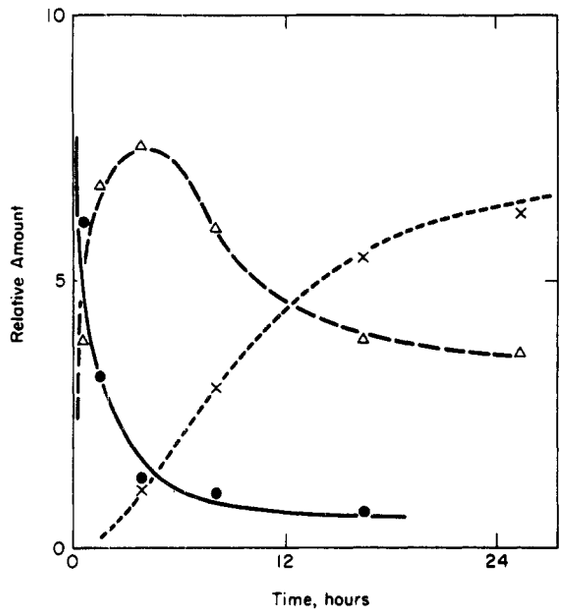

Figure 1. Composition during initial stages of a 30 °C reaction of HCHO with 1 in methanol, K_2CO_3 catalysis (as in Experimental Section). Data taken from ^{13}C NMR methyl signal intensities. (● - ●) **1**; (△ - - - △) **2**; (x - - - x) **4**. Methacrylophenone (**3**), present at a low (ca. 10–15%) equilibrium concentration, is not shown.

mmol) of propiophenone, and 750 mg (5.4 mmol) of potassium carbonate was stirred in 39 mL of methanol for 6 days at room temperature. Proton NMR (60 MHZ) showed a mixture which could be integrated for 10–15 mol % of **3**. Carbon NMR spectroscopy showed **2** and **4** to be present in the ratio of 1:15 compared to 1:4 after only 3 days. The solvent was removed in vacuo without applied heat, and the residual oil was taken up in benzene, washed with water, and dried over sodium sulfate. Fractional distillation gave 6.1 g (55%) of pure **4**: bp 75 °C (0.1 mm); 60-MHz ^1H NMR ($CDCl_3$) δ 1.2 (d, 3, CH_3–C), 3.25 (s, 3, CH_3O), 3.35–3.95 (m, 3, CH, CH_2), 7.2–8.15 (m, 5, ar); mass spectrum *m/e* (rel intensity) 178 (M^+, 5), 163 (3), 146 (25), 136 (16), 105 (100), 77 (74). GC assay showed ca. 16% more of **4** distributed between the forerun (60% pure) and the pot residue.

Anal. Calcd for $C_{11}H_{14}O_2$ (178.2): C, 74.13; H, 7.92. Found: C, 74.19; H, 8.24.

^{13}C Incorporation Experiment. To a solution of 107 mg of **4** diluted to 0.3 mL with 9:1 MeOH:H_2O saturated with K_2CO_3 was added 11 μL of 20% aqueous formaldehyde, 90% ^{13}C. The resulting solution was stored at ambient temperature and observed by ^{13}C NMR spectroscopy periodically. After 3 weeks, the CH_2 signal had doubled, indicating ca. 1% ^{13}C incorporation. Cannizzaro reaction products were evident, as was **5** (see text).

After 8 weeks, incorporation was measured at ca. 1.7%. The solution was worked up and analyzed by gas chromatography–mass spectroscopy, giving values of 1.4–2% ^{13}C incorporation, based on ratios of M^+ to $M^+ + 1$ ions of both **3** and **4**. GC–MS analysis of a trimethylsilylated sample also showed a substance: *m/e* (rel intensity) 280 (M^+, 5), 265 (11), 215 (83), 179 (78), 173 (51), 135 (58), 105 (100), 77 (82), which we consider as further evidence for **5** [$C_{12}H_{15}O_3$–$Si(CH_3)_3$, mol wt 280].

Acknowledgment. Thanks are due to Patricia Cala for the mass spectral experiments, and to Robert Reamer for some of the NMR measurements.

Registry No.—**1** (Ar = Ph), 93-55-0; **3** (Ar = Ph), 769-60-8; **4** (Ar = Ph), 62509-81-3; **5**, 62509-82-4; **5** Me_3Si ether, 62509-83-5; formaldehyde, 50-00-0.

