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Photochemistry of 9-Benzyloxytriptycenes[1)]

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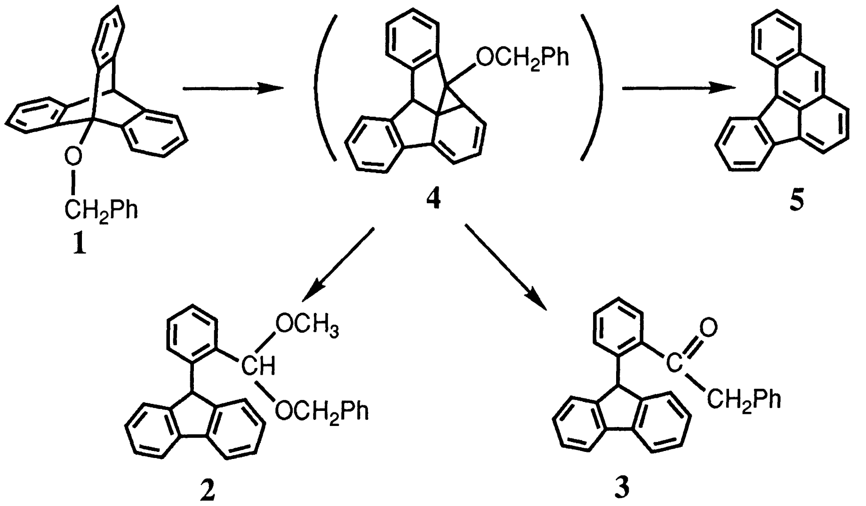
The photochemical reactions of 9-benzyloxytriptycenes in methanol were found to give 2-(9-fluorenyl)benzaldehyde acetals and benzyl 2-(9-fluorenyl)phenyl ketones. Intermediacy of norcaradienes and two kinds of singlet carbenes has been demonstrated by quantum yields, light intensity dependence, competitive reactions, and substituent effects.

The photorearrangement of triptycenes proceeds through the formation of 2-(9-fluorenyl)phenylcarbene intermediates which add internally to the aromatic ring and can be intercepted with alcoholic solvents.[2)] Whereas 9-alkoxytriptycenes show similar reaction patterns, they are unique in that the corresponding α-alkoxycarbenes are formed regiospecifically and undergo further reactions to give 2-(9-fluorenyl)benzaldehyde and alkyl 2-(9-fluorenyl)phenyl ketones in hydrocarbon solvents.[3)] Since the formation of these secondary products are not popular in carbene chemistry and the previous work is based on the product analyses of the almost completed reactions by irradiation with a Vycor-filtered high-pressure mercury lamp, a more detailed study has been carried out with special emphasis on the effects of the wavelength and intensity of light on the early stage of these photoreactions.



Scheme 1.

Irradiation of 1-3 mM methanol solutions of 9-benzyloxytriptycene **1** at 254 nm for a short period (5-30 s) produced a mixture that showed two intense and two weak peaks in HPLC. The one intense and two weak peaks were found to correspond to those of the authentic samples of unreacted **1**, acetal **2**, and ketone **3**.[3] An absorption with λ_{max} at 250 and 350 nm was obtained, when the spectrum of the photolysate was taken with the unirradiated solution of **1** as a reference (Fig. 1). Since neither **2** nor **3** showed absorptions at wavelength longer than 340 nm, the absorption maximum at 350 nm is ascribed to that of a photoproduct of the unidentified HPLC peak. On the basis of the similarity of the shape and absorption maxima to those of the norcaradienes formed by photolysis of parent triptycene and other bridgehead-substituted triptycene derivatives,[4] norcaradiene structure **4** was assigned to the main fraction. This HPLC peak was not found when the photoreacton was carried out to completion by irradiation either at 254 nm or with a Vycor-filtered high-pressure mercury lamp. The yields of **2** and **3** based on consumed **1** were ca. 40% and 30%, respectively, together with 10% **5** and small amounts of unidentified products as determined by HPLC. Efforts to obtain other spectral data for **4** or isolate **4** were unsuccessful either; when concentrated, **4** was converted into hydrocarbon **5**[3,5] by a dark reaction without forming **2** and **3**. Irradiation of the photolyzed (at 254 nm for 30 s) solution at 345 nm showed an increase of **2** at the expense of **4** as shown in Fig. 2. The amount of **1** and **3** did not change during this period.

