CHEMISTRY LETTERS, pp. 257-258, 1975. Published by the Chemical Society of Japan

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

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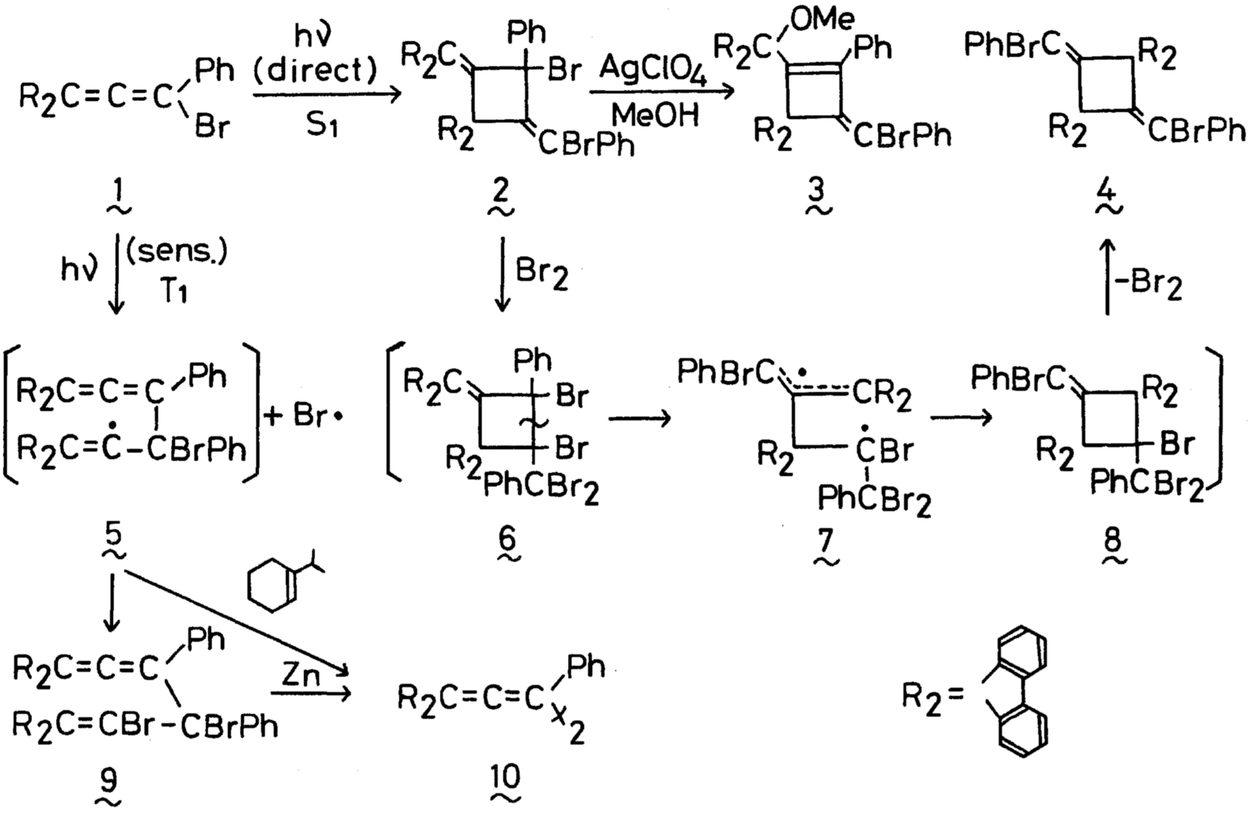
Photodimerization of the title allene afforded 1,1-biphenylene-3-bromo-2-bromobenzylidene-4-fluoren-9-ylidene-3-phenylcyclobutane (2), whereas the photodimerization in the presence of fluorenone afforded 1,1,6,6-bis(biphenylene)-4,5-dibromo-3,4-diphenylhexa-1,2,5-triene (9).

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• affords 9, and elimination of Br• 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.

(Received February 3, 1975)