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THE SYNTHESIS OF BICYCLO[6.2.0]DECAPENTAENE

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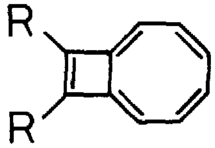
Summary: The parent bicyclo[6.2.0]decapentaene is synthesized for the first time by thermal ring opening of its valence isomer. Thermal dimerization of the compound is also described.

Although a number of bicyclo[6.2.0]decapentaenes have been synthesized,[1] the parent hydrocarbon 1 has remained unknown despite several attempts of synthesis.[2] We wish here to communicate the synthesis and some properties of 1.

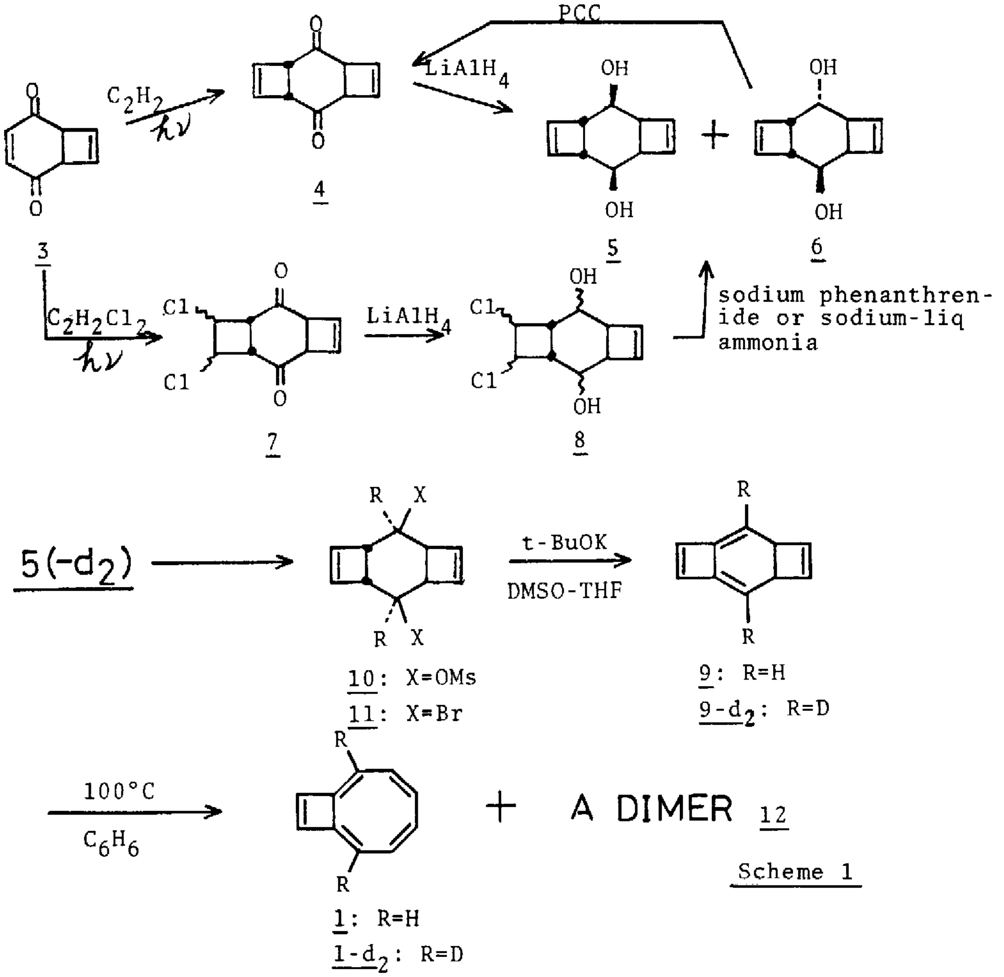


1 : R=H
2 : R=Ph

The synthetic scheme for 1 is *essentially the same* as the one we previously described for the synthesis of 9,10-diphenyl *derivative* 2,[1d] *namely thermal ring opening* of a valence isomer.

Irradiation of bicyclo[4.2.0]octa-3,7-diene-2,5-dione 3[3] in dichloromethane under continuous introduction of acetylene for 4-5 h gave *anti*-[2+2] adduct 4 in poor yield of 10-15%. Reduction of 4 with $LiAlH_4$ in THF gave *cis* and *trans* diol, 5 and 6, in 19 and 77% yield, respectively. An improved yield of the desired *cis* diol 5 was obtained in the following way. Photoreaction of 3 with either Z or E dichloroethylene gave a stereoisomeric mixture of rather unstable [2+2] adducts 7 in fair yield, which was subsequently reduced to a mixture of dichloro-diols 8 ($LiAlH_4$-THF). Treatment of 8 with phenanthrene-sodium[4] in THF provided 5 and 6 in 20 and 24% yield, respectively. Dechlorination with sodium-liquid ammonia[5] gave a similar result. The *trans* diol 6 could be transformed to the *cis* one 5 through oxidation to 4 (pyridinium chlorochromate,[6] CH_2Cl_2-EtOAc, 60-70% yield), although the process is not so effective.

