The present data demonstrate unambiguously that the decomposition of 10-hydroperoxy-8,12-octadecadienoic acid (1) by Fe(III)·BLM proceeds by homolytic cleavage of the peroxide O–O bond, as outlined in Scheme I, which should result in concomitant formation of an activated Fe·BLM. As noted previously,[7b] both the mechanisms of formation and chemical behavior of this species seem consistent with its representation of a high valent metal–oxo [Fe(IV)=O] species less oxidized than the species resulting from admixture of Fe(III)·BLM + H_2O_2 or Fe(II)·BLM + O_2.

It may be noted that the techniques employed here to control and analyze the oxidation states of activated BLM are potentially of more general utility in analyzing the mechanistic course of metal-centered oxygenation/oxidation reactions.

(16) Solvolsis of the *p*-toluensulfonate of octen-3-ol in aqueous acetone, in the presence or absence of 1,1,3,3-tetramethylisoindoline-*N*-oxyl, led to the formation of the isomeric allylic alcohols in a 1:1 ratio. No alkoxyamines could be detected when 1,1,3,3-tetramethylisoindoline-*N*-oxyl was present, thereby demonstrating that 2-octenyl carbonium ions do not react with the nitroxide to give alkoxyamines.

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Telomers of Bent Arenes. Acid-Catalyzed Dimerization and Trimerization of the 1,4-Hexamethylene-Bridged Arenes [6]Paracyclophane, [6](1,4)Naphthalenophane, and [6](1,4)Anthracenophane

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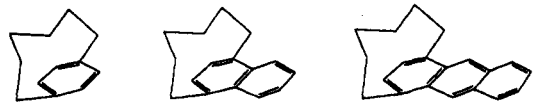
Summary: Whereas treatment of 1,4-hexamethylene-bridged benzene [6]paracyclophane (1) with a catalytic amount of H_2SO_4 gave, as a minor product, dimer **6**, along with isomers **4** and **5**, similar treatment of 1,4-hexamethylene-bridged naphthalene [6](1,4)naphthalenophane (**2**) afforded predominantly dimers **7** and **8**, together with trimers **9** and **10**. The 1,4-hexamethylene-bridged anthracene [6](1,4)anthracenophane (**3**) yielded only trimers **13** and **14**.

It is well-known that alkyl-substituted arenes undergo acid-catalyzed isomerization.[1] Only under extremely drastic conditions, however, does dehydrogenative dimerization, i.e., the Scholl reaction,[2] take place, usually with low efficiency to give low yields of products. On the other hand, short-bridged cyclophanes undergo facile acid-catalyzed isomerization to more stable isomers because a large amount of strain is released thereby.[3] One notable exception is the $AlCl_3$/HCl-promoted skeletal rearrangement of [2.2.2](1,3,5)cyclophane, wherein the formation of intramolecular carbon–carbon bonds between the two aromatic rings leads, at least initially, to a less stable isomer.[4] Here, we report *the first examples of the acid-catalyzed dimerization and trimerization of 1,4-hexamethylene-bridged arenes* which possess severely deformed aromatic nuclei, i.e., [6]paracyclophane (**1**),[3c,5] [6](1,4)naphthalenophane (**2**),[6] and [6](1,4)-anthracenophane (**3**).[6]



1 2 3

Earlier, we reported[3c,7] that the treatment of **1** (5×10^{-2} M CH_2Cl_2 solution) with a catalytic amount of acid (TfH or TFA) at room temperature yielded the corresponding meta and ortho isomers **4** and **5**. However, when a more concentrated solution (1.5×10^{-1} M) of **1** was treated with a catalytic amount of H_2SO_4, the dimer **6**[8] was also formed as a minor product (21%), together with a 1:1 mixture of **4** and **5** (59%). Similar treatment of the naphthalene **2** produced dimers **7**[8] and **8**,[8] which possess meta- and ortho-bridged naphthalenophane units, respectively, as major products (72%). The relative amount of **8** increased as the reaction time was increased, which indicated that **8** was produced by isomerization of **7**. Two minor products, trimers **9**[8] and **10**[8] (15%), were also isolated. The structures of **9** and **10** were inferred from the similarity between their ^1H NMR spectra and those of anthracene trimers **13** and **14**.[9] No monomeric products were detected even after

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(1) For a review, see: McCauley, D. A. *Friedel-Crafts and Related Reactions*; Olah, G. A., Ed.; Wiley-Interscience: New York, 1964; Vol. II, Chapter 24.

