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“Naphtharadialene”, Related Polyenes and Naphthocyclobutenes[1,2]

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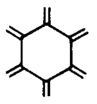
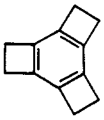
Pyrolysis of either 1,4,5,8-tetrakis(chloromethyl)-2,3,6,7-tetramethylnaphthalene (**4**) or its isomer **5**, in which the positions of the methyl and chloromethyl substituents are interchanged, gives naphtho[2,3:6,7]dicyclobutene[1,8:4,5]dicyclopentene **6**. “Naphtharadialene” **3** is the suggested intermediate. Similar pyrolysis of 2,3-bis(chloromethyl)-1,4,5,6,7,8-hexamethylnaphthalene (**8**) gives the radialene-type product **9** in good yield. Compound **9** adds 2 equiv of bromine to give **10** but adds 1 equiv of dimethyl acetylenedicarboxylate across the 2,3-methylene moieties at room temperature to give the quinone methide **17**. Under kinetic control, **9** similarly adds 1 equiv of sulfur dioxide to give **18**, but under reversible conditions the aromatic bis adduct **19** is formed. Pyrolysis of 2,5-bis(chloromethyl)-1,4,5,8-tetramethylnaphthalene (**15**) gives 4,8-dimethylnaphtho[1,2:5,6]dicyclobutene (**16**), whose X-ray structure is described. The factors involved in forming radialenes vis-à-vis benzocyclobutenes are discussed.

Although alkyl derivatives of hexaradialene have been known for many years[5] and are quite stable crystalline materials,[6] the highly reactive parent hydrocarbon **1** has only recently been prepared.[7-10] In contrast with **1**, its



1



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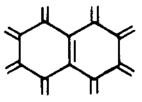

3

aromatic valence tautomer **2** appears to be quite stable.[11] We describe here evidence for the formation of “naphtharadialene” **3**,[1] as a reactive intermediate, and for the formation of certain related polyenes and dicyclobutanaphthalenes.[2]

Results and Discussion

Pyrolysis in a quartz apparatus at 620–640 °C of **4**[12] or of its isomer **5** in which the relative positions of the methyl and chloromethyl substituents were interchanged gave the same product **6** in about 15% yield. The structure was shown to be **6** and not **7** by an X-ray structure determination on a crystal.[13]

There are several possible mechanisms whereby **6** could be formed from **4** and/or **5**. Elimination of 4 equiv of

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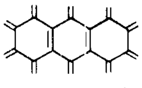
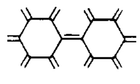
(1) The term radialene refers at present to a single carbocyclic ring, each carbon of which is part of an exocyclic carbon–carbon double bond. Although the structure of **3** does not adhere strictly to this definition, we believe that the meaning of the trivial name we suggest for it (i.e., naphtharadialene) is clear and easier to recognize than the systematic name, which is 1,2,3,4,5,6,7,8-octakis(methylene)-Δ^9-octalin. Furthermore, this type of trivial name is readily extended to polymethylene derivatives of other aromatic hydrocarbons, such as i and ii.



“anthraradialene”

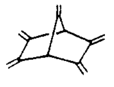
i



“biphenylradialene”

ii

The radialene nomenclature may also be useful for polymethylene derivatives of bicyclic (etc.) systems which have considerable current interest, as for example iii.[4] By use of this method, **3** could be called bicyclo[4.4.0]radialene.



“bicyclo[2.2.1]radialene”

iii

(2) For a preliminary account of this work, see: Hart, H.; Jeffares, M.; Teuerstein, A.; Ward, D. L. *J. Am. Chem. Soc.* **1978**, *100*, 8012.

(3) Inquiries regarding the X-ray structure determinations should be directed to these authors.

(4) Mohraz, M.; Batich, C.; Heilbronner, E.; Vogel, P.; Carrupt, P.-A. *Recl. Trav. Chim. Pays-Bas* **1979**, *98*, 361.

(5) Hopff, H.; Wick, A. K. *Helv. Chim. Acta* **1961**, *44*, 380. Hopff, H.; Gatti, A. *Ibid.* **1965**, *48*, 1289.

(6) Marsh, W.; Dunitz, J. D. *Helv. Chim. Acta* **1975**, *58*, 707.

(7) Barkovich, A. J.; Strauss, E. S.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1977**, *99*, 8321.

(8) Schiess, P.; Heitzmann, M. *Helv. Chim. Acta* **1978**, *61*, 844.

(9) Harruff, L. G.; Brown, M.; Boekelheide, V. *J. Am. Chem. Soc.* **1978**, *100*, 2893.

