

same reaction sequence yielding (3*R*)-3-deuterio-4,4-dimethylcyclohexanone whose CD spectrum was the mirror image of IV and showed the same temperature independence.

- (8) $[R]_{\text{obsd}}$, $[R]$, and $[R]_{\text{eq}}$ refer to the observed rotational strength or to the one calculated for the conformer with the deuterium in the axial and equatorial position, respectively.
- (9) The contributions for the axial and equatorial α -methyl groups were taken from D. N. Kirk and W. Klyne, *J. Chem. Soc., Perkin Trans. 1*, 1076 (1974).
- (10) Obtained by a linear least-squares fit (standard deviation 10%) to the data points in an Arrhenius diagram. The experimental error associated with the $[R]_{\text{obsd}}$ values was ± 0.0015 .
- (11) R. E. Carter and L. Melander, *Adv. Phys. Org. Chem.*, **10**, 1 (1973).
- (12) K. Kuchitsu and L. S. Bartell, *J. Chem. Phys.*, **36**, 2470 (1962).
- (13) A $\pm 1\%$ shift in the equilibrium would result in a change of $[R]_{\text{obsd}} = \pm 0.003$.
- (14) C. Djerassi and W. Klyne, *Proc. Natl. Acad. Sci. U.S.A.*, **48**, 1093 (1962).

Shy-Fuh Lee, Günter Barth, Carl Djerassi*

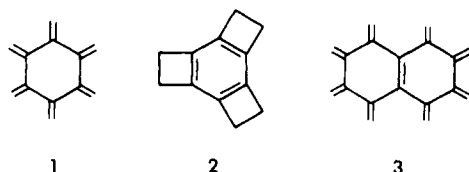
Department of Chemistry, Stanford University
Stanford, California 94305

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Evidence for "Naphtharadialene" (1,2,3,4,5,6,7,8-Octakis(methylene)- Δ^9 -octalin)¹

Sir:

Various precursors have recently been converted by pyrolysis to the reactive and theoretically interesting hydrocarbon hexaradialene (**1**).²⁻⁴ There is no indication yet that **1** cyclizes to the isomeric tricyclobutabenzene (**2**). We describe here novel pyrolysis results which suggest the intermediacy of "naphtharadialene" (**3**),¹ although the isolated product is a cyclized isomer.

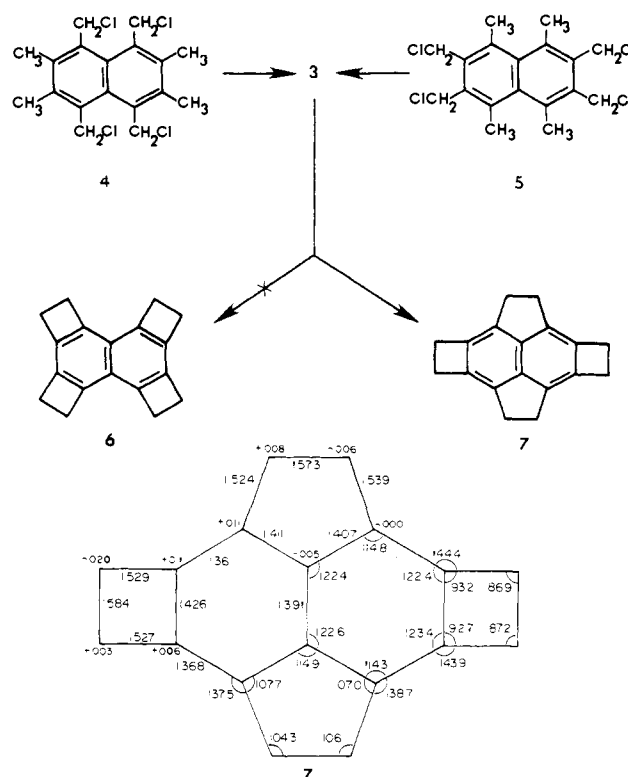


Pyrolysis⁵ of either 1,4,5,8-tetrakis(chloromethyl)-2,3,6,7-tetramethylnaphthalene (**4**)⁶ or its isomer **5**,⁷ in which the relative positions of the methyl and chloromethyl groups are interchanged, in a quartz apparatus⁸ at 620–640 °C and 10^{-4} Torr gave the same product, in $\sim 15\%$ yield. The product was best separated from the crude pyrolyzate by sublimation at 150 °C and 10^{-3} Torr.⁹ It is a yellow crystalline compound (cubes from benzene) which may be handled at room temperature, although samples darken and decompose gradually, particularly in solution. Gradual heating gave no melting point because of progressive decomposition. However, a sample sealed in a capillary and plunged into a bath at 160 °C, and then heated rapidly, melted reproducibly at 175–176 °C.

