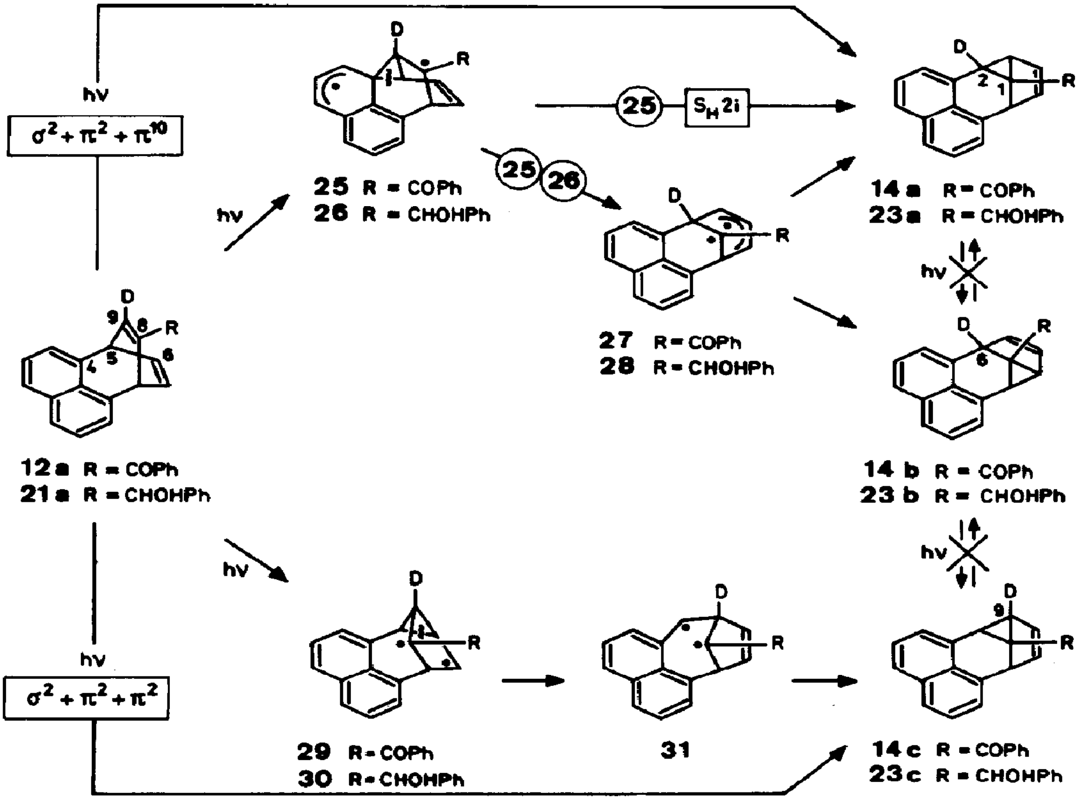

Fig. 1. Reaction scheme for the photorearrangement of **12a** and **21a** to **14a** - **14c** and **23a** - **23c** respectively, showing possible stepwise and symmetry allowed concerted reaction paths.

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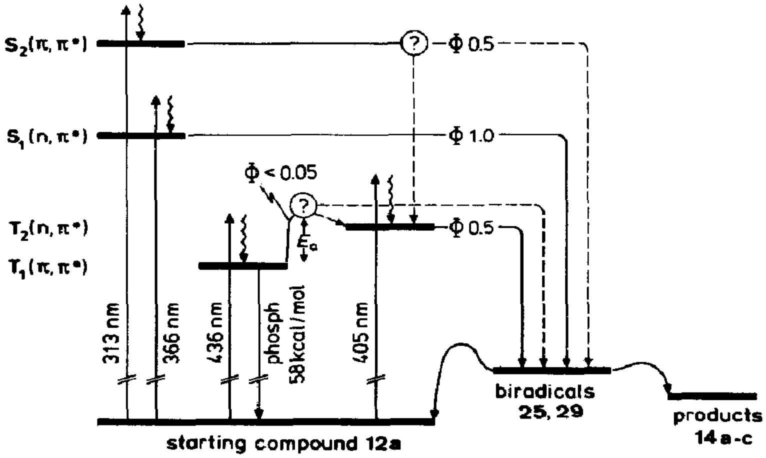


Fig. 2. State and reaction diagram for the di-π-methane rearrangement **12a** → **14a** - **14c**: – – –→, processes not discerned experimentally.