(10) For other recent derivatives of hexaradialene, see: Hart, H.; Sasaoka, M. *J. Am. Chem. Soc.* **1978**, *100*, 4326; Gall, J. H.; Gilmore, C. J.; MacNicol, D. D. *J. Chem. Soc., Chem. Commun.* **1979**, 927.

(11) Nutakul, W.; Thummel, R. P.; Taggart, A. D. *J. Am. Chem. Soc.* **1979**, *101*, 770.

(12) Hart, H.; Reilly, J. L.; Jiang, J. B.-C. *J. Org. Chem.* **1977**, *42*, 2684.

(13) Ward, D. L. *Acta Crystallogr. Sect. B* **1980**, *36*, 963.

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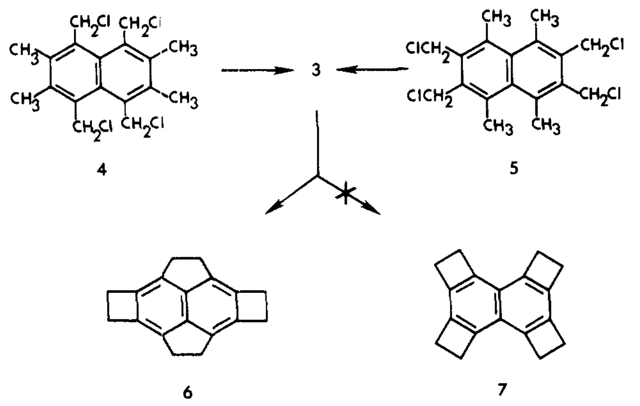
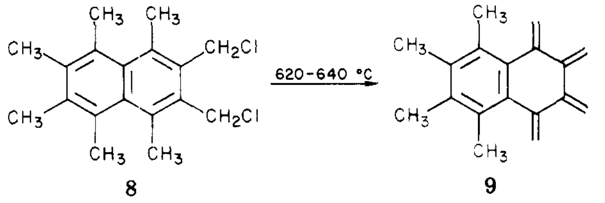
Scheme I



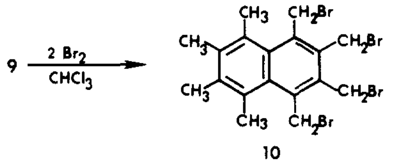
hydrogen chloride from either **4** or **5** would give the "naphtharadialene" **3**, which could cyclize to **6** (Scheme I). Alternatively, each elimination of hydrogen chloride could be followed by cyclization (rearomatization). In this case, the product from either precursor would have to be **7**, which could then thermally isomerize to **6**, presumably via **3**. We believe the former alternative is the more likely and have obtained indirect experimental evidence which supports this belief.

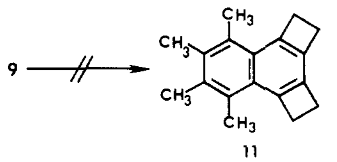
Pyrolysis of the bis(chloromethyl)naphthalene **8** at 620–640 °C gave in 45–55% yield a hydrocarbon to which we assign the radialene-type structure **9**. Although attempts to isolate **9** via column or thin-layer chromatography or by sublimation were unsuccessful and led only to polymers, solutions of **9** in inert solvents such as chloroform were quite stable and could be kept at room temperature for hours before significant decomposition occurred. Furthermore, these solutions, which were obtained directly from the pyrolysis reaction by washing the product from the cold finger of the pyrolysis apparatus, were relatively uncontaminated with other substances (as judged by their NMR spectra). That is, any polymer or byproducts formed during the pyrolysis of **8** did not pass through the hot zone of the pyrolysis tube to the collector. Consequently it was possible to obtain fairly good spectroscopic data on **9**.



The structure of **9** is based on its spectral properties and chemical transformations. The ^1H NMR spectrum of **9** had singlets at δ 2.13 and 2.31 for the aromatic methyl groups and four two-proton peaks at δ 4.92, 5.17, 5.30, and 5.48 for the four sets on vinyl protons. The ^{13}C NMR spectrum had nine peaks, as required by the symmetry of **9**, with appropriate chemical shifts. A chloroform solution of **9** reacted rapidly at 0 °C with 2 equiv of bromine to give the crystalline tetrabromo derivative **10**, mp 173–174 °C, whose structure was clear from its ^1H NMR spectrum (six-proton singlets at δ 2.30 and 2.70 for the aromatic methyl groups and four-proton singlets at δ 4.68 and 5.06 for the methylene protons).

There was no indication in any of the pyrolysis experiments that **9** cyclized to its aromatic isomer **11** (indeed, attempts to bring about this type of cyclization by irradiating solutions of **9** led only to polymeric materials).

