SHORT COMMUNICATIONS

Thermal Dimerization of Tropilidene*1

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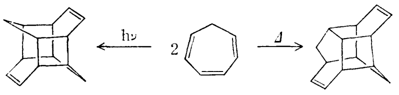
(Received December 12, 1969)

We have found an example of a [6+4] combination between two hydrocarbon molecules[1] in the Diels-Alder reaction for the first time. Although the photochemical dimerization of tropilidene (I) to give a dimer (II)[2] is known, comparable studies with thermal reactions have not hitherto been reported. In the course of our research on the Diels-Alder reactions of tropilidene, we have found that the thermal reaction of I gave a dimer (III).



(II) (I) (III)

Fig. 1

When I was heated in an ampoule at 170°C for 100 hr, vacuum distillation (40—43°C/1 mmHg) of the product followed by silicagel chromatography (pentane) gave colorless prisms (from methanol), mp 157—162°C, $C_{14}H_{16}$, in 26% yield, IR, 3020, 2910, 1641, 1436, 889, 731 cm^{-1}; UV, end absorption; MS, *m/e* 184 (M^+), the base peak was found at *m/e* 92 corresponding to the tropilidene ion $C_7H_8^+$ and the second intense peak at *m/e* 91 (79%) corresponding to the tropylium ion $C_7H_7^+$. The NMR specrtum[3] showed the asymmetric complex olefinic protons multiplet at 6.4—5.2 (4H) and the three groups of multiplets centered at 2.8 (4H, allylic methine), 2.3 (4H, methine) and 1.9 (4H, methylene) respectively. These data strongly suggest the structure of pentacyclo[7,5,0,0^{2,7},0^{5,13}, 0^{6,12}]tetradeca-3,10-diene (III) for this dimer. III was identical in all respects with the authentic sample[4] which was obtained by the Wolf-Kishner reduction of the cycloaddition product of tropone and I.[5]

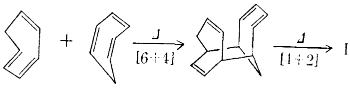


Fig. 2

The formation of III, which may be considered as a concerted [6+4]-cycloaddition[6] followed by an intramolecular Diels-Alder addition, is an additional evidence for the *trans*-[6+4]-cycloaddition.[5,7]

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*1 This paper was presented at the 21st Annual Meeting of the Chemical Society of Japan, Osaka, April, 1968.

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1) Thermal [6+4] co-cycloaddition of two azepine molecules has recently been discovered. I. C. Paul, S. M. Johnson, J. H. Barrett and L. A. Paquette, *Chem. Commun.*, **1969**, 6.

2) G. O. Schenck, J. Kuhls and C. H. Krauch, *Ann. Chem.*, **639**, 20 (1966).

3) Determined on a Varian A-60 instrument in deuteriochloroform and reported as δ units relative to TMS (δ=0).

4) Y. Fujise, Ph. D. Thesis (1967) of Tohoku University (under supervision of Professor Shô Itô). We thank Professor Shô Itô for comparison of this compound.

5) Shô Itô, Y. Fujise and M. C. Woods, *Tetrahedron Lett.*, **1967**, 1059.

6) R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 2046, 4388 (1965).

7) R. C. Cookson, B. V. Drake, J. Hudec and A. Morrison, *Chem. Commun.*, **1966**, 15; Shô Itô, Y. Fujise, T. Okuda and Y. Inoue, This Bulletin, **39**, 1351 (1966).