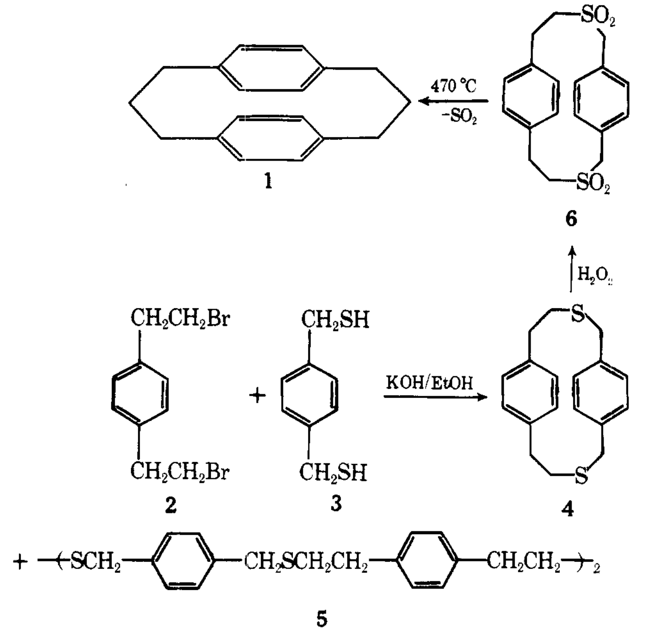

been of the dibenzyl type, affording two-carbon bridges.[12] It is somewhat surprising in retrospect that the three-carbon bridge in 1 is formed so efficiently from an aliphatic/benzyl sulfone where the intermediate aliphatic free radical ($ArCH_2CH_2\cdot$) might be expected to suffer disproportionation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

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

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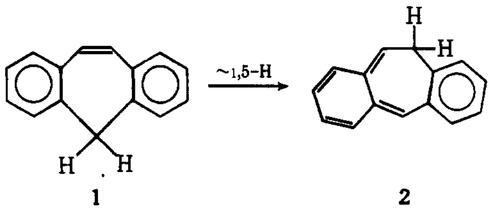
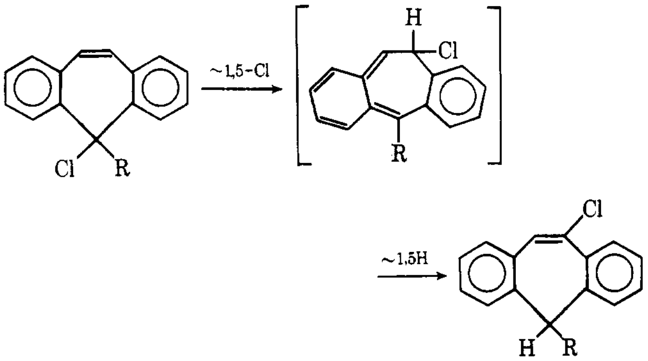
It has long been known that thermal 1,5-sigmatropic hydrogen migrations occur quite readily,[2] particularly in seven-membered ring systems.[3,4] While much work has been done on tropilidene (and substituted tropilidines) and on benzotropilidene (and substituted derivatives) there is a notable paucity 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



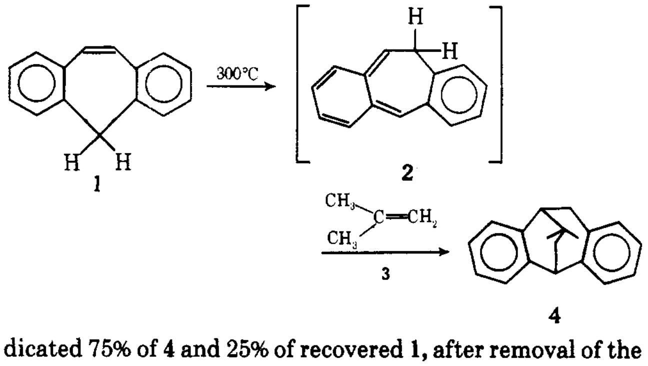
other apparent references to 1,5-sigmatropic rearrangements in 1,2,5,6-dibenzotropilidene systems is by Looker.[6] He employed compounds containing a chlorine atom at carbon 7 together with another bulky substituent and showed that, upon heating, these compounds isomerized by migration of the chlorine to carbon 3. The postulated mechanism involved a 1,5-sigmatropic chlorine migration followed by a 1,5-hydrogen rearrangement.[6b]

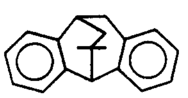


We now report, for the first time, direct evidence for the intermediacy of 2 formed by the thermal reorganization of 1 by trapping in a Diels–Alder reaction.