(2) Balaban, A. T.; Nenitzescu, C. D. *Friedel-Crafts and Related Reactions*; Olah, G. A., Ed.; Wiley-Interscience: New York, 1964; Vol. II, Chapter 23.

(3) (a) Hopf, H.; Marquard, C. *Strain and Its Implication in Organic Chemistry*; de Meijere, A.; Blechert, S., Eds.; Kluwer Academic: Dordrecht, 1989; pp 297–332. (b) Jenneskens, L. W.; de Boer, H. J. R.; de Wolf, W. H.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1990**, *112*, 8941–8949. (c) Tobe Y.; Ueda, K.-I.; Kakiuchi, K.; Odaira, Y.; Kai Y.; Kasai, N. *Tetrahedron* **1986**, *42*, 1851–1858.

(4) Boekelheide, V.; Hollins, R. A. *J. Am. Chem. Soc.* **1973**, *95*, 3201–3208.

(5) Kane, V. V.; Wolf, A. D.; Jones, M., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 2643–2644. Kammula, S. L.; Iroff, L. D.; Jones, M., Jr.; van Straten, J. W.; de Wolf, W. H.; Bickelhaupt, F. *Ibid.* **1977**, *99*, 5815.

(6) Tobe, Y.; Takahashi, T.; Ishikawa, T.; Yoshimura, M.; Suwa, M.; Kobiro, K.; Kakiuchi, K.; Gleiter, R. *J. Am. Chem. Soc.* **1990**, *112*, 8889–8894.

(7) Careful reexamination of the products revealed that a small amount of dimer **6** was formed even under these conditions. The treatment of **1**–**3** with a catalytic amount of TFA resulted in product distributions similar to those obtained on treatment with H_2SO_4.

(8) The spectroscopic characteristics and other analytical data, which are given in the supplementary material, are in accord with the assigned structure.

(9) Characteristic ^1H NMR signals ($CDCl_3$) for the vinyl and methine protons of **9**, **10**, **13**, and **14** are as follows. **9**: δ 6.17 (d, J = 6.8 Hz), 5.79 (d, J = 7.3 Hz), 5.60 (dd, J = 8.8, 8.3 Hz), 3.51 (d, J = 5.4 Hz), 3.26 (d, J = 6.8 Hz), 2.94 (br m), 2.86 (d, J = 6.8 Hz). **10**: δ 6.06 (d, J = 7.0 Hz), 5.66 (d, J = 7.3 Hz), 5.61 (dd, J = 9.2, 8.1 Hz), 3.48 (br m), 3.45 (d, J = 5.9 Hz), 3.19 (d, J = 7.0 Hz), 2.91 (d, J = 7.3 Hz). **13**: 6.46 (d, J = 7.0 Hz), 5.95 (d, J = 7.3 Hz), 5.66 (t, J = 8.0 Hz), 3.71 (d, J = 5.8 Hz), 3.49 (d, J = 7.0 Hz), 3.39 (br m), 3.04 (d, J = 7.0 Hz). **14**: 6.31 (d, J = 6.8 Hz), 5.84 (d, J = 6.8 Hz), 5.65 (dd, J = 8.8, 8.3 Hz), 3.82 (br m), 3.64 (d, J = 5.9 Hz), 3.43 (d, J = 6.3 Hz), 3.13 (d, J = 7.3 Hz).