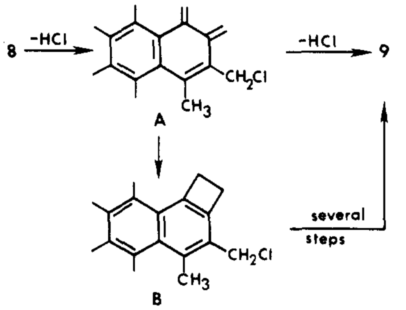




Consequently it seems unlikely that **7** would be an intermediate in the formation of **6** from the pyrolysis of **4** or **5**. On the other hand, the formation of **9** from **8** lends credibility to our suggestion that the initial pyrolysis product of **4** and **5** is in fact the "naphtharadialene" **3**.

The cyclization of this radialene to **6** rather than to **7** is probably a matter of thermodynamics. It seems likely that **6**, with two five-membered rings and two four-membered rings fused to the naphthalene framework, is probably a less strained compound than **7**.[14]

Hydrocarbon **9** could be formed from **8** by several paths. Elimination of the first equivalent of hydrogen chloride should give A which could then either lose a second equivalent of HCl to give **9** directly or rearomatize to B which could go on to **9**. Some analogues of A are known to rearomatize. For example, **12** is an intermediate in two syntheses of **13**.[15-17] However, whether A is converted to **9** or to B is a matter of the relative rates of HCl elimination vs. ring closure. It seems most likely that A is converted directly to **9**, because the second HCl elimination does not involve disruption of an aromatic ring. Similar arguments apply to the formation of **3** from **4** or **5** and indeed to **1** from tris(chloromethyl)mesitylene.[8,9]



Once **9** is formed, ring closure becomes less likely because aromatization is no longer a driving force for the first cyclization. A similar rationale can be used to explain why **1** does not cyclize to **2**.[18]

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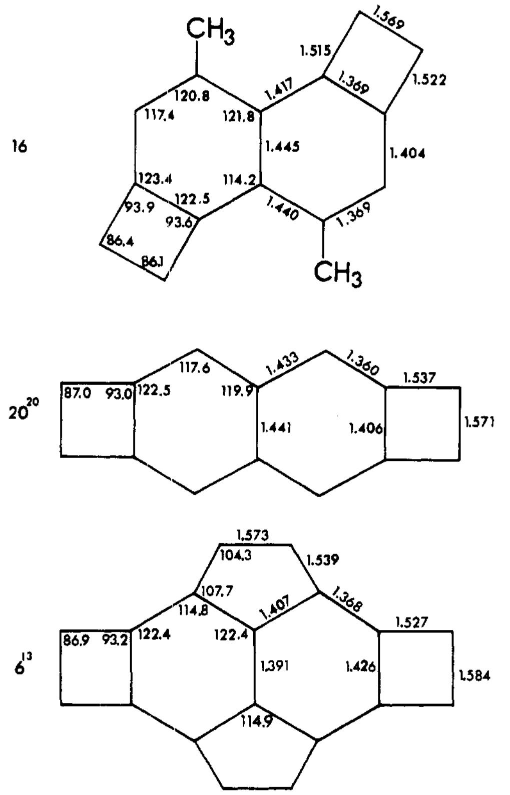
[14] We would expect that **7** (as yet unknown) will isomerize to **6** under our pyrolysis conditions. The cyclization of **3** to **6**, although it can be represented in a concerted manner involving eight of the nine double bonds in **3**, probably proceeds via diradical intermediates which should be readily accessible thermally from **3**.

[15] Cava, M. P.; Shirley, R. L.; Erickson, B. W. *J. Org. Chem.* **1962**, *27*, 755.

[16] Ewing, G. D.; Boekelheide, V. *Synthesis* **1979**, 427.

[17] For alternate preparations of **13**, see: Thummel, R. P.; Cravey, W. E.; Nutakul, W. *J. Org. Chem.* **1978**, *43*, 2473.

16

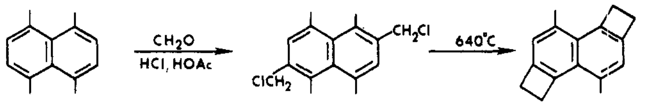


20^{20}

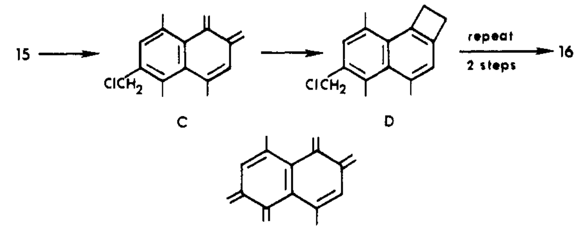
6^{13}

Figure 1. Comparison of bond angles and bond distances in three dicyclobutanaphthalenes.