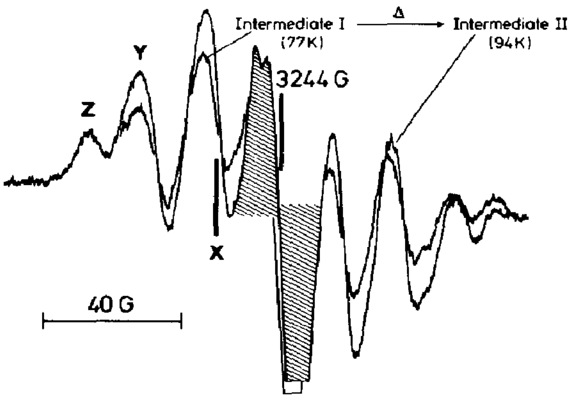
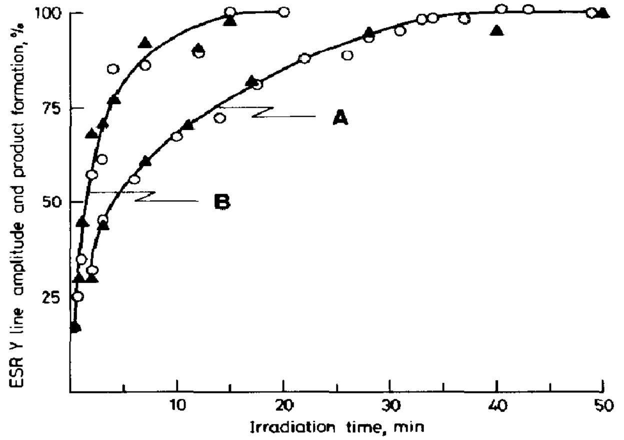


Fig. 3. ESR spectra of **12** after irradiation at 77 K (intermediate I; spectrum with smaller amplitudes) and after subsequent warming to 94 K and recooling to 77 K (intermediate II; spectrum with larger amplitudes): $D' = 58$ G; $E' = 4$ G. The shaded portions are caused by radical byproducts.

ous wavelengths and triplet sensitization with donors of different triplet energies; see Fig. 2). At 298 K the primary photoreaction occurs directly from the $S_1$ $(n,\pi^*)$ and $T_2(n,\pi^*)$ states and it proceeds from $T_1(\pi,\pi^*)$ and from $S_2(\pi,\pi^*)$ either directly or via $T_2$. At lower temperatures on direct irradiation, the $S_1 \rightarrow T$ intersystem crossing and triplet reaction compete with the reaction from the singlet. The processes at room temperature are summarized in Fig. 2. The energy and nature of the lowest-lying $T_1$ state of **12** were determined by phosphorescence at 77 K and by a laser flash photolysis measurement of the rate constants of triplet energy transfer to **12** as a function of the sensitizer energy ($E_T = 51$ - 69 kcal mol$^{-1}$). Quantum yields of selective direct excitations to $S_1$, $S_2$, $T_1$ and $T_2$ and of sensitizations to $T_1$ and $T_2$ by donors of $E_T = 62$ - 69 kcal mol$^{-1}$ completed the information necessary for the diagram in Fig. 2.



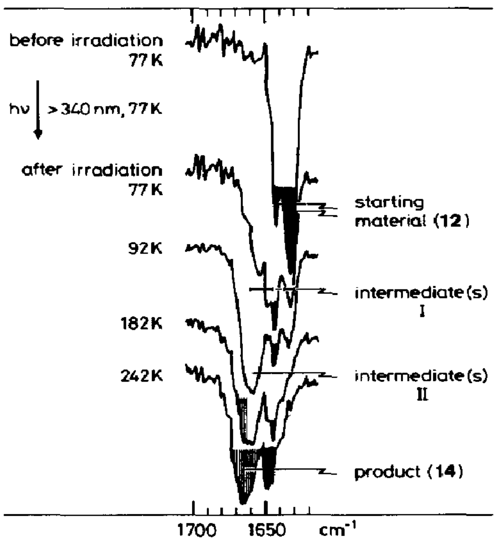


Fig. 4. Comparison between the ESR signal intensity of intermediate I and the formation of product **14** as a function of the irradiation time: curve A, excitation using a wavelength of 313 nm; curve B, excitation using a wavelength greater than 340 nm; ▲, ESR signal of the biradical at 77 K; ○, product formation after warming to room temperature. The maxima of the ESR intensity and of the formation of product **14** are taken as the 100% values of these parameters. The plots have not been normalized with respect to the different intensities of the two excitation wavelengths.

Fig. 5. IR spectra of **12** at 77 K before irradiation and after irradiation using a wavelength greater than 340 nm for 30 min during the warm-up from 77 to 242 K. The band shapes of **12** (■) and **14** (▨) at 242 K are the same as those of the appropriate reference samples at 242 K. Of the twelve frozen-out rotamers, after irradiation only one was still present in the temperature range 77 - 182 K and the build-up of **14** started to show at 182 K.