Results and Discussion

When 1,2,5,6-dibenzotropilidene (1) was heated at 300 °C (24 h) with excess isobutylene (3) an adduct was formed which we have identified as 5,10-ethano-12,12-dimethyldibenzo[*a*,*d*]cycloheptane (4). Gas chromatographic analysis indicated 75% of 4 and 25% of recovered 1, after removal of the excess 3. Preparative VPC afforded pure 4 with the following properties which serve to prove the structure: high-resolution mass spectral molecular weight found 248.1568 (calcd for $C_{19}H_{20}$, 248.1565); NMR (60 MHz, CCl_4) δ 0.83 (3 H, s, $C_{12}CH_3$), 1.18 (3 H, s, $C_{12}CH_3$), 6.91–7.21 (8 H, m, ArH), and 1.8–4.0 (6 H, m, $CHCH_2$). The 100-MHz spectrum of the δ 1.8–4.0 region showed quite clearly two distinct AMX systems, thus proving the structure of the adduct as 4 rather than the isomeric 5 which would not be expected to show this NMR pattern. By assuming that the doubly benzylic tertiary C_5 hydrogen is the one at lowest field and that the two largest coupling constants are those between geminal hydrogens,[7] the following assignments can be made: H_5, δ 3.61 (dd); H_{13} and $H_{13'}$, δ 1.80 (dd) and 2.05 (dd); H_{10}, δ 2.59 (t); H_{11} and $H_{11'}$, δ 2.89 (dd) and 3.39 (dd). By direct measurement of the splittings of the multiplets the following approximate coupling constants were obtained: $J_{H_5-H_{13}} \simeq 5.5$; $J_{H_5-H_{13'}} \simeq 1.5$; $J_{H_{13}-H_{13'}} \simeq 13$; $J_{H_{10}-H_{11}} = J_{H_{10}-H_{11'}} \simeq 4$; $J_{H_{11}-H_{11'}} \simeq 17.5$ Hz.





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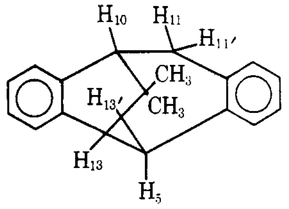
The simplest mechanistic explanation for the formation of 4 is initial rearrangement of 1 to 2 by a 1,5-sigmatropic hydrogen migration followed by a Diels–Alder reaction with 3. Molecular models indicate that 4 is the more thermodynamically stable adduct formed from what is most likely the more favorable transition state. In an attempt to see if 4 was the kinetically or thermodynamically controlled product we tried the reaction at 220 °C. Only starting materials were recovered. Thus a clear-cut distinction cannot be made.



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It should also be pointed out that a small amount of the isomeric adduct 5 might have escaped analytical detection but it is clear that the vast majority of the product is 4, proving conclusively that 2 is indeed formed from 1 in a thermal reaction.

Conclusion

1,2,4,5-Dibenzotropilidene (2) is formed thermally from 1,2,5,6-dibenzotropilidene (1) by a 1,5-sigmatropic hydrogen migration and it can be trapped with isobutylene as the Diels–Alder adduct (4).

Experimental Section

NMR spectra were determined with a Varian A-60A or an HA-100 high-resolution spectrometer, using Me_4Si as internal reference on 5–10% solutions in CCl_4. The mass spectrum was determined on a Du Pont Model CEC 21-110B mass spectrometer. Vapor phase chromatography was performed with a thermal conductivity detector instrument using He carrier gas. Relative yields based on VPC peak areas were not corrected for thermal conductivity differences of the components.