The product had the following spectral properties. The high resolution mass spectrum showed a parent and base peak at m/e 232.12509 (calcd for $C_{18}H_{16}$ 232.12520). The ¹H NMR spectrum ($CDCl_3$, 180 MHz) consisted of two singlets with equal intensity at δ 3.24 and 3.26,¹⁰ and the ¹³C NMR spectrum ($CDCl_3$) had aliphatic carbon signals at δ 29.12 and 29.49 and aromatic carbon signals at δ 132.67, 137.39, and 139.95.¹¹

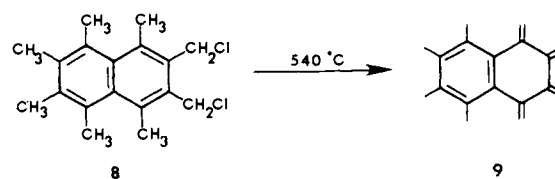
These NMR data do not permit an unequivocal choice between structures **6** and **7** for the pyrolysis product (Scheme I). Both compounds have D_{2h} symmetry and the proton and carbon-13 chemical shifts of model compounds are similar.^{12,13} Consequently it was necessary to carry out an X-ray structure determination on a crystal. The correct structure is **7**. The molecule is essentially planar, with the bond angles and distances shown.¹⁴

Scheme I



The formation of **7** from both **4** and **5** is striking, since it requires bond formation between methyl carbons in the precursors. This result strongly suggests the intermediacy of **3**, since stepwise elimination of hydrogen chloride and ring closure can only lead to **6**. Experiments designed to isolate and/or trap **3** are under way.¹⁵

In partial support for the intermediacy of **3**, pyrolysis of the bis(chloromethyl)naphthalene **8**¹⁶ at 540 °C and 10^{-4} Torr gave a good yield of the relatively stable radialene type product **9**: ¹H NMR δ 2.13 (s, 6 H), 2.31 (s, 6 H), 4.92 (d, 2 H, $J = 1.5$



Hz), 5.17 (br s, 2 H), 6.30 (br s, 2 H), 5.48 (d, 2 H, $J = 1.5$ Hz).

Acknowledgment. We are indebted to the National Science Foundation (CHE 77-05956) for financial support of this research.

References and Notes

- The term "radialene" generally refers to a single carbocyclic ring, each carbon of which is part of an exocyclic carbon-carbon double bond. Although the trivial name "naphtharadialene" which we suggest here for **3** does not adhere strictly to this definition, it is descriptive and much simpler than the systematic name.
- A. J. Barkovich, E. S. Strauss, and K. P. C. Vollhardt, *J. Am. Chem. Soc.*, **99**, 8321 (1977).
- P. Schiess and M. Heitzmann, *Helv. Chim. Acta*, **61**, 844 (1978).
- L. G. Harruff, M. Brown, and V. Boekelheide, *J. Am. Chem. Soc.*, **100**, 2893 (1978).
- We follow here the elegant experimental design of others^{3,4} and also our own earlier interest in benzocyclobutene synthesis via hydrogen chloride eliminations: H. Hart and R. W. Fish, *J. Am. Chem. Soc.*, **82**, 749 (1960); H. Hart, J. A. Hartlage, R. W. Fish, and R. R. Rafofs, *J. Org. Chem.*, **31**, 2244 (1966).
- H. Hart, J. L. Reilly, and J. B.-C. Jiang, *J. Org. Chem.*, **42**, 2684 (1977).
- Compound **5** was obtained by chloromethylation of 1,4,5,8-tetramethylnaphthalene: mp 263–266 °C dec; NMR ($CDCl_3$) δ 2.62 (s, 12 H), 4.83 (s, 8 H). We are indebted to Mr. David Makowski for this preparation, and for

