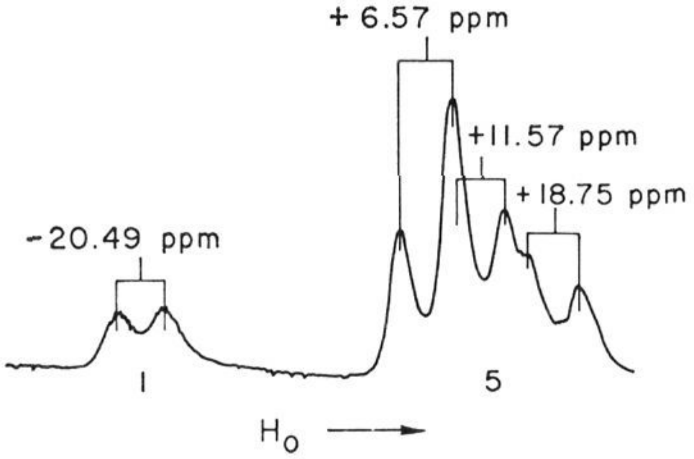

Figure 1. The ^{11}B nmr spectrum of $(B_6C_2H_8)Mn(CO)_3^-$ in deuterioacetone at 32 Mc/sec. Chemical shifts measured relative to $BF_3\cdot O(C_2H_5)_2$.

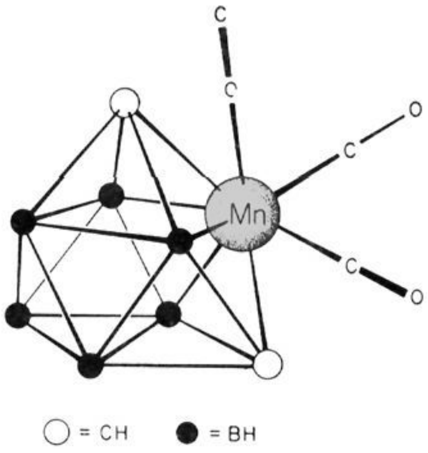

Figure 2. Proposed structure for $(B_6C_2H_8)Mn(CO)_3^-$.

ammonium salt of I in tetrahydrofuran solution contained a band at 2540 cm^{-1}, ascribed to B–H stretch, and carbonyl stretching bands at 2000 and 1920 cm^{-1}. Electronic spectra were determined in acetonitrile solution [λ_{max} mμ (ϵ): 215 (sh) (~36,000), 287 (sh) (11,000), and 423 (4250)].

Figure 1 presents the 32-Mc/sec ^{11}B nmr spectrum of tetramethylammonium I in deuterioacetone solution. Taking the low-field doublet of relative intensity 1, a 1:2:2:1 pattern of doublets is easily discerned. Similar ^{11}B nmr spectra of the $BH_2(py)_2^+$ salt of I gave essentially the same result except for the fact that the high-field array integrated with a relative intensity of 6 due to the broad ^{11}B resonance of the cation.[3] The ^1H nmr spectrum of tetramethylammonium I contained a sharp singlet at τ 6.27 of relative intensity 12 which was assigned to the cation and a single resonance of relative intensity 2 at τ 4.3. The latter resonance was assigned to two equivalent protons attached to the carbon atoms of the $B_6C_2H_8^{-2}$ ligand.

The equivalence of the two carbon atoms and the 1:2:2:1 ^{11}B nmr population coupled with the other characterization data suggests that the structure presented in Figure 2 approximates the structure of I. In this structure the $Mn(CO)_3$ moiety occupies a position between two equivalent apical carbon atoms. The third apical position must then be occupied by a boron atom, and this atom appears to reside at low field in the ^{11}B nmr spectrum.[4]

The appearance of $Mn_2(CO)_{10}$ in the reaction products suggests that $BrMn(CO)_5$ functions as an oxidizing agent which degrades either the $B_7C_2H_{11}^{-2}$ ion or an intermediate which contains seven boron atoms to produce the observed B_6 ligand.

Further work is in progress with this and similar systems which will be reported elsewhere.

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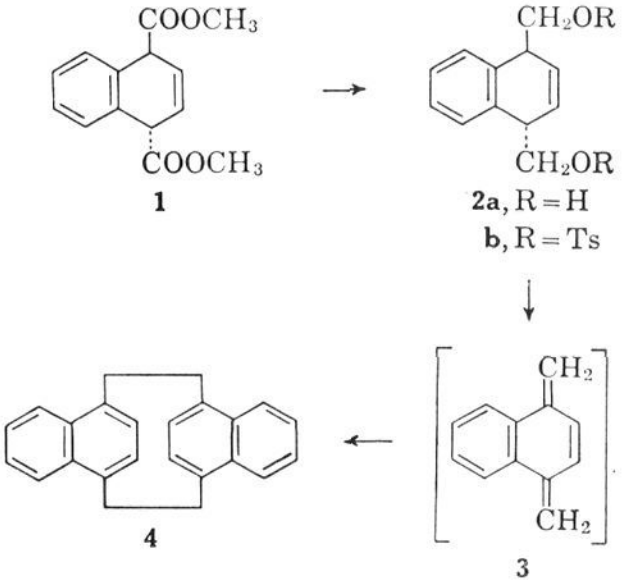
A Novel Synthesis of [2.2]Paracyclophanes

Sir:

[2.2]Paracyclophanes (*e.g.*, **4, 8**) are an interesting group of substances since they exhibit unusual transannular effects.[1] Unfortunately, all the methods known for the synthesis of simple members[2-6] involve a cyclization step which proceeds in rather unsatisfactory yield (not above 25%).[7] We now describe a new synthesis of this class of compound using a cyclization step which proceeds in considerably higher yield than those obtained previously.