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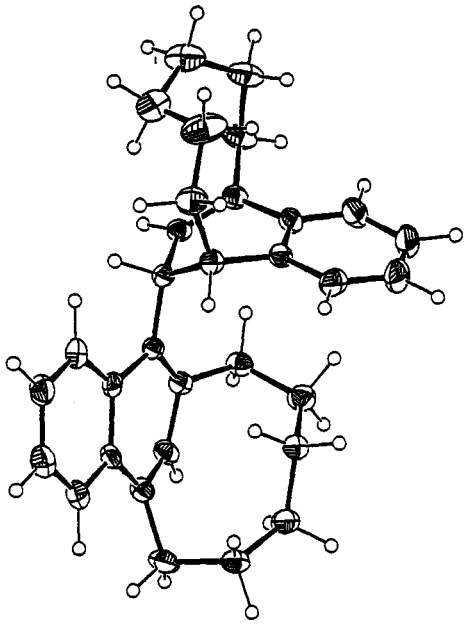
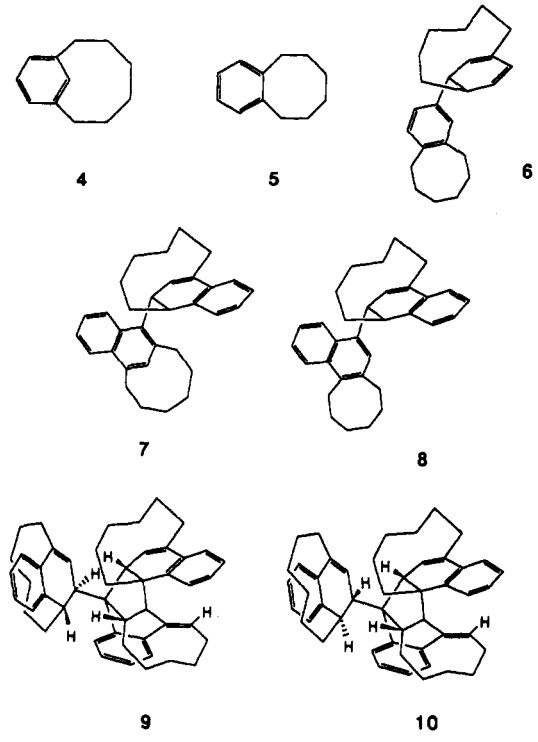


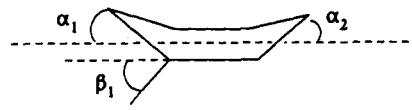
Figure 1. Molecular structure of dimer 7.

solutions of 2 as dilute as 1.8×10^{-3} M were treated with acid.



The structure of the [6](1,3)naphthalenophane[10] derivative 7 was elucidated by X-ray crystallographic analysis (Figure 1).[11] Values of the angles α_1, α_2, and β—which are measures of the extent to which the aromatic ring is deformed into a boat conformation—are listed in Table I for compound 7 and also for 8,11-dichloro[5]metacyclophane (11)[12] and the 2-oxa[6]metacyclophane derivative 12.[13] It should be noted that α_1 of 7 is only slightly smaller than that of 11 but is much greater than that of 12. The other deformation angles, α_2 and β, of 7 are much smaller than those of 11. The overall extent to which the aromatic ring of 7 is deformed seems to be larger than that of the oxa[6]metacyclophane 12 and is probably a consequence the greater flexibility of the naphthalene ring relative to the benzene ring.

Table I. Deformation Angles of [n](1,3)-Bridged Cyclophanes



compd	α_1 (deg)	α_2 (deg)	β (deg)
7	25.3	4.6	13.2, 18.8
11[12]	26.8	12	48
12[13]	17.0	6.4	22.9, 20.1

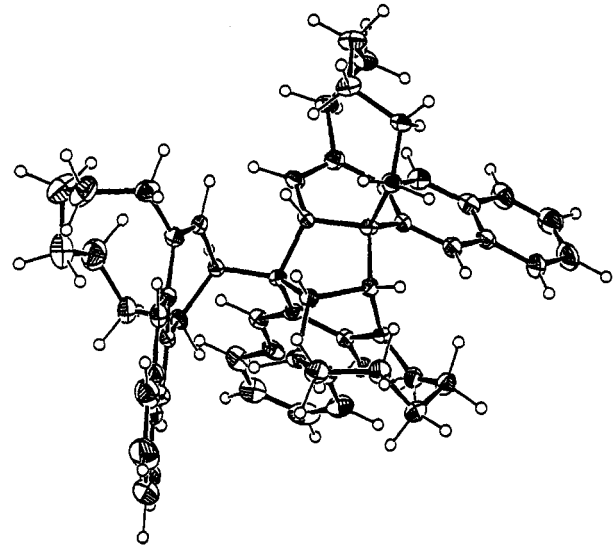
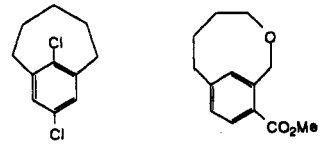


Figure 2. Molecular structure of trimer $13 \cdot 2CH_2Cl_2$. For the sake of clarity, the solvent molecules are not shown.



11 12

Treatment of the anthracene 3 with H_2SO_4 under similar conditions afforded only trimers. The structure of the major trimeric product 13[8] (43%) was established by X-ray crystallographic analysis (Figure 2).[14] A minor product, 14[8] (8%), was also isolated and is believed to be a stereoisomer of 13, on the basis of similarities between the ^1H NMR spectra of the two compounds.[9] No monomeric

(10) Although [6](1,3)naphthalenophane has been prepared, its molecular structure is yet to be determined, see: Parham, W. E.; Johnson, D. R.; Hughes, C. T.; Meilahn, M. K.; Rinehart, J. K. *J. Org. Chem.* **1970**, *35*, 1048–1053. The shortest-bridged [n](1,3)naphthalenophane described so far is the [5]-homologue, see: Grice, P.; Reese, C. B. *J. Chem. Soc., Chem. Commun.* **1980**, 424–425.