- preliminary pyrolysis experiments.
- (8) The compound was sublimed with gentle heat into a quartz tube packed with quartz beads, and pyrolysis products were collected on a cold finger (-78°C) ~ 1 cm from the hot zone; chloroform was then distilled from another vessel to wash the product from the cold finger into a collection tube.
 - (9) Chromatography on silica gel or basic alumina destroyed the product. It could be purified on Florisil (hexane eluant), but some decomposition occurred if contact with Florisil was prolonged.
 - (10) At 60 MHz, only a sharp singlet at δ 3.25 is seen.
 - (11) The limited solubility and the long relaxation time of the ring carbons caused the lowest field peak to be weak and difficult to observe.
 - (12) For example, the methylene protons of naphtho[a]cyclobutene and naphtho[b]cyclobutene appear at δ 3.25 and δ 3.28, respectively (R. P. Thummel, W. E. Cravey, and W. Nutakul, *J. Org. Chem.*, **43**, 2473 (1978)), and those of acenaphthene and several pyracene derivatives occur in the range of δ 3.37–3.49 (L. A. Carpino and S. Gowecke, *J. Org. Chem.*, **29**, 2824 (1964) and B. M. Trost, G. M. Bright, C. Frihart and C. Brittelli, *J. Am. Chem. Soc.*, **93**, 737 (1971)). The methylene carbons appear at δ 28.27 and 29.26 in naphtho[a]cyclobutene (we are indebted to Professor Thummel for sending us various spectra for comparison) and at δ 31.5 in pyracene (B. M. Trost and W. B. Herdle, *J. Am. Chem. Soc.*, **98**, 4080 (1976)). Although these data tend to favor **6** over **7**, it is difficult to predict how the combined presence of four- and five-membered rings in **7** will affect the ^1H and ^{13}C chemical shifts.
 - (13) Other spectral data of the product follow: 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 cm^{-1} (w); UV (5:2 methylene chloride–acetonitrile) λ_{max} 360 nm (ϵ 310), 335 (620), 309 (4790), 298 (6040), 286 (4630), 270 (sh), 240 (47 500); a methylene chloride solution irradiated at 298 nm showed fluorescence with a maximum at 355–360 nm. The ultraviolet spectrum shows some similarity to that of pyracene (A. G. Anderson, Jr., and R. H. Wade, *J. Am. Chem. Soc.*, **74**, 2274 (1952)).
 - (14) $R = 4.6\%$, $R_w = 3.5\%$, estimated standard deviation 0.004–0.008 Å and 0.3–0.6°. Details of the structure will be reported in *Acta Crystallogr.*
 - (15) The quartz beads, following the pyrolysis of either **4** or **5**, were coated with a hard, steely-gray bright mirror which was extremely difficult to remove mechanically, but which could be removed by combustion. This type of mirror was not produced during the pyrolysis of **8**, suggesting that it may be a polymer of **3**, reminiscent of the films produced from *p*-xylylene vapors (L. A. Errede and M. Szwarc, *Q. Rev., Chem. Soc.*, **12**, 301 (1959)).
 - (16) H. Hart and A. Oku, *J. Org. Chem.*, **37**, 4269 (1972).

Harold Hart,* Mark Jeffares
Avraham Teuerstein, Donald L. Ward

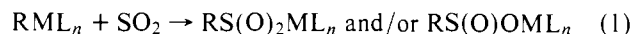
Department of Chemistry, Michigan State University
East Lansing, Michigan 48824

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A Radical-Chain Mechanism for Some Sulfur Dioxide "Insertion" Reactions in Organocobaloximes

Sir:

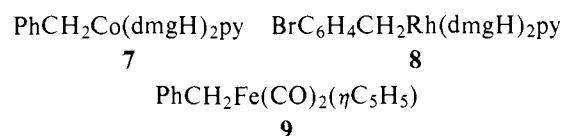
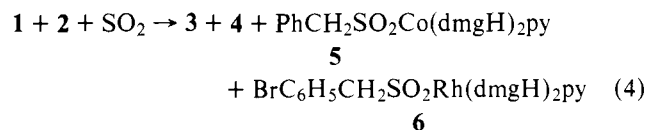
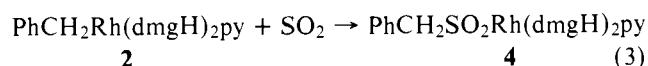
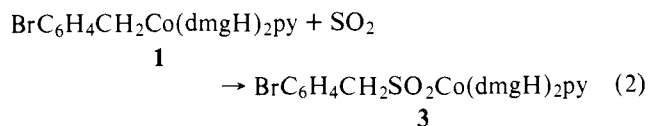
Sulfur dioxide insertion is one of the more common reactions of σ -bonded organometallic complexes;¹ it occurs with many organic derivatives of both main group and transition elements (eq 1). However, despite the appreciable body of careful work on the kinetics, products, and stereochemistry of these reactions, there is no comprehensive picture of the mechanisms which may operate.



We here describe some simple experiments which demonstrate that, in the case of certain organocobaloximes,² organorhodoximes, and possibly in the case of some organoiron complexes under appropriate conditions, the reaction is not a true insertion into the carbon–metal bond, but is an intermolecular process in which the organic and metal fragments of the "insertion" product do not originate from the same molecule of organometallic substrate.

Thus, 4-bromobenzylbis(dimethylglyoximate)pyridinecobalt(III) (**1**) and benzylbis(dimethylglyoximate)pyridine-rhodium(III) (**2**) separately undergo "insertion" in liquid SO_2 in sealed tubes at ambient temperature within 2 h to give the corresponding products **3** and **4**, respectively² (eq 2, 3). Under identical conditions, an equimolar mixture of **1** and **2** reacts to give *four* products, **3**, **4**, **5**, and **6**³ (eq 4). In the early stages product **4** is formed faster than **5** and **6**, and **3** is formed slowest

of all. No rearrangement of **1** and **2** into **7** and **8** takes place during the reaction,⁴ and separate experiments in which reaction 3 is carried out in the presence of the insertion product **3** show that no conversion of **3** and **4** into **5** and **6** occurs.⁵

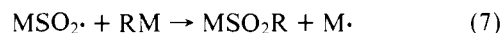
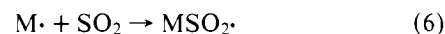


Following our several recent observations of chain reactions involving homolytic displacements at carbon centers,⁶ we propose that these apparent sulfur dioxide insertion reactions involve the radical-chain mechanism outlined below.

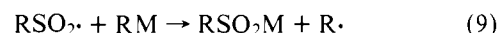
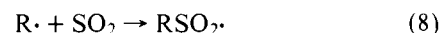
Initiation:⁷



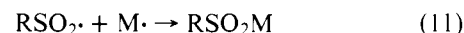
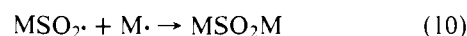
Propagation:



and/or



Termination:



The radical nature of the reaction is apparent from observations that (i) the reactions of SO_2 with alkylcobaloximes at low temperatures, e.g., with $\text{PhCH}_2\text{CH}_2\text{Co}(\text{dmgH})_2\text{py}$, are markedly photocatalyzed⁸ and (ii) the rates of thermal reaction of SO_2 with alkylcobaloximes are variable and subject to induction periods and to catalysis by admixture with the more reactive benzyl- or allylcobaloximes or with cobaloxime(II). While we cannot rule out some reaction through the propagation steps 8 and 9, we prefer the mechanism involving predominantly reactions 5, 6, 7, and 10 for the following reasons.

(a) α -Toluenesulfonyl radicals, generated by chlorine atom abstraction from the corresponding α -toluenesulfonyl chloride by cobaloxime(II) (eq 12), react with allylcobaloximes to give high yields of the benzyl(allyl)sulfone (**10**, eq 13), but no "insertion" product **5** can be detected.⁹ Moreover, only small yields of **5** are formed in the reaction of α -toluenesulfonyl chloride with **7** despite significant formation of chlorocobaloxime(III) via eq 12.