References and Notes

(1) R. C. Fuson, W. E. Ross, and C. H. McKeever, *J. Am. Chem. Soc.*, **60**, 2935 (1938).
(2) (a) J. H. Burkhalter and R. C. Fuson [*J. Am. Chem. Soc.*, **70**, 4184 (1948)] noted that low yield rendered the method of ref 1 impractical. (b) J. Colonge and G. Weinstein [*Bull Soc. Chim. Fr.*, 462 (1952)] claimed higher yields with "potasse alcoolique" catalyzed reaction of commercial trioxane in ethanol. We obtained no detectible (NMR or TLC) reaction whatsoever using either KOH/C_2H_5OH or KOC_2H_5 with *s*-trioxane (Aldrich Chemical Co.) under their conditions. (c) L. G. Heeringa and M. G. J. Beets [*Recl. Trav. Chim. Pays-Bas*, **76**, 213 (1957)] repeated the reaction with acetophenone and found the product to be different from what had been originally claimed.[1] (d) On the other hand, Pl. A. Plattner and J. Wyss [*Helv. Chim. Acta*, **24**, 483 (1941)] found the product of *hydroxy*methylation *without purification* (our italics) to be convenient for the preparation of 2-methyl-1-indanone.
(3) To be published elsewhere.
(4) Cf. T. I. Temnikova and N. A. Oshueva, *J. Gen. Chem. USSR* (*Engl. Transl.*), **33**, 1368 (1962); and R. C. Fuson, W. E. Ross, and C. H. McKeever, *J. Am. Chem. Soc.*, **61**, 414 (1939).
(5) From M. S. D., Canada. Prior thermal depolymerization of the reagent would, of course, have been possible, but less convenient.
(6) From Aldrich Chemical Co.
(7) Boiling points are uncorrected. Elemental analyses were performed by Mr. J. P. Gilbert and associates of these laboratories. ^1H NMR spectra were obtained on a Perkin-Elmer R-24A spectrometer in $CDCl_3$, unless otherwise noted. ^{13}C NMR data were obtained with a Varian CFT-20 FT spectrometer, referenced to external Me_4Si in acetone-d_6. Mass spectral analyses were obtained on a Finnigan 3200, GC inlet, operated at 70 eV.

A Convenient Synthesis of [3.3]Paracyclophane

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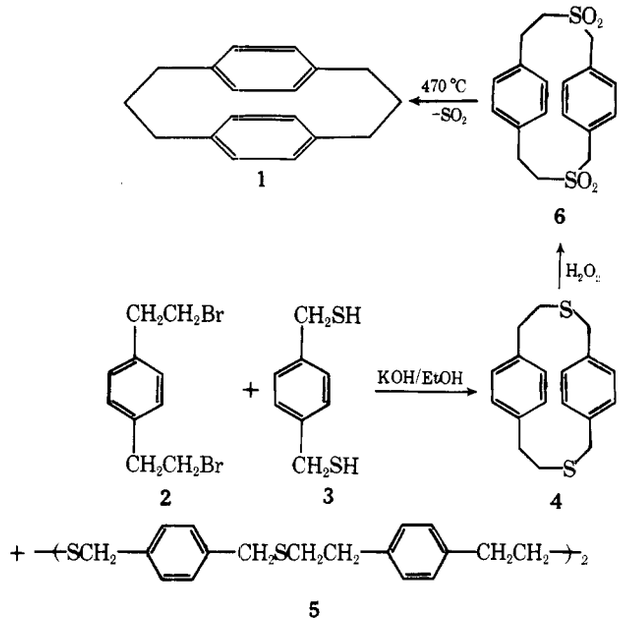
[3.3]Paracyclophane (**1**) is a pivotal structure among the [*m.m*]paracyclophanes. It is intermediate in ring size between [2.2]paracyclophane, where ring strain and transannular effects are pronounced, and [4.4]paracyclophane, where these effects are absent.[1] While some chemical and physical studies of **1** have been reported,[1,2] it has been much less studied than, for example, the more readily available[3] [2.2]paracyclophane. Chemical transformations for which the ring size in **1** is particularly suited have been neglected because this ring system is not easily accessible. Of the three reported syntheses of **1**, the first[4] utilizes 1,3-diphenylpropane as starting material, involves an acyloin ring closure, and gives the final product in an overall yield of about 0.1%. Two more recent and improved syntheses utilize diazomethane[5] or solvolytic[6] ring expansion routes from [2.2]paracyclophane, itself prepared in low yield (10%) by the most convenient method,[3] and provide **1** in overall yields of 7–19%, the latter involving preparative GLC isolation.

Our interest[7] in novel structures derivable from **1** necessitated a synthetically less expensive route to this compound. We now report for **1** a new synthesis which is particularly convenient and which does not require at any stage the use of special separation procedures.