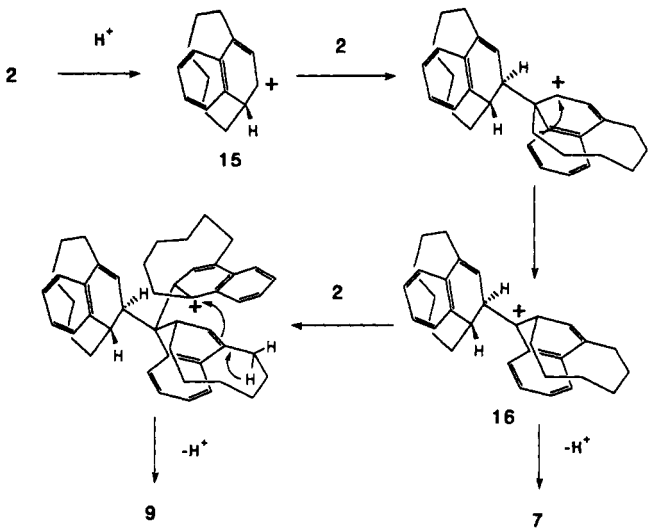
(11) Diffraction intensities were measured with a Rigaku four-circle diffractometer that used Ni-filtered Cu Kα radiation. Crystal data for 7: triclinic, $P\bar{1}$, a = 12.751 (4) Å, b = 11.551 (4) Å, c = 9.592 (2) Å, α = 109.95 (3)°, β = 96.82 (3)°, γ = 63.67 (2)°, V = 1189.3 (6) Å^3, Z = 2, D_c = 1.175 g cm^{-3}, R = 0.116 for 3176 observed reflections.

(12) Jenneskens, L. W.; Klamer, J. C.; de Boer, H. J. R.; de Wolf, W. H.; Bickelhaupt, F.; Stam, C. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 238–239.

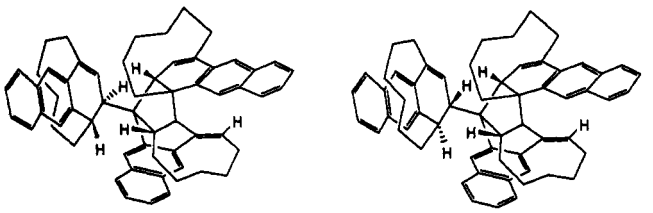
(13) Shea, K. J.; Burke, L. D.; Doedens, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 5305–5306.

(14) Crystal data for $13 \cdot 2CH_2Cl_2$: triclinic, $P\bar{1}$, a = 16.499 (3) Å, b = 14.299 (4) Å, c = 11.106 (2) Å, α = 100.61 (2)°, β = 88.03 (2)°, γ = 77.26 (2)°, V = 2469.0 (9) Å^3, Z = 2, D_c = 1.279 g cm^{-3}, R = 0.108 for 5258 observed reflections.

Scheme I



or dimeric products could be detected even after dilute (1.3×10^{-3} M) solutions of 3 were treated with acid.



The formation of dimers 6–8 and trimers 9, 10, 13, and 14 can be readily explained by positing a series of electrophilic attacks by intermediate cations on the respective substrates, as is shown in Scheme I for the naphthalene 2. It should be noted that, in the case of 2, electrophilic attack on the second substrate molecule takes place before the migration of the hexamethylene bridge of the cation 15, and that attack on the third molecule of substrate occurs before loss of proton from the meta-bridged dimeric cation 16. The last attack takes place at a less hindered site (C-2) in the aromatic core. The pronounced tendency of 2 and 3 to telomerize rather than isomerize can be explained in terms of the enhanced reactivity arising from the high HOMO level and the large double-bond character of the C-1–C-2 bond of the acene cores of the molecules.[15] In summary, we have observed, for the first time, an acid-catalyzed telomerization of bridged arenes, the aromatic rings of which are severely deformed into boat conformations by the presence of a 1,4-hexamethylene bridge.