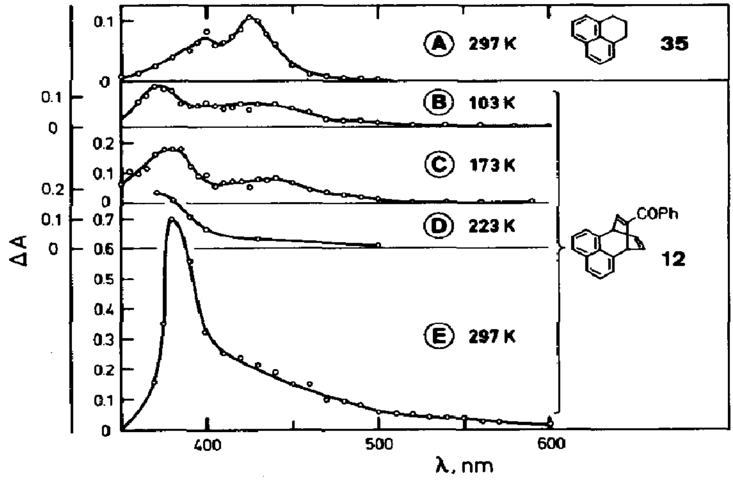
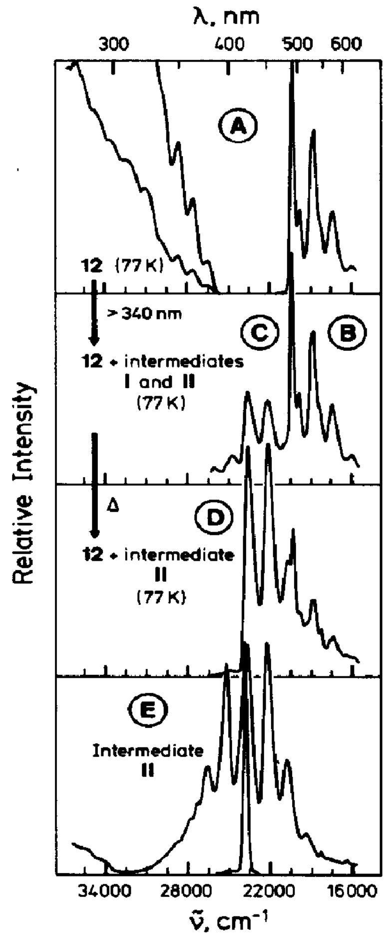


Fig. 6. Transient spectra obtained on laser flash photolysis of **12** and **35** using excitation at $\lambda = 265$ nm (spectra A and B) and at $\lambda = 353$ nm (spectra B - E). Spectra B and C are attributed to the $T_1$ state of **12**. Spectrum E arises from intermediate II: lifetime $\tau = 20 \pm 4$ ns at 278 - 363 K in benzene; extinction coefficient $\varepsilon_{max} \lesssim 2500$ dm$^3$ mol$^{-1}$ cm$^{-1}$.



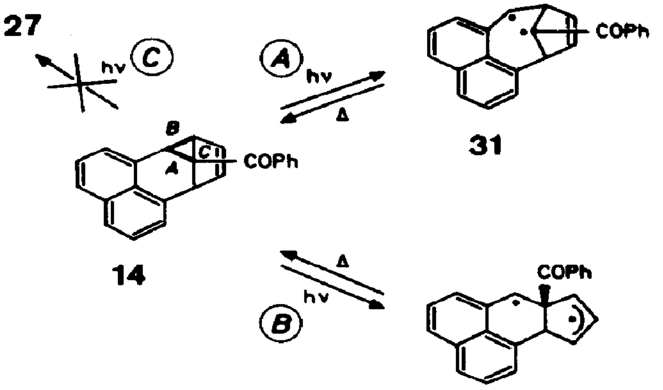


Fig. 7. Emission at 77 K (all spectra corrected; emission at $\lambda = 491$ nm (spectrum A) and at $\lambda = 450$ nm (spectrum E); excitation at $\lambda = 355$ nm (spectra A - E): spectrum A, phosphorescence and excitation of **12**; spectrum B, residual phosphorescence of **12**; spectrum C, fluorescence of intermediate II (some possible emission at about 25 000 $cm^{-1}$ from intermediate I may be present) immediately after exhaustive irradiation at 77 K; spectrum D, as spectrum C but immediately after reaching maximum intensity; spectrum E, fluorescence and excitation of intermediate II after computer-aided subtraction of the phosphorescence of spectrum C.

Fig. 8. Reaction scheme showing thermally reversible photocleavages as possible mechanisms for the dissipation of the excitation energy in **14**.

The rearrangement **12a** → **14a** - **14c** proceeds along three reaction paths evolving from the two primary photochemical processes of naphthyl–vinyl and vinyl–vinyl bonding in the $\beta$ position to the benzoyl group (**12, 25** and **29**).

Two ground state triplet diradical intermediates such as **25** and **27** were shown for the first time in di-$\pi$-methane photochemistry to intervene consecutively and in accordance with expectation based on previously proposed mechanisms [2]. Each of these intermediates was characterized by electron spin resonance (ESR) spectroscopy (Figs. 3 and 4) and by IR spectroscopy (Fig. 5); in addition, the second intermediate was characterized by laser flash photolysis (Fig. 6) and by fluorescence and fluorescence excitation (Fig. 7).

The failure of products **14a** - **14c** to interconvert photochemically is ascribed to efficient energy dissipation through the thermally reversible photocleavage of bonds A and/or B in the three-membered ring as shown in the scheme in Fig. 8.

## *References*

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2 H.E. Zimmerman, in P. de Mayo (ed.), *Rearrangements in Ground and Excited States*, Vol. 3, Academic Press, New York, 1980, pp. 131 - 166.