The transformation of 5 to tricyclic tetraene 9 was examined in two pathways: via dimesylate 10 and via dibromide 11. The dimesylate 10 was obtained in 94% yield by reaction of 5 with CH_3SO_2Cl in dichloromethane using triethylamine as a base. The dibromide 11 was prepared in ca 30% yield by treatment of 5 with CBr_4-PPh_3[7] or NBS-PPh_3[8] in refluxing acetonitrile. Treatment of either 10 or 11 with t-BuOK (2-3 equiv) in DMSO-THF (2:1) under argon atmosphere at 0-25°C gave 9 [colorless oil; δ (C_6D_6) 3.38 (2H, d, J=3.2 Hz), 5.27 (2H, d, 3.2 Hz), 6.08 (2H, s), 6.48 (2H, s)[9]; UV: see Fig. 3] in 5-8% yield. Similarly, using $LiAlD_4$ for the reduction of 4, was obtained dideuterated tetraene 9-d_2 [δ (C_6D_6) 3.38 (2H, s), 6.08 (2H, s), 6.48 (2H, s)]. All the attemtps to improve the yield of 9 under various conditions have been unsuccessful. (Scheme 1)



Scheme 1

As expected, heating of 9 at 100°C in benzene yielded 1 accompanied by formation of a dimer 12. When the reaction of 9-d_2 was traced by means of ^{1}H-NMR spectroscopy (Fig. 1), the decrease of 9-d_2 obeyed the first-order rate law [$t_{1/2}$ (100°C)=95 min] with less than half rate of that for 2 [$t_{1/2}$ (100°C)=40 min^{10}]. While 1-d_2 reached its maximum concentration in about 2 h and thereafter decreased, dimer 12-d_4 slowly increased over the reaction time. These results indicate that dimer 12 is derived from two molecules of 1.

Although sensitive to air, 1 and 12 could be isolated by silica gel column chromatography without appreciable decomposition. The hydrocarbon 1 is a red-orange oil. The ^{1}H-NMR spectrum in C_6D_6 (Fig. 2) is quite simple, exhibiting only two singlets at δ 6.18 and 7.32 in the integrated ratio of 3:1. With 1-d_2, the ratio becomes 2:1. The electronic spectrum is shown in Fig. 3 compared with those of 2 and 9. The mass spectrum shows peaks at m/e 130 (25%), 129 (43%), 128 (M^+, 100%), 127 (44%), 126 (17%), 115 (10%), and 102 (37%).[11]

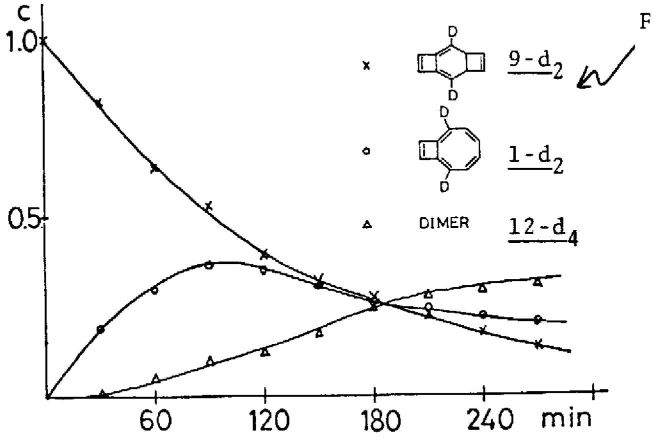


Fig. 1 Plot of relative concentration of 1-d_2, 9-d_2, and 12-d_4 vs. time at 100°C in C_6D_6. Data are calculated from the integrated areas of the ^{1}H-NMR signals using the benzene signal as an internal standard. The initial concentration of 9-d_2 is ca. 2 x 10^{-1} M.

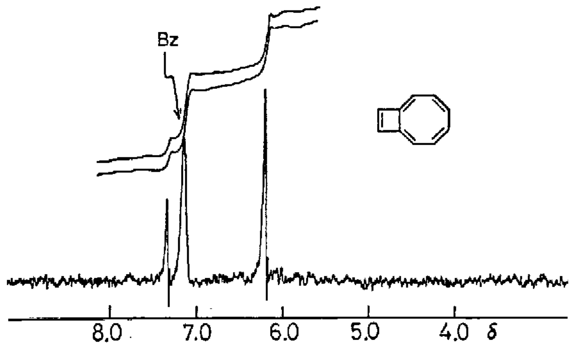


Fig. 2 ^{1}H-NMR spectrum of 1 in C_6D_6

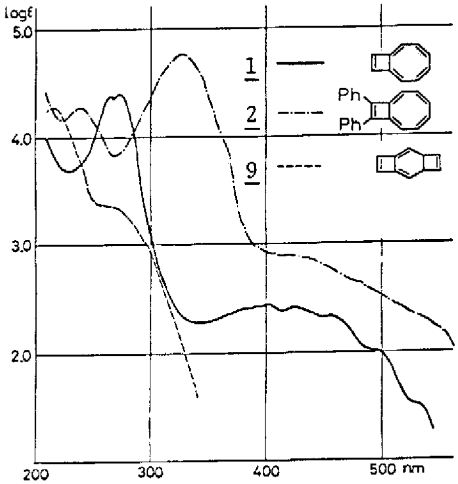


Fig. 3 Electronic spectra of 1, 2, and 9 in cyclohexane

Since the spectral properties of 1 resemble those of 2, it would be expected that 1 has a similar molecular geometry to 2,[12] that is, an almost planar conformation, a long central bond length, and a rather small bond alternation of the peripheral bonds.