Treatment of *p*-bis(2-hydroxyethyl)benzene[8] with 48% hydrobromic acid gives the corresponding dibromide **2** in 72% yield. Addition of a dilute solution of **2** and *p*-xylene-α,α'-dithiol (**3**) in benzene to hot alcoholic potassium hydroxide affords 2,13-dithia[4.4]paracyclophane (**4**) and 2,13,22,33-tetrathia[4.4.4.4]paracyclophane (**5**) in yields of 39 and 6%, respectively. The yields in this reaction have not been optimized; higher dilution conditions than we employed would likely increase the ratio of **4** to **5**. Oxidation of **4** with 30% hydrogen peroxide provides the disulfone **6** quantitatively. The disulfone on pyrolysis at 470 °C under diminished pressure gives essentially pure **1** (94%) as a cold trap condensate. The pyrolysis requires rather simple apparatus, proceeds to completion in a matter of seconds on a 100-mg scale, and can be done repetitively to yield appreciable quantities of **1** in a short time.

Ring contraction by sulfone pyrolysis has been used to advantage by others[9–11] for the preparation of bridged aromatic compounds. In virtually all cases, however, the sulfones have



been of the dibenzyl type, affording two-carbon bridges.[12] It is somewhat surprising in retrospect that the three-carbon bridge in 1 is formed so efficiently from an aliphatic/benzyl sulfone where the intermediate aliphatic free radical ($ArCH_2CH_2\cdot$) might be expected to suffer disproportionation reactions.[13]

Having established for the first time that three-carbon bridged cyclophanes may be produced by sulfone pyrolysis, derivatives of 1 not easily obtained from the hydrocarbon itself may now be accessible by suitable modifications of 2 and 3.

Experimental Section

p-Bis(2-bromoethyl)benzene (2). The procedure given here is more convenient than the reported[14] one which involves a sealed tube reaction. A mixture of p-bis(2-hydroxyethyl)benzene[8] (4.0 g, 24 mmol), 48% HBr (12.5 mL), and concentrated H_2SO_4 (2.5 mL) was heated at the reflux temperature for 24 h and then diluted with water. The precipitate of dibromide was crystallized from EtOH to give white needles: yield 5.0 g (72%); mp 70–71 °C (lit.[14] mp 72–73 °C); ^1H NMR ($CDCl_3$) δ 3.14 (m, 4 H), 3.55 (m, 4 H), 7.17 (s, 4 H).

2,13-Dithia[4.4]paracyclophane (4). A solution of 2 (5.63 g, 19.2 mmol) and commercial p-xylene-α,α'-dithiol (3.27 g, 19.2 mmol) in 1 L of benzene was added dropwise over 70 h to a refluxing solution of 4.5 g of KOH in 1 L of 90% EtOH. This addition was carried out under nitrogen and with vigorous stirring. After an additional 2 h at the reflux temperature, the mixture was cooled and solvents were removed under diminished pressure. The resulting yellow gum was triturated with CCl_4 at room temperature. The extracts were treated with charcoal, the solvent was removed, and the resulting solid was crystallized from EtOH to give 4: yield (two crops) 2.24 g (39%); mp 182–182.5 °C; ^1H NMR ($CDCl_3$) δ 2.70 (A_2B_2, 8 H), 3.35 (s, 4 H), 6.70 (s, 8 H); MS m/e (rel intensity) 300 (100, M^+).

Anal. Calcd for $C_{18}H_{20}S_2$: C, 71.94; H, 6.70; S, 21.34. Found: C, 71.84; H, 6.71; S, 21.22.

2,13,22,33-Tetrathia[4.4.4.4]paracyclophane (5). In a reaction identical in all respects with the one described above, the crude reaction mixture was subjected to column chromatography on alumina (CCl_4). This gave first 4 (39%) followed by 5 which was crystallized from $CHCl_3$–hexane: yield 0.36 g (6%); mp 135–135.5 °C; ^1H NMR ($CDCl_3$) δ 2.57 (broad s, 16 H), 3.67 (s, 8 H), 6.88 (s, 8 H), 7.22 (s, 8 H); MS m/e (rel intensity) 600 (100, M^+).

Anal. Calcd for $C_{36}H_{40}S_4$: C, 71.94; H, 6.70; S, 21.34. Found: C, 71.84; H, 6.66; S, 21.17.

2,13-Dithia[4.4]paracyclophane 2,2,13,13-Tetroxide (6). A solution of 4 (0.22 g, 0.73 mmol) and 30% H_2O_2 (9 mL) in xylene–acetic acid (2:1, 45 mL) was heated with stirring at 80 °C for 5 h. The mixture was concentrated under reduced pressure (caution!) and 50 mL of ether was added to precipitate the disulfone 6. This was washed well with ether to give a white powder, highly electrostatic and insoluble in common solvents, yield 0.26 g (97%) decomposition temperature above 340 °C. This material was used for the pyrolysis described below. IR (KBr) 1300 cm^{-1} ($-SO_2-$); MS m/e (rel intensity) 364 (4, M^+), 236 (100, $-2SO_2$).