We performed an additional pyrolysis which bears on the cyclization of intermediates such as A. During the preparation of 5 (via the complete chloromethylation of 1,4,5,8-tetramethylnaphthalene) we isolated small amounts of a bis(chloromethyl) product and by suitable manipulations were able to increase its yield to 43%. Pyrolysis of that compound gave a hydrocarbon whose structure was established as 16 by X-ray. Consequently the bis(chloromethyl) compound must be 15.[19] In this case, the second loss of hydrogen chloride requires disruption of an aromatic system; we suspect that here, therefore, the sequence of steps involves successive eliminations and cyclizations and that polyene E is probably not an intermediate in the conversion of 15 to 16.



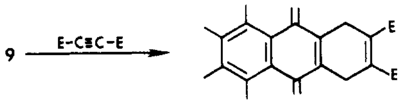
14 15 16



C D E

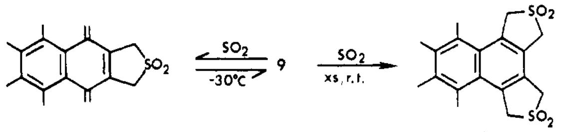
In summary, then, if a single benzenoid ring contains two (or more) chloromethyl substituents with adjacent methyl groups (as in 4, 5, or 8), the second elimination of hydrogen chloride will occur easily and predominate over cyclobutene formation. In this case a radialene-type product will be formed. Once the radialene is formed the driving force for cyclization, i.e., aromatization, is no longer present. But if each benzenoid ring contains only one pair of adjacent chloromethyl and methyl groups (as in 15 or simpler examples such as *o*-(chloromethyl)toluene), elimination will be followed by cyclization to the benzocyclobutene-type product.

It seemed of some interest to study the Diels–Alder chemistry of 9, to determine which diene moiety (1,2- or 2,3-) would react with dienophiles. Treatment of 9 with dimethyl acetylenedicarboxylate (DMAC) at room temperature gave a crystalline adduct identified from its spectra as the quinone methide 17. The ^{1}H NMR spectrum showed two singlets for the aromatic methyls (δ 2.27, 2.44), a singlet for the ester methyls (δ 3.80), a singlet for the methylene groups (δ 3.40), and two broad singlets for the two sets of vinyl protons (δ 5.30, 5.51).



17 (E = CO_2CH_3)

The reaction of 9 with sulfur dioxide was interesting. At −30 °C rapid reaction occurred to give 18, which could be isolated as a crystalline material. With excess SO_2 at room temperature, however, the product was the bissulfone 19; this product could also be obtained by treating chloroform solutions of 18 with SO_2. The structures of 18 and 19 were readily apparent from their spectra. Thus the kinetic Diels–Alder adduct with either DMAC or sulfur dioxide involves addition to the 2,3-methylene moiety; in the case of SO_2, this addition is reversible and the thermodynamically more stable, fully aromatic bis adduct can be obtained.



18 19

Comparison of 16 with Other Dicyclobutanaphthalenes. In Figure 1, the bond angles and bond distances of 16 are compared with those of naphtho[*b*,*g*]dicyclobutene (20)[20] and 6. The naphthalene framework bond distances are approximately the same in 16 and in 20, relatively independent of whether the cyclobutane rings are fused at bonds *a* and *f* (16) or *b* and *g* (20). The only significant difference is some shortening of the C1–C8a

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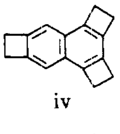
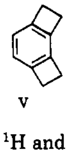
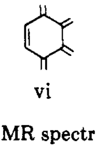
[18] Some analogues of 11 are known. Compounds iv (Bilyard, K. G.; Garratt, P. J.; Underwood, A. J.; Zahler, R. *Tetrahedron Lett.* **1979**, 1815) and v (Thummel, R. P. *J. Am. Chem. Soc.* **1976**, *98*, 628; Thummel, R. P.; Nutakul, W. *J. Org. Chem.* **1977**, *42*, 300) have been prepared by routes which do not involve *o*-quinonedimethide intermediates. Compound v has also been obtained in very low yield (Giovanni, E.; Vuilleumier, H. *Helv. Chim. Acta* **1977**, *60*, 1452) by a pyrolytic route, but it is not known whether any vi (analogue of 9) is also formed in that reaction.



iv

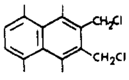


v



vi

[19] It was not possible from the ^{1}H and ^{13}C NMR spectra to distinguish 15 from its isomers vii and viii or 16 from its isomers ix and x.