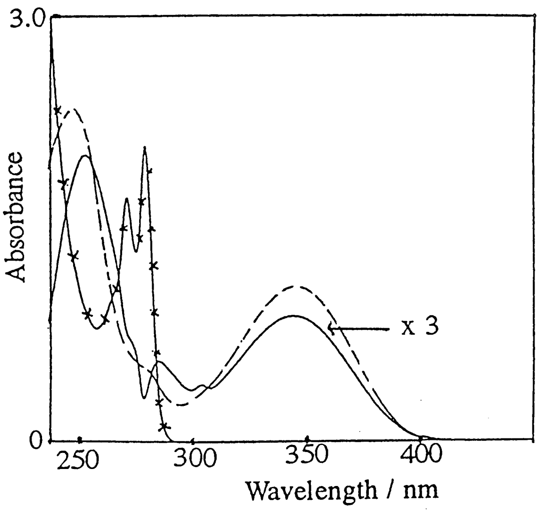


Fig. 1. Absorption spectra of **1** (x--x), the photolysate of **1** (——) with the unirradiated solution of **1** as a reference, and the authentic norcaradiene from triptycene[4] (----) in methanol.

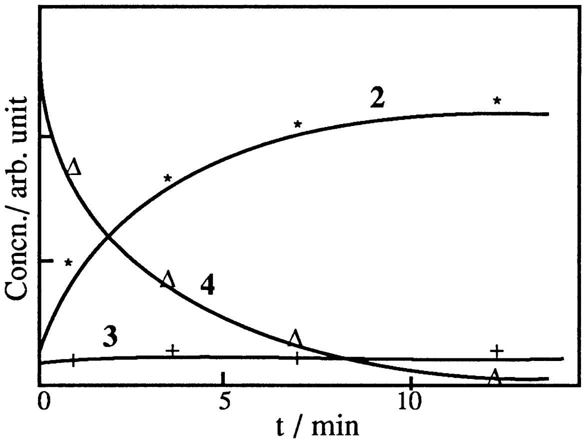


Fig. 2. Appearance of **2** at the expense of **4** by irradiation at 345 nm.

In order to delineate the mechanism of this reaction (Scheme 1), we have studied some quantum yields, light intensity dependence, competitive reactions, and substituent effects. The results are as follows.

1) The quantum yields of the photoreactions were measured for less than 5% decrease of the substrates and formation of the products by a standard method with potassium ferroperoxalate as a chemical actinometer. Those of the formation of **4**, **2**, and **3** were 0.15, 0.002, and 0.001, respectively, at 254 nm. 2) The quantum yields

for the disappearance of **4** and formation of **2** and **3** were 0.014, 0.012, and 0.001, respectively, at 334 nm. 3) The dependence of the initial rates of formation on the light intensity has been studied at 254 nm using a set of calibrated density filters and analyzed in terms of Eq. 1, where k, c and I are the initial rate constant, a proportionality constant, and the light intensity, respectively. The n values were obtained as 0.75 ± 0.14,

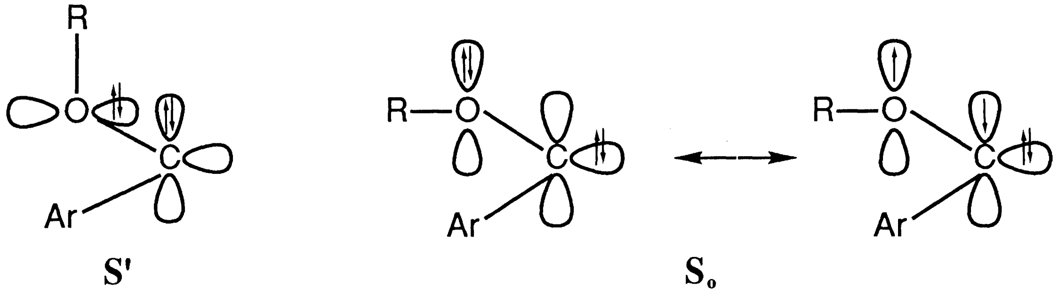
$$k = c\,I^n \qquad (1)$$

1.51 ± 0.27, and 1.42 ± 0.25 for the formation of **4**, **2**, and **3**, respectively. The results deviated from integers but were more or less consistent with the one-photon formation of **4** and the two-photon processes for **2** and **3**. 4) Relative rates of the reaction of variously substituted benzyl derivatives of **1** (p-X-$C_6H_4CH_2$ instead of $PhCH_2$) by competitive reactions. The results are summarized in Table 1. All substituents enhance the reactivity irrespective of the nature of the sbstituents. A subtle effect of the bridgehead substitution on the the regioselectivity of the reaction is reported and ascribed to differences in reaction rates rather than those of radiationless deactivations.[6] 5) The ratios of the quantum yields of the formation of **3**, (Φ_X/Φ_H) were obtained for **1** and variously substituted benzyl derivatives (see Table 1). The ratios are smaller for electron-donating substituents indicating that the rearrangement of the carbenes to the ketones is electrophilic.

