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

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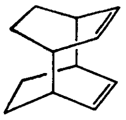
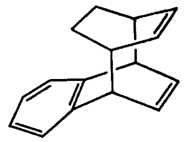
Summary 5,6,11,12-Tetrahydro-5,12;6,11-diethenodibenzo[*a,e*]cyclo-octene (*pp*′-dinaphthalene) (**5**) has been synthesized and its thermal and photochemical behaviour has been examined.

TRICYCLO[4.2.2.2^{2,5}]DODECA-3,7-DIENE (**1**)[1] and the benzo-fused 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**).


(1)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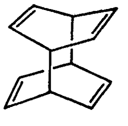
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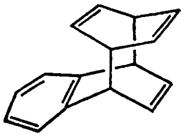
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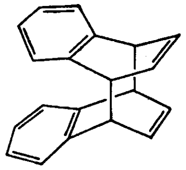
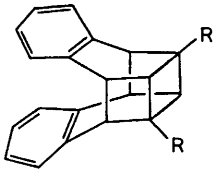
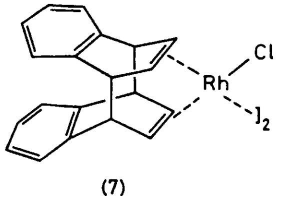

(5)

The alkaline hydrolysis of the cage diester (**6a**)[4] derived from the photodimerization of methyl naphthalene-2-carboxylate gave the diacid (**6b**),† m.p. 203—205 °C, quantitatively. The brominative decarboxylation of (**6b**) by Cristol's modification of the Hunsdiecker reaction[5] 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; ^{1}H n.m.r. (CDCl$_3$) δ 3·28 (br. d, 4H), 4·28 (d, *J* 5 Hz, 4H), and 6·92 (br. s, 8H); ^{13}C n.m.r. (CDCl$_3$) δ 33·5 (d), 45·7 (d), 126·3 (d), 128·2 (d), and 137·8 (s) p.p.m.; u.v. λ_{max}(CH$_2$Cl$_2$) 276 (ϵ 427) and 268 (479) nm.

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 phosphite (80% yield): m.p. 87·5—88·5 °C; ^{1}H n.m.r. (CDCl$_3$) 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; ^{1}H n.m.r. (CDCl$_3$) 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); ^{13}C n.m.r. (CDCl$_3$) δ 23·2 (t), 42·4 (d), 125·5 (d), 126·7 (d), and 143·0 (s) p.p.m.; u.v. λ_{max}(CH$_2$Cl$_2$) 274 (ϵ 646) and 267 (617) nm.

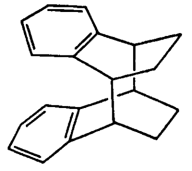


(6)



(7)

a; R = CO$_2$Me
b; R = CO$_2$H
c; R = Br
d; R = H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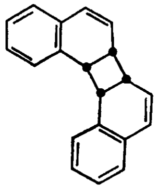
(9)

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 ^{1}H 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.

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