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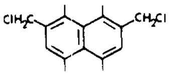
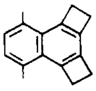


viii



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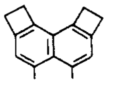

x

[20] Thummel, R. P.; Nutakul, W. *J. Am. Chem. Soc.* **1978**, *100*, 6171.

bond in **16** (1.417 Å) (cf. that bond in **20** (1.433 Å)). The bond angles of the naphthalene framework in the two compounds are, however, quite different because of the different positions of ring fusion in the two compounds. The angles in the four-membered rings, as well as the bond lengths in these rings, are quite similar.

In **6** the naphthalene framework shows two important bond-length variations from **16** and **20**; the central C4a–C8a bond is shortened (from 1.44 to 1.39 Å) and the C2–C3 bond is lengthened (from 1.40 (5) to 1.426 Å) as a consequence of fusion of two five-membered rings to the structure. Although the four-membered-ring bond angles in all three compounds are nearly the same, **6** contains an even longer single bond in the four-membered ring (1.584 Å) than do **16** and **20** (1.57 Å); this again is a clear consequence of including C1, C8 and C4, C5 of the naphthalene framework in five-membered rings.

Experimental Section

General Procedures. ^{1}H NMR spectra were recorded on a Varian T-60 or Bruker WH-180 spectrometer, and ^{13}C NMR spectra were recorded on a Varian CFT-20 or on the Bruker spectrometer. Chemical shifts are in parts per million (δ) from internal Me_4Si. Infrared spectra were measured on a Perkin-Elmer 237 grating spectrometer and are calibrated against a polystyrene film. UV spectra were obtained with a Cary 17 spectrometer. Mass spectra were obtained at 70 eV, using a Finnegan 4000 with the INCOS data system, operated by Mr. Ernest Oliver. High-resolution mass spectra were performed by the NIH regional facility, biochemistry department, Michigan State University. Melting points are uncorrected. Microanalyses were performed by Spang Microanalytical Laboratory, Eagle Harbor, MI.

2,3,6,7-Tetrakis(chloromethyl)-1,4,5,8-tetramethylnaphthalene (5).[21] A mixture of 1,4,5,8-tetramethylnaphthalene[22] (3.0 g, 16.3 mmol), paraformaldehyde (15 g, 0.5 mol), concentrated hydrochloric acid (40 mL), glacial acetic acid (50 mL), and phosphoric acid (12 mL) was heated with stirring at 120 °C for 12 h. The cooled mixture was poured into a mixture of ice and water (200 mL), and the solid yellow-brown product was filtered, dissolved in methylene chloride (250 mL), washed with aqueous sodium bicarbonate (3 × 100 mL), and dried ($MgSO_4$). Evaporation of the solvent gave 3.2 g (52%) of crude **5**.[23] The product is sufficiently pure for pyrolysis but can be further purified by chromatography over silica gel (chloroform eluant) and/or by recrystallization from hexane–ethyl acetate. For pure **5**: mp 263–266 °C dec; IR (KBr) 1450 (m), 1380 (s), 1230 (m) cm^{-1}; NMR ($CDCl_3$) δ 2.62 (12 H, s, methyls), 4.83 (8 H, s, methylenes); mass spectrum, *m/e* (relative intensity) 380 (24), 379 (100), 378 (35), 376 (27) 343 (27), 309 (15).

Anal. Calcd for $C_{18}H_{20}Cl_4$: C, 57.17; H, 5.33. Found: C, 57.21; H, 5.35.

General Pyrolysis Procedure. The starting material was either sublimed with gentle heat or fed by means of an Archimedes screw (Figure 2) into a quartz tube (2-cm diameter) loosely packed with quartz cylinders (3-mm diameter and ~8 mm in length). The tube was heated externally to the desired temperature, and the apparatus was under vacuum, usually at 10^{-4} torr. The product was collected on a cold finger cooled to −78 °C with dry ice and located about 1 cm from the hot zone. Product could be collected from the cold finger by distilling solvent (usually CCl_4 or $CDCl_3$) over it directly in the pyrolysis apparatus or by removing the cold finger and rinsing it with solvent.