[3.3]Paracyclophane (1). The pyrolysis apparatus consisted of a hinged horizontal cylindrical furnace of the combustion tube type and a 25 × 1.5 cm Pyrex combustion tube sealed at one end and connected to a vacuum pump through a U-tube trap held at −77 °C. The U-tube contained a loose cotton plug to help trap condensate and was positioned as close as possible to the exit end of the furnace. The pyrolysis tube and cold trap assembly was so supported to allow some motion of the tube along the furnace length. Disulfone 6 (92 mg, 0.25 mmol) was placed at the sealed end of the pyrolysis tube, the system pressure reduced to 0.1 mm, and then the tube placed in the furnace (preheated to 470 °C) such that the sample end protruded outside the furnace. After several minutes, the sample end of the tube was pulled fully into the heating zone. Pyrolysis occurred immediately, was complete within 45 s, and provided an off-white solid in the cold trap. The content of the trap was washed out with $CHCl_3$, and the solvent removed to give essentially pure 1 yield 56 mg (94%). The NMR spectrum shows no contaminant and fully agrees, as does the MS, with the reported[1] values. A portion of the pyrolysate was crystallized from EtOH, mp 104.5–105.5 °C (lit.[5] mp 105–105.5 °C).

Registry No.—1, 2913-24-8; 2, 4542-72-7; 3, 105-09-9; 4, 62587-08-0; 5, 62587-09-1; 6, 62587-10-4; p-bis(2-hydroxyethyl)benzene, 5140-03-4.

References and Notes

(1) M. Sheehan and D. J. Cram, *J. Am. Chem. Soc.*, **91**, 3544 (1969).
(2) M. Sheehan and D. J. Cram, *J. Am. Chem. Soc.*, **91**, 3553 (1969).
(3) H. E. Winberg and F. S. Fawcett, *Org. Synth.*, **42**, 83 (1962). For a recent review of cyclophane syntheses, particularly those of the [2.2] type, see F. Vögtle and P. Neumann, *Synthesis*, 85 (1973).
(4) D. J. Cram, N. L. Allinger, and H. Steinberg, *J. Am. Chem. Soc.*, **76**, 6132 (1954).
(5) D. J. Cram and R. C. Helgeson, *J. Am. Chem. Soc.*, **88**, 3515 (1966).
(6) E. Hedaya and L. M. Kyle, *J. Am. Chem. Soc.*, **88**, 3667 (1966).
(7) D. T. Longone and J. A. Gladysz, *Tetrahedron Lett.*, 4559 (1976).
(8) Prepared from commercial p-phenylenediacetic acid by hydride reduction of the diethyl ester using the published method: K. B. Augustinsson and H. Hasselquist, *Acta Chem. Scand.*, **17**, 953 (1963).
(9) E. Vögtle, *Angew. Chem.*, **81**, 258 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 274 (1969).
(10) H. A. Staab and M. Haenel, *Chem. Ber.*, **106**, 2190 (1973).
(11) V. Boekelheide and R. A. Hollins, *J. Am. Chem. Soc.*, **95**, 3201 (1973).
(12) For a recent exception see F. Vögtle and J. Grütze, *Angew. Chem.*, **87**, 543 (1975); *Angew. Chem., Int. Ed. Engl.*, **14**, 559 (1975).
(13) The formation of free radicals in this type of sulfone pyrolysis has been inferred[10,12] rather than rigorously demonstrated. A referee has suggested that the absence of free-radical side reactions may imply an alternative mechanism such as an ion pair or cage radical rearrangement of the Stevens type, followed by loss of SO_2 from a sulfinic acid intermediate.
(14) P. Ruggli and W. Theilheimer, *Helv. Chim. Acta*, **24**, 899 (1941).

Formation and Trapping of 1,2,4,5-Dibenzotropilidene (10*H*-Dibenzo[*a,d*]cycloheptene)[1a]

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It has long been known that thermal 1,5-sigmatropic hydrogen migrations occur quite readily,[2] particularly in seven-membered ring systems.[3,4] While much work has been done on tropilidene (and substituted tropilidines) and on benzotropilidene (and substituted derivatives) there is a notable paucity of work on these migrations in 1,2,5,6-dibenzotropilidene (5*H*-dibenzo[*a,d*]cycloheptene, 1). In an earlier publication in which we reported the pyrolytic conversion of 1 into anthracene and 9-methylanthracene[5] we suggested that the initial step involved a 1,5-sigmatropic hydrogen migration to produce 2 which then gave the observed products. The only