1,2,5,6-Dibenzotropilidine (5*H*-dibenzo[*a*,*d*]cycloheptatriene, 1) was prepared by Dr. Alan S. Ross by the reduction of 5*H*-dibenzo[*a*,*d*]cyclohepten-5-one (12 g, 58 mmol) with aluminum isopropoxide (36 g, 0.18 mol) using the method described by Wendler et al.,[8] yield 7.8 g (41 mmol), 71%, mp 127–130 °C (uncorrected) (lit.[8] 123–128 °C).

Diels–Alder Reaction of 1,2,4,5-Dibenzotropilidene (10*H*-Dibenzo[*a*,*d*]cycloheptene, 2) to Produce 5,10-Ethano-12,12-dimethyldibenzo[*a*,*d*]cycloheptane (4). A mixture of 100 mg of 2 and 2 g of isobutylene (3) were heated in a 50-mL steel bomb at 300 °C for 24 h. VPC analysis (5 ft × 0.25 in. column packed with 10% Apiezon L on 60/80 mesh Chromosorb P, 200 °C) showed two components. The minor one (25%) was shown to be starting material (2) while the second (75%) was shown, after preparative VPC using the above column, to be 4 (see text for details).

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Registry No.—1, 256-81-5; 2, 256-80-4; 3, 115-11-7; 4, 62549-87-5.

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Synthesis of Sodium Formate-^{13}C and Oxalic Acid-$^{13}C_2$

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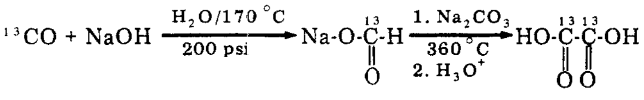
Compounds labeled with stable isotopes such as D, ^{13}C, ^{15}N, or ^{18}O have recently been shown[1,2] to be very useful for the diagnosis of diseased states in man because they lack the potential danger of their radioactive analogues, are not toxic at moderate levels in the body, and are easily identified in labeled molecules by mass spectrometry. Our research program required large amounts of oxalic acid-$^{13}C_2$ (1) for incorporation studies involving compounds of biological interest to be used in the production of $^{13}CO_2$ for breath tests.[3]

A review of the literature concerning suitable laboratory preparations of oxalic acid revealed only two convenient methods for the incorporation of a double $^{13}C_2$ label: (1) the reductive coupling of CO_2 over molten sodium or potassium,[4,5] which proved to be unsuitable because of low yields (10–17%), and (2) the pyrolysis of sodium formate.[6,7] Preliminary experiments with nonlabeled sodium formate, pyrolyzed to 360 °C, produced only a trace of oxalic acid,[8] and generated considerable amounts of sodium carbonate. However, the yield of oxalic acid was increased substantially by the pyrolysis of sodium formate with a 2-molar equivalence of sodium carbonate. The excess sodium carbonate appeared to keep the desired oxalic acid from deteriorating to carbonate at elevated temperatures.



$$^{13}CO + NaOH \xrightarrow[200\ \text{psi}]{H_2O/170\ ^\circ C} Na\text{-}O\text{-}\overset{13}{C}(=O)\text{-}H \xrightarrow[360\ ^\circ C;\ 2.\ H_3O^+]{1.\ Na_2CO_3} HO\text{-}\overset{13}{C}(=O)\text{-}\overset{13}{C}(=O)\text{-}OH$$

2 1

In the first effort to prepare the precursor sodium formate-^{13}C, it was found that a stirred solution of sodium hydroxide under CO at 1 atm showed little uptake of the gas. However, when the CO was charged into a reaction bomb under pressure, over a stirred solution of hot sodium hydroxide, the gas was quantitatively consumed. Reaction with 90% ^{13}CO under these experimental conditions resulted in >99% yield of ^{13}C-labeled sodium formate. Pyrolysis of this sodium formate-^{13}C at 360 °C for 30 min, while intimately mixed with a molar excess of sodium carbonate, resulted in the formation of oxalic acid-$^{13}C_2$ in >90% overall yields.