Acknowledgment. We thank to the Crystallographic Research Center of the Institute for Protein Research and the Instrumental Analysis Center of the Faculty of Engineering, Osaka University, for the use of X-ray and NMR and MS facilities, respectively. We are also grateful to the Ministry of Education, Science, and Culture for partial support of this work through a Grant-in-Aid for Scientific Research on Priority Areas (Grant No. 02230217).

Supplementary Material Available: Experimental details of the preparation and isolation of dimers 6–8 and trimers 9, 10, 13, and 14; spectroscopic characteristics and other analytical data; labeled ORTEP drawings and tables of interatomic bond distances and angles, fractional atomic coordinates, and anisotropic thermal parameters for atoms other than hydrogen for 7 and 13·2CH_2Cl_2 (19 pages). Ordering information is given on any current masthead page.

(15) For unusual reactions of 2 and 3, see: Tobe, Y.; Takahashi, T.; Kobiro, K.; Kakiuchi, K. *Tetrahedron Lett.* **1991**, *32*, 359–362; *J. Am. Chem. Soc.*, in press.

B-[3-((Diisopropylamino)dimethylsilyl)allyl]diisopinocampheylborane: An Excellent Reagent for the Stereoselective Synthesis of Anti Vicinal Diols

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Summary: Aldehydes reacted stereoselectively with *B*-[3-((diisopropylamino)dimethylsilyl)allyl]diisopinocampheylborane, derived from (+)- and (−)-α-pinene, to provide, on workup with hydrogen peroxide, (3*S*,4*R*)- and (3*R*,4*S*)-dihydroxy-1-alkenes, respectively.

Recently Brown and co-workers have introduced several allyl- and crotylboranes that are spectacularly useful for the conversion of aldehydes into homoallylic alcohols.[1,2] The methods are particularly useful for the preparation of 4-hydroxy- and 4-hydroxy-3-methyl-1-alkenes. In all cases, the products were formed with both excellent relative and absolute stereochemical control. This chemistry is exemplified by the *E* and *Z* isomers of *B*-(crotyl)diisopinocampheylborane (**1a,b**) both of which are available in high enantiomeric purity from the commercial *B*-methoxy compound **1c**.[3] On reaction with aldehydes, the *E* reagent **1a** gave the anti[4] homoallylic alcohol **2**, whereas the *Z* isomer produced the corresponding syn compound **3**. In addition, the antipodal reagents corresponding to **1a** and **1b** are also readily available.[3] Thus, the enantiomers of the anti and syn homoallylic alcohols **2** and **3** are also easily synthesized with outstanding stereochemical control. Since homoallylic alcohols may be oxidized to reveal protected β-hydroxy aldehyde systems, the Brown methodology has found considerable use as a masked aldol strategy in

(1) For example, see: Racherla, U. S.; Brown, H. C. *J. Org. Chem.* **1991**, *56*, 401. Jadhav, P. K.; Bhat, K. S.; Perumal, P. T.; Brown, H. C. *J. Org. Chem.* **1986**, *51*, 432. Brown, H. C.; Bhat, K. S. *J. Am. Chem. Soc.* **1986**, *108*, 5919. Brown, H. C.; Randad, R. S.; Bhat, K. S.; Zaidlewicz, M.; Racherla, U. S. *J. Am. Chem. Soc.* **1990**, *112*, 2389. Srebmik, M.; Ramachandran, P. V. *Aldrichimica Acta* **1987**, *20*, 9 and references therein.

(2) For examples of alternative methods to prepare homoallylic alcohols from allylboranes, see: Mikhailov, B. M.; Pozdnev, V. F. *Izv. Acad. Nauk SSSR, Ser. Khim.* **1967**, 1477. For a review of addition of crotylboronates to aldehydes, see: Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 555. Roush, W. R.; Halterman, R. L. *J. Am. Chem. Soc.* **1986**, *108*, 294 and references therein. Midland, M. M.; Preston, S. B. *J. Am. Chem. Soc.* **1982**, *104*, 2330. Garcia, J.; Kim, B.-M.; Masamune, S. *J. Org. Chem.* **1987**, *52*, 4831.

(3) Either antipode is commercially available from Aldrich. Brown, H. C.; Desai, M. C.; Jadhav, P. K. *J. Org. Chem.* **1982**, *47*, 5065. Brown, H. C.; Jadhav, P. K. *J. Am. Chem. Soc.* **1983**, *105*, 2092.

(4) Masamune, S.; Choy, W. *Aldrichimica Acta* **1982**, *15*, 47.

0022-3263/91/1956-5243$02.50/0