The rather slow thermal dimerization of 1 even at 100°C contrasts with the quite rapid dimerization of benzocyclobutadiene,[13] which may reflect some aromatic stabilization of 1.

The dimer 12 is an yellow oil and shows the following spectral properties: m/e 256 (M^+, 49%), 255 (100%), 239 (68%), 229 (49%), 178 (46%); δ (C_6D_6) 5.0-6.5 (multiplet with strong peaks at 5.7); λ (cyclohexane) 229 (log ε 4.58), 300 nm (sh, 4.03). These data resemble those of octalene[14] and suggest the structure to be cyclooct[c]octalene 12a or cyclooct[b]octalene 12b[15] which are expected to be formed as shown in Scheme 2. The identity has been, however, still uncertain, although we at present rather prefer 12a because the resonance contribution of 1C was suggested to be negligible by the X-ray analysis of 2.[12] The further structural elucidation of the dimer will be the subject of the future publication

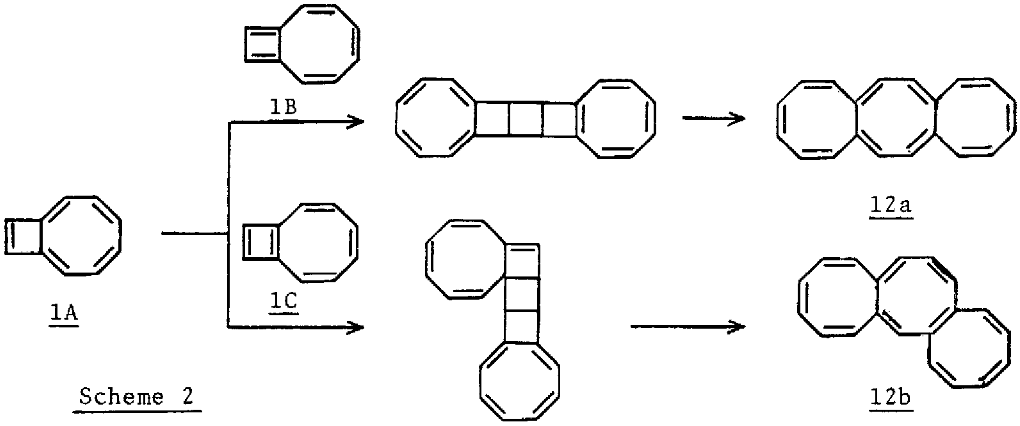
4: m.p. 111°C; ν (KBr) 1690, 1560 cm^{-1}; δ ($CDCl_3$) 3.92 (s), 6.27 (s) (1:1).

5: m.p. 126°C; ν (KBr) 3240, 1560, 1045, 1033 cm^{-1}; δ (CD_3OD) 3.22 (4H, m), 4.20 (2H, m), 6.0-6.5 (4H, m).

6: m.p. 165°C; ν (KBr) 3390, 3310, 1560, 1038, 1024 cm^{-1}; δ (CD_3OD) 3.2 (4H, m), 4.17 (2H, m), 6.13 (4H, s).

10: m.p. 104-110°C decomp.; δ ($CDCl_3$) 3.03 (6H, s), 3.53 (4H, m), 4.93 (2H, m), 6.18 (2H, s), 6.33 (2H, s).

11: m.p. 61°C; δ (CCl_4) 3.83 (4H, m), 4.15 (2H, m of d, J=10 Hz), 6.16 (2H, s), 6.35 (2H, s).



Scheme 2

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9) The chemical shifts in C_6D_6 were calculated taking the benzene signal as δ 7.15.

10) The half-life, $t_{1/2}$(100°C)=90 min, for 2 in ref. 1d is an error and should be corrected as described in the text. It was mistaken for that at 93°C.

11) Although ^{13}C-NMR spectrum of 1 has not yet been obtained, that of 2 shows the nucleus carbons at δ ($CDCl_3$, TMS) 108.57 (C-2,7), 122.61, 123.14 (C-3∼6), 137.90 (C-1,8), and 149.26 (C-9,10). The relatively high-field chemical shifts of C-2∼7 may suggest some polar character of 2.

12) C. Kabuto and M. Oda, the preceding paper.

13) A review: M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds," p 180, Academic Press, New York and London, 1967.

14) E. Vogel, H-V. Runzheimer, F. Hogrefe, B. Baasner, and J. Lex, Angew. Chem. Int. Ed., 16, 871 (1977).

15) There can be one more isomer for cyclooctaoctalene, namely, cyclooct[a]-octalene. Although the available data do not exclude this structure, we hardly find simple rationalization for the formation of it from 1.

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