Naphtho[2,3:6,7]dicyclobutene[1,8:4,5]dicyclopentene (6). Pyrolysis of either **4** or **5** (100–300-mg scale) at 620–640 °C (10^{-4} torr) gave **6**. The product was recovered from the crude pyrolyzate either by sublimation at 10^{-3} torr and 150 °C or by rapid chromatography over Florisil (hexane eluant).[24] The yield of pure **6** (yellow cubes from benzene) was about 15%. Gradual heating gave no melting point because of progressive decomposition, but samples sealed in a capillary and plunged in a bath preheated to 160 °C and heated rapidly melted reproducibly at 175–176 °C: IR (KBr) 2900–2920 (s), 2820 (s), 1600 (m), 1478 (w), 1440 (w), 1416 (m), 1365 (s), 1272 (m), 1212 (m), 1192 (m), 1154 (w), 815 (w), 760 (w), 713 (w), cm^{-1}; UV (5:2 CH_2Cl_2–CH_3CN) λ_{max} 360 nm (ϵ 310), 335 (620), 309 (4790), 298 (6040), 286 (4630), 270 (sh), 240 (47 500);[25] a methylene chloride solution of **6** irradiated at 298 nm showed strong fluorescence, λ_{max} 355–360 nm; ^{1}H NMR ($CDCl_3$, 180 MHz) δ 3.24, 3.26 (8 H each, s); ^{13}C NMR ($CDCl_3$) δ 147.84, 137.29, 132.60, 29.47, 29.10;[26] mass spectrum, *m/e* (relative intensity) 232 (100), 217 (15), 216 (13), 215 (23), 203 (18), 202 (15); high-resolution mass spectrum, calcd for $C_{18}H_{16}$ 232.12520, found 232.12509.

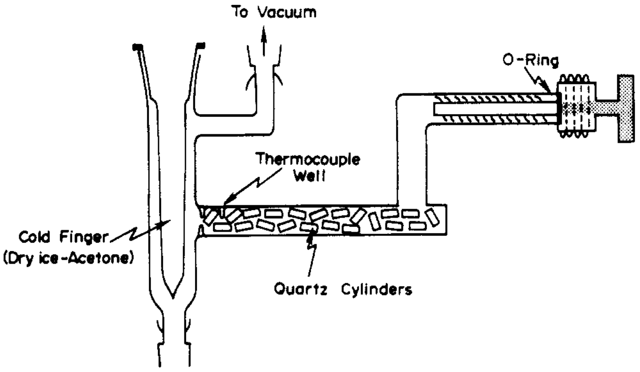

Figure 2. Pyrolysis apparatus with screw feed. Feed tube is precision bore glass, and screw threads are machined to fit it closely. Compound to be pyrolyzed lies as a powder between the threads.

1,2,3,4-Tetrakis(methylene)-5,6,7,8-tetramethyl-1,2,3,4-tetrahydronaphthalene (9). Pyrolysis of 2,3-bis(chloromethyl)-1,4,5,6,7,8-hexamethylnaphthalene (**8**)[27] (150–300-mg scale) at 620–640 °C (10^{-4} torr) gave **9** in at least 45–55% yield (the yield is calculated on the amount of **10** or **17** isolated on treatment of the crude pyrolyzate with bromine or dimethyl acetylenedicarboxylate, respectively, and assuming that the second reaction in each case is quantitative). For **9**: IR (CCl_4) 2920 (m), 1620 (w), 1580 (sh), 1550 (m), 1255 (m), 1225 (m), 1010 (m), 985 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.13 (6 H, s), 2.31 (6 H, s), 4.92 (2 H, d, J = 1.5 Hz), 5.17 (2 H, d, J = 0.5 Hz), 5.30 (2 H, d, J = 0.5 Hz), 5.48 (2 H, d, J = 1.5 Hz); ^{13}C NMR ($CDCl_3$) δ 145.50, 145.07, 135.31 (aromatic), 133.26, 129.27 (ring vinyl), 115.20, 105.71 (methylene), 17.98, 16.93 (methyls).

1,2,3,4-Tetrakis(bromomethyl)-5,6,7,8-tetramethylnaphthalene (10). The pyrolyzate from 230 mg of **8**, dissolved in chloroform (5 mL), was treated dropwise at 0 °C with a solution of bromine (0.2 mL) in chloroform (2 mL). After addition was complete the solution was washed successively with 1 N sodium thiosulfate and water and dried (Na_2SO_4). Evaporation of the solvent and recrystallization from ethanol–benzene gave 230 mg (55% from **8**) of **10**: mp 173–174 °C dec; NMR ($CDCl_3$) δ 2.30 (6 H, s), 2.70 (6 H, s), 4.68 (4 H, s), 5.06 (4 H, s); mass spectrum, *m/e* (relative intensity) 558, 556, 554 (all <1%), 479 (5), 477 (13), 475 (13), 473 (5), 398 (9), 396 (15), 394 (9), 317 (67), 315 (67), 236 (100).

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[21] We are indebted to Mr. David Makowski for first developing this preparation.

[22] Sy, A.; Hart, H. *J. Org. Chem.* **1979**, *44*, 7.