This synthesis is a convenient, inexpensive, and high-yield procedure for the preparation of a new two-carbon, $^{13}C_2$-labeled molecule. Oxalic acid-$^{13}C_2$ is now readily available as a reactive precursor for labeling experiments with larger molecules.

Experimental Section

Sodium Formate-^{13}C (2). Into a 300-mL Parr pressure bomb were placed 6.0 g (0.15 mol) of sodium hydroxide, 20 mL of water, and a stirring bar. The apparatus was sealed and a tank of 90% ^{13}CO (Stohler Isotope Chemicals, Inc.) attached utilizing minimum dead volume connections. After evacuation of the trapped air, the reaction bomb was charged at 200 psi with 0.15 mol (3.3 L) of 90% ^{13}CO, heated to 170 °C, and stirred for 12 h. During that time the pressure slowly rose to 400 psi and finally dropped to 40 psi. After 12 h the bomb was cooled to reveal only a very slight pressure. The bomb was opened, the solution removed and transferred by pipet, and the water rotary evaporated away to yield 10.2 g (99% yield) of sodium formate-^{13}C: mp 250–252 °C; IR (KBr) 2810 and 2715 ($^{13}HC{=}O$), 1550 and 1365 ($^{13}CO_2Na$), 1317 and 763 cm^{-1}.

Oxalic Acid-$^{13}C_2$ (1). The above 10.2 g (0.15 mol) of sodium formate-^{13}C was intimately ground with 31.8 g (0.30 mol) of Na_2CO_3 and placed in an open-ended glass tube. The tube and contents were pyrolyzed in a pyrolysis oven to 360 °C over a period of 30 min. After cooling, the contents of the tube were transferred to a 500-mL beaker with a minimum amount of water. Concentrated HCl was added to reach a pH 1.0. Crystals of oxalic acid were filtered off (5.1 g) and the mother liquor evaporated to dryness. The residue of sodium chloride and product was sublimed under vacuum ($\approx 7 \times 10^{-2}$ Torr) at 200 °C for 2 h to yield another 1.2 g of pure oxalic acid-$^{13}C_2$.[9] Total yield[10] was 6.3 g (93.3%) of oxalic acid-$^{13}C_2$: mp 99–100 °C dec; IR (KBr) 3425 and 3280 ($^{13}CO_2H$), 1120 and 715 cm^{-1}; mass spectrum *m/e* (rel intensity)[11] 92 (M^+, 0.06), 58 (3), 47 (50), 46 (100), 45 (22), and 30 (21).

Acknowledgments. The author gratefully acknowledges the support of the Cottrell Research Starter Grant, administered by Research Corporation, and the generous gift of the labeled carbon monoxide by Stohler Isotope Chemicals, Inc. The author also is indebted to Dr. Donald Chichester for his help in editing this manuscript.

Registry No.—**1**, 62654-02-8; **2**, 23102-86-5; sodium hydroxide, 1310-73-2; ^{13}CO, 1641-69-6.

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(8) Yields were monitored by titrating reaction solutions with 0.001 M $KMnO_4$ until a red color persisted [*Chem. Abstr.*, **9**, 2043 (1915)] and by classical color reactions for oxalic acid [L. H. Chernoff, *J. Am. Chem. Soc.*, **42**, 1784 (1920)] using resorcinol and H_2SO_4.

(9) Sublimation at 105 °C under vacuum for 12 h yielded 1.4 g of oxalic acid on a duplicate run (total yield 6.5 g, 96%). Additional labeled material was separated from the NaCl crystal lattice by dissolving in water, rotary evaporation, and repeating sublimation.

(10) The labeled and nonlabeled oxalic acid gave satisfactory spectroscopic properties (IR and MS) when compared to each other and authentic oxalic acid.

(11) Mass spectral analyses were performed using a 70-eV Du Pont 490-F mass spectrometer. Samples were probe distilled directly into the ion source of the mass spectrometer.

Photoreduction of Bridgehead Halides with Organotin Hydride

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Dissolving metals reduce strained bridgehead halides.[1] The yields in these reactions are generally satisfactory only when