Methyl *trans*-1,4-dihydronaphthalene-1,4-dicarboxylate (**1**)[8] was reduced with lithium aluminum hydride to the diol **2a**,[9] which on treatment with *p*-toluenesulfonyl



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(1) See R. C. Helgeson and D. J. Cram, *J. Am. Chem. Soc.*, **88**, 509 (1966), and earlier papers in the series. For a review, see B. H. Smith, "Bridged Aromatic Compounds," Academic Press Inc., New York, N. Y., 1964.

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(4) H. E. Winberg, F. S. Fawcett, W. E. Mochel, and C. W. Theobald, *ibid.*, **82**, 1428 (1960); H. E. Winberg and F. S. Fawcett, *Org. Syn.*, **42**, 83 (1962).

(5) L. A. Errede and J. P. Cassidy, *J. Am. Chem. Soc.*, **82**, 3653 (1960); L. A. Errede, R. S. Gregorian, and J. M. Hoyt, *ibid.*, **82**, 5218 (1960); L. A. Errede, *ibid.*, **83**, 949 (1961).

(6) (a) D. T. Longone and C. L. Warren, *ibid.*, **84**, 1507 (1962); (b) D. T. Longone and F-P. Boettcher, *ibid.*, **85**, 3436 (1963); (c) D. T. Longone and M. T. Reetz, *Chem. Commun.*, 46 (1967).

(7) J. H. Golden (*J. Chem. Soc.*, 3741 (1961)) has reported that tetrabenzo[2.2]paracyclophane (the 9,10-dianthracene analog of **4** and **8**) is formed in 40–63% yield by treatment of 9,10-di(chloromethyl)-anthracene and 9,10-di(bromomethyl)anthracene with sodium iodide, but the application of this method to the synthesis of simpler members has not been described.

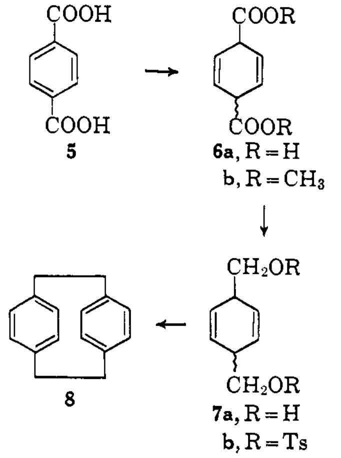
(8) Substance **1** is readily prepared from naphthalene by successive treatment with sodium and carbon dioxide, followed by esterification (T. M. Lyssy, *J. Org. Chem.*, **27**, 5 (1962)).

(9) S. Hsi-Kwei Jiang, *Hua Hsüeh Hsüeh Pao*, **23**, 351 (1957) (*Chem. Abstr.*, **52**, 15481 (1958)).

chloride (2.4 equiv) and pyridine at room temperature gave the ditosylate **2b** (mp 144–145°) in 65% over-all yield. Solvolysis of **2b** with boiling pyridine for 5 hr led to [2.2]paracyclonaphthane (**4**, mp 297–300°) as sole product in 90% yield. Substance **4** showed a molecular ion peak at *m/e* 308 in the mass spectrum and exhibited essentially the same ultraviolet and nmr spectra as those of the known *anti* isomer (mp 299–301°), obtained previously in 3% yield by a Hofmann elimination.[3b,10] The conversion of **2b** to **4** probably involves the *p*-xylylene derivative **3** (or an equivalent species) as an intermediate. As already pointed out for a related reaction,[6c] the dimerization of **3** to **4** must involve a multistep process since the Woodward–Hoffmann selection rules[11] do not allow a direct thermal 6 + 6 electrocyclic reaction.

In order to determine whether the synthesis could be applied to [2.2]paracyclophanes not containing fused aromatic rings, we investigated the synthesis of [2.2]-paracyclophane (**8**) itself by an analogous route.