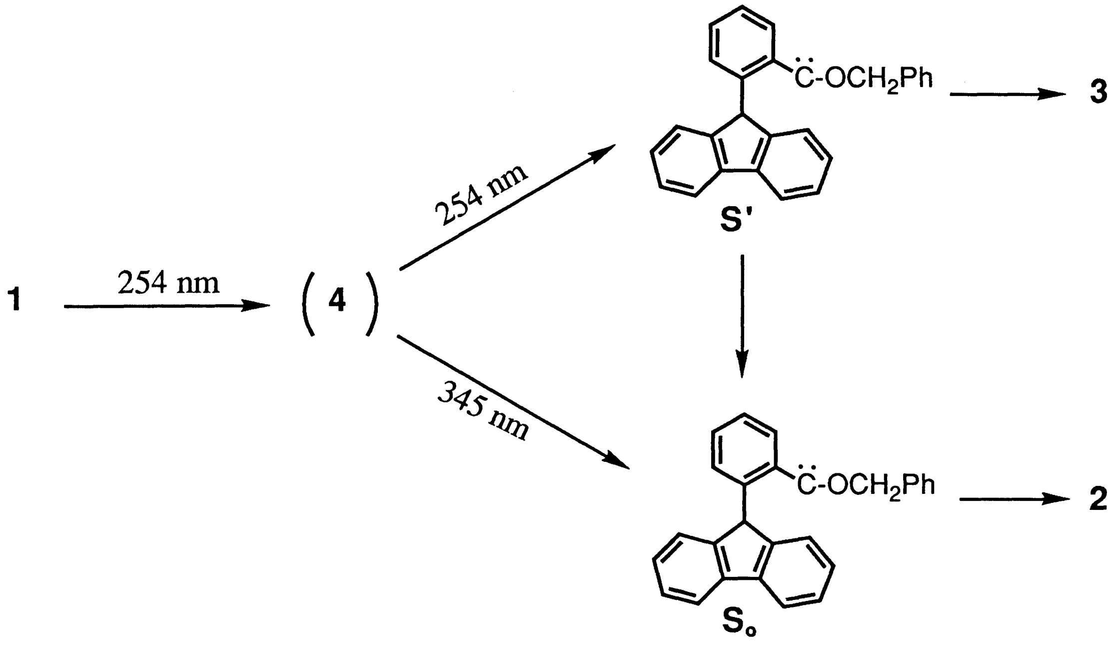
Table 1. Effects of the *p*-substituent X of the benzyl group on the relative rates of the reaction of **1** and Φ_X/Φ_H for the formation of **3**

X	H	F	Cl	CH_3	OCH_3
Relative rates of reaction of **1**	1.0	1.6	1.2	1.4	2.3
Φ_X/Φ_H for formation of **3**	1.0	1.05	1.07	0.33	0.31

All the above observations require the intermediacy of **4** and most of **2** and **3** are formed by two-photon processes. Selective formation of **2** from **4** by irradiation at longer wavelength and formation of **3** plus **2** at 254 nm requires the intermediacy of two kinds of singlet carbenes. In reference to the electronic configuration of the carbene species involved in Wolff rearrangement,[7] two structures S and S' are postulated (Scheme 2). The former undergoes OH insertion pre-dominantly, whereas the migration of the benzyl group to the divalent carbon could also take place in the latter in the higher energy S' state. All the results are interpreted in terms of Scheme 3.



Scheme 2.



Scheme 3.

References

1) Dedicated to Professor Emeritus Osamu Simamura of The University of Tokyo on the occasion of his 80th birthday.

2) H. Iwamura and K. Yoshimura, J. Am. Chem. Soc., 96, 2652 (1974); H. Iwamura, Chem. Lett., 1974, 1205.

3) H. Iwamura and H. Tukada, Chem. Lett., 1976, 1045 ; H. Iwamura and H. Tukada, Tetrahedron Lett., 1978, 3451.

4) Absorption maxima (log ε) are at 249 (4.26), 345 (3.89) nm, 248.5 (4.23), 347 (3.89) nm, and 340 nm for the norcaradienes from triptycene (Ref. 2 and: T. D. Walsh, J. Am. Chem. Soc., 91, 515 (1969), 9,10-bis(2-cyano-2-methyletyl)triptycene (H. Iwamura, J. Chem. Soc.,Chem. Commun., 1973, 232), and 9-azatriptycene (T. Sugawara, N. Nakashima, K. Yoshihara, and H. Iwamura, J. Am. Chem. Soc., 105, 859 (1983), respectively. Since the HPLC peak hight of **4** was nearly the same as that of **1** after 10% of decrease by irradiation when detected at 254 nm, ε of **4** at 254 nm is supposed to be about ten times higher than that of **1** (ε=1270).

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