

PHOTODIMERIZATION OF 3,3-BIPHENYLENE-1-BROMO-1-PHENYLALLENE

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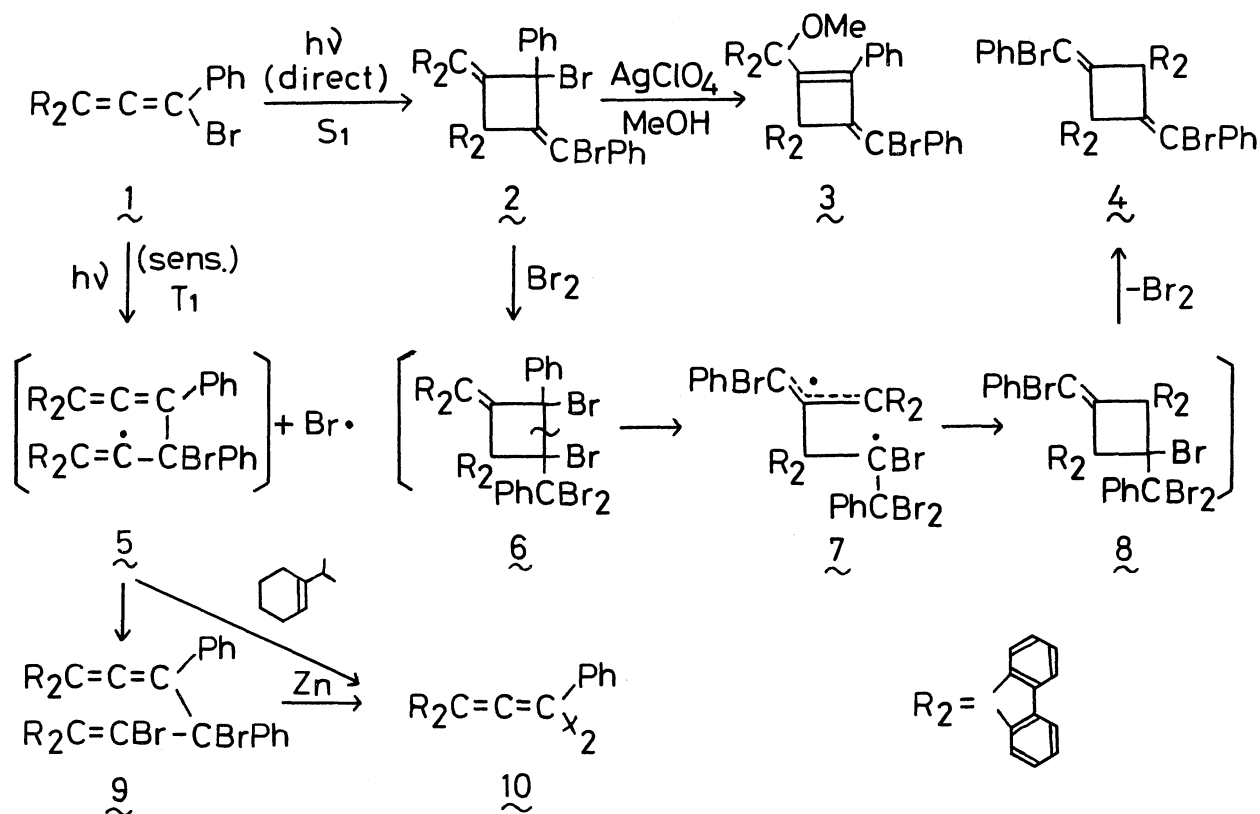
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Photodimerization of the title allene afforded 1,1-biphenylene-3-bromo-2-bromobenzylidene-4-fluoren-9-ylidene-3-phenylcyclobutane (2), whereas the photodimerization in the presence of fluorenone afforded 1,1,6,6-bis(biphenylene)-4,5-dibromo-3,4-diphenylhexa-1,2,5-triene (9).

Although thermal dimerization of allenes have been extensively studied,¹⁾ photodimerization of allenes has yet been reported.²⁾ We found that the photodimerization of the title allene (1) affords 1,3-dimethylenecyclobutane and hexa-1,2,5-triene, and that the photodimerization contrasts with thermal dimerization of allene which affords 1,2-dimethylenecyclobutane derivative.

A solution of 1 in benzene was irradiated³⁾ for 1.5 hr to afford 1,1-biphenylene-3-bromo-2-bromobenzylidene-4-fluoren-9-ylidene-3-phenylcyclobutane (2, 30%, mp 233-234°C, λ_{\max} 372 nm (ϵ , 5,100), m/e 690 (M^+ , rel intensity 2), 611 (M^+-Br , 12), 530 (M^+-Br_2 , 100), 453 (530-Ph, 25)) and 1,1,6,6-bis(biphenylene)-4,5-dibromo-3,4-diphenylhexa-1,2,5-triene (9, 10%, mp 181-181.5°C, λ_{\max} 313 nm (ϵ , 10,200), ν_{\max} 1930 cm^{-1}). The structures of these photodimers were elucidated on the basis of the spectral data shown in parentheses and of the following reactions. The reaction of 2 with $AgClO_4$ in THF-MeOH afforded 3,3-biphenylene-4-bromobenzylidene-2-(9-methoxyfluoren-9-yl)-1-phenylcyclobutene (3, mp 242-242.5°C, λ_{\max} 352 nm (ϵ , 13,600), ν_{\max} 1100 cm^{-1} , nmr ($CDCl_3$): 2.0-3.2 (m, 26H), 7.80 τ (s, 3H)). The debromination of 9 with Zn-powder afforded 10 (70%, mp 173.5-174°C).⁴⁾ When 2 was treated with Br_2 in $CHCl_3$ at 40°C for 10 min, 2 was isomerized into 1,1,3,3-bis(biphenylene)-2,4-bis(bromobenzylidene)cyclobutane (4, mp 257-258°C, λ_{\max} 357 nm (ϵ , 14,800), m/e 690 (M^+)) in a quantitative yield. A plausible pathway of the rearrangement is as follows: Ring cleavage of 6 which formed initially by the addition of Br_2 to 2, affords biradical intermediate (7). Debromination of 8 which produced by ring closure of 7 finally affords 4.

When the photodimerization of 1 was carried out in the presence of fluorenone for 1 hr, 9 (46%) and 10 (5%) were obtained, but not any cyclic dimer. This reaction can be well interpreted by



assuming radical (5) as an intermediate. Recombination of 5 with $Br\cdot$ affords 9, and elimination of $Br\cdot$ from 9 affords 10. Because the photodimerization of 1 in the presence of 1-isopropylcyclohexene as a radical scavenger afforded 10 as the major product (40%) in addition to a small amount of 9 (10%), the above interpretation is not unreasonable.

References

- 1) See, e.g., D. R. Taylor, Chem. Rev., 67, 342 (1967).
- 2) The only reported example in the photodimerization of cumulene is limited to the case of tetraphenylbutatriene in the solid state which affords 1,3-dialkenylidenecyclobutane. Z. Berkovitch-Yellin, M. Lahav, and L. Leiserowitz, J. Amer. Chem. Soc., 96, 918 (1974).
- 3) Irradiation was carried out with a 400W high-pressure mercury lamp through a Pyrex filter.
- 4) F. Toda and Y. Takehira, Chem. Commun., in press.
- 5) The permanganate oxidation of 4 afforded benzoic acid and 2,2,4,4-bis(biphenylene)cyclobutane-1,3-dione.

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