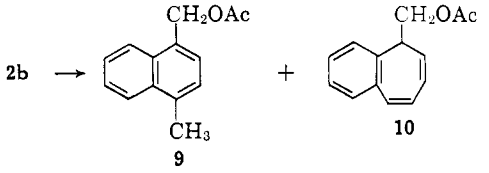
Terephthalic acid (**5**) on Birch reduction with sodium (6 equiv) in liquid ammonia and ethanol,[12] followed by continuous ether extraction of the product, gave a mixture of *cis*- and *trans*-1,4-dihydroterephthalic acids (**6a**, mp >300°) in 65% yield (80% conversion).[13]

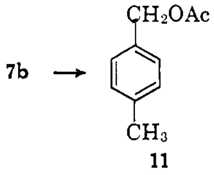


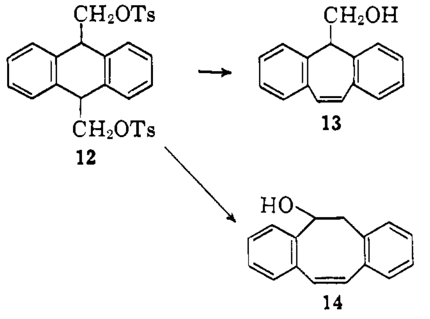
Esterification with diazomethane in ether led to the corresponding dimethyl ester **6b** (mp *ca.* 50–80°). The nmr spectrum of **6b** showed the absence of the isomeric dimethyl 2,5-dihydroterephthalate, while the melting point range indicated the presence of both stereoisomers. Lithium aluminum hydride reduction of **6b** and treatment of the resulting diol **7a** with *p*-toluenesulfonyl chloride gave the ditosylate **7b** (mp 125–127°) in 60% yield (based on **6b**).

Solvolysis of **7b** with boiling pyridine for 3 hr led to [2.2]paracyclophane (**8**, mp 284–286°), isolated in 40% yield as the sole product by direct crystallization. The substance showed a molecular ion peak at *m/e* 208 in the mass spectrum and exhibited essentially the same ultraviolet, infrared, and nmr spectra as those reported for **8** (mp 285–287°).[3] The yield compares favorably with the best one obtained previously (11–17% by Hofmann degradation of (*p*-methylbenzyl)trimethylammonium hydroxide).[4]

Solvolysis of the ditosylates **2b** and **7b** under different conditions led to other products. Boiling **2b** with acetic acid for 7 hr gave 60% of a *ca.* 1 : 1 mixture of the acetates **9** and **10**,[15] but no **4** was isolated. Similar treatment of **7b** led to 55% *p*-methylbenzyl acetate (**11**) as the sole product, identified by direct comparison with an authentic sample.[17] Essentially the same results were obtained when the acetic acid solvolyses of **2b** and **7b** were carried out in the presence of sodium acetate or sodium dihydrogen phosphate buffers. By comparison,







cis-9,10-bis(hydroxymethyl)-9,10-dihydroanthracene ditosylate (**12**) on solvolysis with acetic acid (and subsequent saponification) has been shown by other workers to give mainly the cycloheptatriene derivative **13**, while acetic acid buffered with sodium acetate led mainly to the cyclooctatrienol derivative **14**.[18]

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[10] [2.2]Paracyclonaphthane (**4**) has recently been converted to novel polycyclic compounds by photosensitized autoxidation and by photoisomerization (H. H. Wasserman and P. M. Keehn, *J. Am. Chem. Soc.*, **88**, 4522 (1966); **89**, 2770 (1967)).

[11] R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046 (1965).

[12] Essentially the conditions described for the reduction of benzoic acid to 1,4-dihydrobenzoic acid were used (M. E. Kuehne and B. F. Lambert, *Org. Syn.*, **43**, 22 (1963)).

[13] 1,4-Dihydroterephthalic acid (**6a**) has been prepared previously by other methods,[14] but the presently described synthesis was found to be the most convenient one.

[14] A. Baeyer, *Ann.*, **251**, 257 (1889); C. Mettler, *Ber.*, **39**, 2933 (1906); P. C. Condit, U. S. Patent 2,477,579 and 2,477,580 (Aug 2, 1949) (*Chem. Abstr.*, **43**, 7839 (1949)); I. L. Mador and T. S. Soddy, U. S. Patent 2,960,544 (Nov 15, 1960) (*Chem. Abstr.*, **55**, 9308 (1961)).

[15] This assignment is based on the nmr spectrum (60 Mcps, CCl_4). This spectrum showed the bands of authentic **9**,[16] as well as bands assigned to **10**, consisting of a 4 H multiplet at τ 3.16–4.46 (olefinic protons), a 2 H doublet (J = 8 cps) at 5.52 (methylene protons), a 1 H multiplet at 6.45–7.06 (methine proton), and a 3 H singlet at 8.03 (methyl protons).

[16] G. Lock and R. Schneider, *Chem. Ber.*, **84**, 636 (1951).

[17] See G. W. K. Cavill and D. H. Solomon, *J. Chem. Soc.*, 3943 (1954).

[18] E. Cioranescu, A. Bucur, M. Banciu, and C. D. Nenitzescu, *Rev. Roumaine Chim.*, **10**, 141 (1965) (*Chem. Abstr.*, **63**, 11456 (1965)); see also J. Rigaudy and P. Tardieu, *Compt. Rend.*, **248**, 1538 (1959); E. D. Bergmann and M. Rabinovitz, *Bull. Res. Council Israel*, **8A**, 172 (1959) (*Chem. Abstr.*, **55**, 3535 (1961)).

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