[23] If, as sometimes happens, the NMR spectrum at this point still shows a significant peak in the aromatic proton region, the crude product can be taken up in glacial acetic acid (60 mL). Paraformaldehyde (6.0 g), hydrochloric acid (40 mL), and phosphoric acid (12 mL) are added, and the mixture is heated at 120 °C for 4 h and then worked up as described. This usually results in complete chloromethylation.

[24] The quartz cylinders, after the pyrolysis of either **4** or **5**, were coated with a hard, steely-gray thin bright mirror which was difficult to remove mechanically but which could be removed by combustion. This type of mirror was not produced during the pyrolysis of **8** or **15**; it may be a polymer of **3** and is reminiscent of the films produced by *p*-xylylene vapors (Errede, L. A.; Szwarc, M. *Q. Rev., Chem. Soc.* **1959** *12*, 301).

[25] Compare with pyracene: Anderson, A. G., Jr.; Wade, R. H. *J. Am. Chem. Soc.* **1952**, *74*, 2274.

[26] For comparison with the ^{13}C NMR spectra of pyracene and naphtho[2,3:6,7]dicyclobutene, respectively, see: Trost, B. M.; Herdle, W. B. *J. Am. Chem. Soc.* **1976**, *98*, 4080; Thummel, R. P.; Nutakul, W. *Ibid.* **1978**, *100*, 6171.

[27] Hart, H.; Oku, A. *J. Org. Chem.* **1972**, *37*, 4269.

2,3-Bis(methoxycarbonyl)-9,10-bis(methylene)-5,6,7,8-tetramethyl-1,4,9,10-tetrahydroanthracene (17). The pyrolyzate from 250 mg of **8** in 5 mL of $CDCl_3$ was stirred at room temperature with excess (300 mg) dimethyl acetylenedicarboxylate for 2 h, after which reaction was complete (NMR). The solvent was removed under reduced pressure and the solid residue was triturated with petroleum ether (bp 30–60 °C) and filtered. Recrystallization from hexane–benzene gave 160 mg (52% based on **8**) of **17** as light yellow crystals: mp 278–280 °C; IR (KBr) 2960 (m), 1735 (m), 1265 (m) cm^{-1}; NMR ($CDCl_3$) δ 2.27 (6 H, s, aromatic methyls), 2.44 (6 H, s, aromatic methyls), 3.40 (4 H, s, methylene), 3.80 (6 H, s, methoxyl), 5.30 and 5.51 (each 2 H, br s, vinyl); mass spectrum, *m/e* (relative intensity) 378 (100), 345 (28), 331 (26), 319 (67), 287 (29), 260 (66); high-resolution mass spectrum, calcd for $C_{24}H_{26}O_4$ 378.18311; found 378.18393.

Reaction of 9 with Sulfur Dioxide. Sulfur dioxide was bubbled into a solution containing approximately 60 mg of **9** in 2 mL of $CDCl_3$ at −30 °C for 2 min. The solution was poured into 50 mL of petroleum ether (bp 30–60 °C) and the resulting precipitate was filtered and recrystallized from hexane–tetrahydrofuran to give 53 mg (49%) of **18**: no melting point (decomposes on heating); NMR ($CDCl_3$) δ 2.23 (6 H, methyls), 2.40 (6 H, s, methyls), 4.10 (4 H, s, methylenes), 5.26 and 5.36 (2 H each, br s, vinyls).

When the same reaction was carried out at room temperature with excess sulfur dioxide, or when a chloroform solution of **18** was similarly treated, the product isolated as above was **19**, as small white crystals from chloroform–hexane: mp >300 °C (the solid became red at about 280 °C); IR (KBr) 3025 (m), 2990 (m), 2935 (m), 2870 (m), 1400 (w), 1322 (m), 1318 (s), 1268 (m), 1245 (m), 1220 (m), 1148 (s), 1110 (s) cm^{-1}; NMR ($CDCl_3$) δ 2.36 (6 H, s, methyls), 2.55 (6 H, s, methyls), 4.23 (4 H, s, methylenes), 4.83 (4 H, s, methylenes); mass spectrum, *m/e* (relative intensity) 364 (22), 300 (22), 236 (100); high-resolution mass spectrum, calcd for $C_{18}H_{20}O_4S_2$ 364.08029, found 364.08118.

