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Synthesis and Reactions of 5,6,11,12-Tetrahydro-5,12;6,11-diethenodibenzo-[a,e]cyclo-octene (pp'-Dinaphthalene)

By Yoshito Tobe,* Fumiaki Hirata, Katsuhiko Nishida, Hisashi Fujita, Koji Kimura, and Yoshinobu Odaira

(Department of Petroleum Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan)

Summary 5,6,11,12-Tetrahydro-5,12;6,11-diethenodibenzo[a,e]cyclo-octene (pp'-dinaphthalene) (5) has been synthesized and its thermal and photochemical behaviour has been examined. TRICYCLO[$4.2.2.2^{2,5}$]DODECA-3,7-DIENE (1)¹ and the benzofused analogue (2)² have been shown to exhibit remarkable reactivity due to the extensive interactions between the two proximate but non-conjugated double bonds. On the other hand, the chemistry of more interesting molecules such as tricyclo $[4.2.2.2^{2,5}]$ dodeca-3,7,9,11-tetraene (pp'-dibenzene) (3) and the monobenzo-derivative (pp'-cycloadduct between benzene and naphthalene) (4) has not yet been investigated; (3) is unknown and the synthesis of (4) was reported only recently.³ We now report the synthesis and thermal and photochemical reactions of the dibenzo-derivative of (3), 5,6,11,12-tetrahydro-5,12;6,11-diethenodibenzo[a,e]cyclooctene (5).



The alkaline hydrolysis of the cage diester $(6a)^4$ derived from the photodimerization of methyl naphthalene-2carboxylate gave the diacid (6b),† m.p. 203-205 °C, quantitatively. The brominative decarboxylation of (6b) by Cristol's modification of the Hunsdiecker reaction⁵ afforded the dibromide (6c), m.p. 212-214 °C (decomp.), in 77% yield; the subsequent debromination of (6c) with tri-n-butyltin hydride in tetrahydrofuran (254 nm irradiation) furnished the hydrocarbon (6d) in 63% yield: m.p. 204-206 °C; ¹H n.m.r. (CDCl₃) δ 3·28 (br. d, 4H), 4·28 (d, J 5 Hz, 4H), and 6.92 (br. s, 8H); ¹³C n.m.r. (CDCl₃) δ 33.5 (d), 45.7 (d), 126.3 (d), 128.2 (d), and 137.8 (s) p.p.m.; u.v. $\lambda_{\max}(CH_2Cl_2)$ 276 (ϵ 427) and 268 (479) nm.

(5)

Treatment of (6d) with bis(norbornadienyl)rhodium chloride in chloroform gave the rhodium complex (7), m.p. >320 °C (decomp.), in 68% yield. The tetraene (5) was liberated from (7) by treatment with triphenyl phos-



phite (80% yield): m.p. 87.5-88.5 °C; 1H n.m.r. (CDCl₃) δ 3.78 (d, J 2 Hz, 4H), 6.52 (d, J 2 Hz, 4H), and 6.70 (br. s, 8H). The structure of (5) was confirmed by its catalytic hydrogenation to give the hydrocarbon (8) which was also obtained as a major product of the reduction of the rhodium complex (7) with sodium borohydride in methanol:⁶ m.p. 200-204 °C; ¹H n.m.r. (CDCl₃) δ 1.60 (dd, J 2, 10 Hz, 4H), 2.50 (d, J 10 Hz, 4H), 3.44 (d, J 2 Hz, 4H), and 6.60-6.90 (m, 8H); ¹³C n.m.r. (CDCl₃) δ 23.2 (t), 42.4 (d), 125.5 (d), 126.7 (d), and 143.0 (s) p.p.m.; u.v. $\lambda_{max}(CH_2Cl_2)$ 274 (ϵ 646) and 267 (617) nm.