2,6-Bis(chloromethyl)-1,4,5,8-tetramethylnaphthalene (15). A mixture of 1,4,5,8-tetramethylnaphthalene[22] (0.92 g, 5 mmol), paraformaldehyde (1.70 g), glacial acetic acid (36 mL), and concentrated hydrochloric acid (20 mL) was heated with stirring at 85–90 °C for 6 h and then allowed to stand at room temperature for 12 h. The mixture was poured into ice water (200 mL) and filtered. The solid was dissolved in ether (50 mL), washed successively with water, 10% aqueous sodium bicarbonate, and water, and then dried ($MgSO_4$). Evaporation of the solvent and recrystallization of the residue from hexane–ethyl acetate gave 604 mg (43%) of **15** as white crystals: mp 174–175 °C; ^1H NMR (CCl_4) δ 2.69 (12 H, s, methyls), 4.63 (4 H, s, methylenes), 6.98 (2 H, br s, aromatic); ^{13}C NMR ($CDCl_3$) δ 136.94, 134.01, 133.31, 132.75, 131.09 (aromatic), 45.62 (methylene), 26.87, 19.36 (methyls); mass spectrum, *m/e* (relative intensity) 282 (53), 280 (82), 247 (35), 245 (100), 210 (20), 195 (23), 179 (35).

4,8-Dimethylnaphtho[1,2:5,6]dicyclobutene (16). Pyrolysis of 100 mg (0.355 mmol) of **15** at 640 °C (10^{-4} torr) gave, after purification by sublimation, 35 mg (47%) of pure **16** as colorless crystals: mp 196–197 °C; ^1H NMR ($CDCl_3$) δ 2.65 (6 H, s, methyls), 3.18 (4 H, t, $J = 0.2$ Hz), 3.58 (4 H, t, $J = 0.2$ Hz), 6.97 (2 H, s, aromatic); ^{13}C NMR ($CDCl_3$) δ 140.95, 139.68, 133.21, 129.25, 122.11 (aromatic), 32.81, 29.63 (methylenes), 20.81 (methyl); mass spectrum, *m/e* (relative intensity) 208 (100), 193 (53), 178 (29), 165 (19); high-resolution mass spectrum, calcd for $C_{16}H_{16}$ 208.12520, found 208.12578.

X-ray Structure of 16. Crystals of **16** are monoclinic; space group $P2_1/c$; $a = 8.304$ (3), $b = 5.060$ (2), $c = 13.510$ (7) Å, $\beta = 101.60$ (3)°; $Z = 2$; $M = 208.30$; $\rho_c = 1.244$ g cm^{-3}. Lattice dimensions were determined by using a Picker FACS-I diffractometer and Mo $K\alpha_1$ ($\lambda = 0.70926$ Å) radiation.

Intensity data were measured by using Mo $K\alpha$ radiation ($2\theta_{max} = 50°$), yielding 978 total unique data points and, based on $I > 2\sigma(I)$, 804 observed data points. The data were reduced;[28] the structures were solved by direct methods.[29] The refinement was by full-matrix least-squares techniques.[30] The final R value was 0.047. The final difference Fourier map showed densities ranging from +0.20 to −0.21, with no indication of missing or incorrectly placed atoms except a possible disorder of the methyl hydrogen atoms. The occupancy ratio of the possible alternate set of hydrogen positions to the reported set would appear to be less than 0.3.

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Registry No. 3, 69153-84-0; **4**, 62571-60-2; **5**, 69153-86-2; **6**, 69153-85-1; **8**, 39654-48-3; **9**, 74420-19-2; **10**, 74420-20-5; **15**, 74420-21-6; **16**, 74420-22-7; **17**, 74420-23-8; **18**, 74420-24-9; **19**, 74420-25-0; 1,4,5,8-tetramethylnaphthalene, 2717-39-7.

Supplementary Material Available: Data for the X-ray structure of **16** are available as Table I, positional and thermal parameters and standard deviations; Table II, anisotropic thermal parameters and standard deviations; Table III, distances; Table IV, angles; Table V, observed structure factors, standard deviations, and differences (8 pages). Ordering information is given on any current masthead page.

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Synthesis of Cyclic Carbonates from Carbon Dioxide and Epoxides in the Presence of Organoantimony Compounds as Novel Catalysts

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The reactions of carbon dioxide (**1**) with epoxides **2** to form cyclic carbonates **3** were carried out in the presence of organoantimony compounds as catalysts. Pentavalent organoantimony compounds, especially tetraphenylstibonium bromide (**4b**) and triphenylantimony dibromide (**4d**), are found to be more active catalysts than trivalent compounds, and the reactivity of compounds **2** seems to be in the following order: propylene oxide (**2b**) > styrene oxide (**2d**) > ethylene oxide (**2a**) > (chloromethyl)ethylene oxide (**2c**). The ring-opening polymerizations of **2b** and **2d** are also examined by using **4b** and **4d**, and it is found that they have no effect on the polymerization. On the basis of the results obtained, a reasonable scheme is proposed for the reaction.

There has been much attention given to synthetic utilization of carbon dioxide (**1**) along with various organometallic compounds. For example, alternating copolymers of **1** and epoxides **2** were synthesized by the use of orga-

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