The diene (1) and the compound (2) have been shown to undergo facile Cope rearrangement at 90 and 80 °C, respectively.^{1,2} It is significant that compound (5) is more labile than (1) or (2); it was converted quantitatively into the Cope rearrangement product (9), m.p. 102-103 °C, even at ambient temperature: the half-life for the rearrangement at 40 °C in chloroform was about 120 min.[‡] More interestingly, in contrast with the case of (1) and (2), § the irradiation of an acetone solution of (5) gave the [4 + 4] cycloreversion product, naphthalene, as the major product along with the [2 + 2] cycloadduct (6d) in a ratio of 2:1. Thus the cleavage of the bonds joining together the two naphthalene rings of the tetraene (5) occurred with extreme ease compared with those of the diene (1) and the triene (2) presumably because of the additional steric and/or electronic interactions between the fused aromatic rings.

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- † All new compounds gave satisfactory analytical and spectral data.
- [‡] Determined from the decrease in the ¹H n.m.r. signal at δ 6.52.

§ It was reported that the intramolecular [2 + 2] cycloadditions of (1) and (2) took place efficiently to afford the corresponding cage compounds on irradiation in the presence of a sensitizer: refs. 1 and 2.

- P. E. Eaton and U. R. Chakraborty, J. Am. Chem. Soc., 1978, 100, 3634.
 N. C. Yang and J. Libman, J. Am. Chem. Soc., 1972, 94, 9228.
 K. T. Mak, K. Srinivasachar, and N. C. Yang, J. Chem. Soc., Chem. Commun., 1979, 1038.
 P. J. Collin, D. B. Roberts, G. Sugowdz, D. Wells, and W. H. F. Sasse, Tetrahedron Lett., 1972, 321; T. Teitei, D. Wells, and W. H. F. Sasse, Tetrahedron Lett., 1972, 321; T. Teitei, D. Wells, and W. H. F. Sasse, Tetrahedron Lett., 1972, 321; T. Teitei, D. Wells, and W. H. F. Sasse, Tetrahedron Lett., 1972, 321; T. Teitei, D. Wells, and W. H. F. Sasse, Tetrahedron Lett., 1972, 321; T. Teitei, D. Wells, and W. H. F. Sasse, Tetrahedron Lett., 1972, 321; T. Teitei, D. Wells, and W. H. F. Sasse, Tetrahedron Lett., 1972, 321; T. Teitei, D. Wells, and W. H. F. Sasse, Tetrahedron Lett., 1972, 321; T. Teitei, D. Wells, and W. H. F. Sasse, Tetrahedron Lett., 1972, 321; T. Teitei, D. Wells, and W. H. F. Sasse, Tetrahedron Lett., 1972, 321; T. Teitei, D. Wells, and W. H. F. Sasse, Tetrahedron Lett., 1972, 321; T. Teitei, D. Wells, and W. H. F. Sasse, Tetrahedron Lett., 1972, 321; T. Teitei, D. Wells, and W. H. F. Sasse, Tetrahedron Lett., 1972, 321; T. Teitei, D. Wells, and W. H. F. Sasse, Tetrahedron Lett., 1972, 321; T. Teitei, D. Wells, and W. H. F. Sasse, Tetrahedron Lett., 1972, 321; T. Teitei, D. Wells, and W. H. F. Sasse, Tetrahedron Lett., 1972, 321; T. Teitei, D. Wells, and W. H. F. Sasse, Tetrahedron Lett., 1972, 321; T. Teitei, D. Wells, and Y. K. F. Sasse, Tetrahedron Lett., 1972, 321; T. Teitei, D. Wells, and Y. K. F. Sasse, Tetrahedron Lett., 1972, 321; T. Teitei, D. Wells, and Y. K. F. Sasse, Tetrahedron Lett., 1972, 321; T. Teitei, D. Wells, and Y. K. F. Sasse, Tetrahedron Lett., 1972, 321; T. Teitei, D. Wells, and Y. K. F. Sasse, Tetrahedron Lett., 1972, 321; T. Teitei, D. Wells, and Y. K. F. Sasse, Tetrahedron Lett., 1972, 321; T. Teitei, D. Y. K. K. F. Sasse, Tetrahedron Lett., 1972, 321; T. Teitei, D. Y. K. W. H. F. Sasse, Aust. J. Chem., 1976, 29, 1783.
 ⁵ S. J. Cristol and W. C. Firth, J. Org. Chem., 1961, 26, 280.
 ⁶ P. E. Eaton and D. R. Patterson, J. Am. Chem. Soc., 1978, 100, 2573.

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