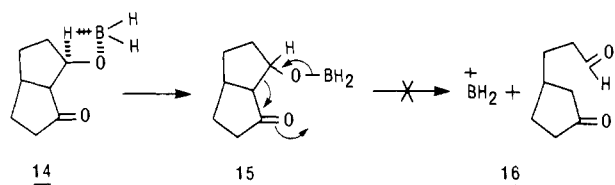
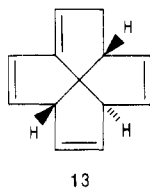


Scheme IV



products of transannular cyclization **10a** and **10b** are interesting in their own right, the failure of the "aldol approach" to provide the [5.5.5]fenestrane system was disappointing.

Because of the recent success in conversion of a related tetracyclo[6.6.0.0^{1,5}.0^{8,12}]tetradecane-2,7,9,14-tetraone¹⁶ into a tetrol via reduction by diborane-THF without ring cleavage, the analogous reduction of **11** seemed worthy of pursuit despite the negligible solubility of **11** in THF. Treatment of **7** (Scheme I) with osmium tetroxide, followed by oxidation with Jones reagent,⁶ gave a 70% yield of the diketo diacid **9c** prepared earlier by Mitschka.^{6,9} This diacid was cyclized to **11** under conditions previously reported.^{6,9} The tetraketone **11** was then stirred in borane-THF³ to provide a 92% yield of stereoisomeric tetrols represented by structure **12**¹⁸ (Scheme III). The mixture of tetrols was then heated in refluxing HMPA^{3,19} for 48 h to give staurane-2,5,8,11-tetraene (**1**)²⁰ (80%) accompanied by the bridgehead alkene **13**²¹ (20%) in 61% overall yield. The tetraene **1** was



separated from **13** by flash chromatography. The solid that resulted was triturated with pentane and purified further by sublimation. Staurane-2,5,8,11-tetraene (**1**) is a white solid (mp 90 °C, sealed capillary) which will sublime on standing. The proton NMR spectrum of **1**, as expected, is very simple consisting of two singlets at δ 3.48 and 5.33. The IR spectrum of **1** is completely consistent with the assigned structure; moreover, the carbon NMR spectrum [δ (CDCl₃) 66.00 (s), 66.36 (d), 131.83 (d)] is definitive for a molecule with such *D*_{2d} symmetry.

The reason for the successful conversion of **11** into **12** without retro-aldol fragmentation can be readily discerned from the mechanism of diborane reduction, as illustrated in Scheme IV. Since the reduction is run in the absence of strong nucleophiles, the conversion of **14** into **15** can occur without carbon-carbon bond cleavage.¹¹ Rupture of the O-BH₂ bond (see **15**) to permit a retro-aldol reaction would generate the high-energy ⁺BH₂ species (see **16**) and hence does not take place. The diborane-THF reduction of **11** is significant for it has recently been employed for the reduction of other β -dicarbonyl systems related to **14**.¹⁶ Since cleavage of the β -dicarbonyl carbon-carbon bonds of 2,8-dioxo-substituted *cis*-bicyclo[3.3.0]octanes (see **11** and **14**) can now be completely avoided, this method represents an important

advance in the use of the condensation of 1,2-dicarbonyl compounds with **5** for the preparation of polyquinanes and polyquinenes.

The successful synthesis of **1** from **4** and **5** shows conclusively that the reaction of 1,2-dicarbonyl compounds with **5** serves not only as a route to natural products²² and polyquinanes^{4,23} but also provides a facile approach to polyquinenes. The 3,4-disposition of the two carbonyl groups (see **7** and **11**) in the diquinane framework is responsible for the simplicity of this approach. Research is in progress at present to study the chemistry of this tetraene **1**, as well as that of its bridgehead isomer **13**.

Acknowledgment. This research was supported by a grant from the National Science Foundation (CHE-7910302) and by the donors of the Petroleum Research Fund, administered by the American Chemical Society. We thank Frank Laib and Mary Rodgers for excellent technical assistance and Noel F. Wittaker for mass spectra.

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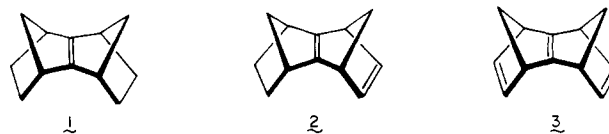
syn-Sesquinorbornatriene and Its Quadricyclane Valence Isomer

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The small deviations from planarity experimentally observed about the double bond in structurally simple norbornenes¹ are recognized to be significantly amplified (to 16–18°) in derivatives of *syn*-sesquinorbornene (**1**).² The phenomenon has commanded



considerable theoretical attention.^{3,4} More recently, introduction of a second double bond as in **2** has been found to enhance the level of downward pyramidal distortion (>20°)⁵ and to be accompanied by substantial deshielding of the central olefinic carbon

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(2) (a) Watson, W. H.; Galloy, J.; Bartlett, P. D.; Roof, A. A. M. *J. Am. Chem. Soc.* **1981**, *103*, 2022. (b) Paquette, L. A.; Charumilind, P.; Böhm, M. C.; Gleiter, R.; Bass, L. S.; Clardy, J. *Ibid.* **1983**, *105*, 3136. (c) Paquette, L. A.; Hayes, P. C.; Charumilind, P.; Böhm, M. C.; Gleiter, R.; Blount, J. F. *Ibid.* **1983**, *105*, 3148. (d) Paquette, L. A.; Hsu, L.-Y.; Gallucci, J. C.; Korp, J. D.; Bernal, I.; Kravetz, T. M.; Hathaway, S. J. *Ibid.* **1984**, *106*, 5743.

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(5) (a) Paquette, L. A.; Green, K. E.; Gleiter, R.; Schäfer, W.; Gallucci, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 8232. (b) Bartlett, P. D.; Combs, G. L., Jr. *J. Org. Chem.* **1984**, *49*, 625.

(17) Deshpande, M.; Jawdoskiuk, M.; Cook, J. M., unpublished results.

(18) One of the tetrols has been crystallized and characterized: mp 228–229 °C; ¹³C NMR (CD₃OD) δ 42.33 (t), 49.38 (d), 69.75 (s), 69.91 (d), 78.31 (d); mass spectrum (CI/CH₄), *m/e* 241 (M + 1, 8), 223 (5.5), 205 (33.5), 187 (100), 169 (33). The remainder of the material, an oil, has been characterized by IR, NMR, and mass spectroscopy, as well as by high-resolution mass spectrometry.

(19) Monson, R. S. *Tetrahedron Lett.* **1971**, 567. Monson, R. S.; Priest, D. N. *J. Org. Chem.* **1971**, *36*, 3826. Lomas, J. S.; Sagatys, D. S.; Dubois, J.-E. *Tetrahedron Lett.* **1972**, 165.

(20) **1**: mp 90 °C (sealed capillary); IR (KBr) 3070, 2900, 1610 cm⁻¹ (weak); ¹H NMR (CDCl₃) δ 3.48 (s, 4 H) and 5.33 (s, 8 H); mass spectrum (EI), *m/e* 168 (M⁺, 73), 167 (100), 166 (17), 165 (53); high-resolution mass spectrum calcd for C₁₃H₁₂ 168.0939; found 168.0958.

(21) **13**: This compound, an oil available in only small quantities, has been characterized by mass spectrometry and ¹³C NMR spectroscopy. All other compounds gave satisfactory CH analysis and/or high-resolution mass spectra.

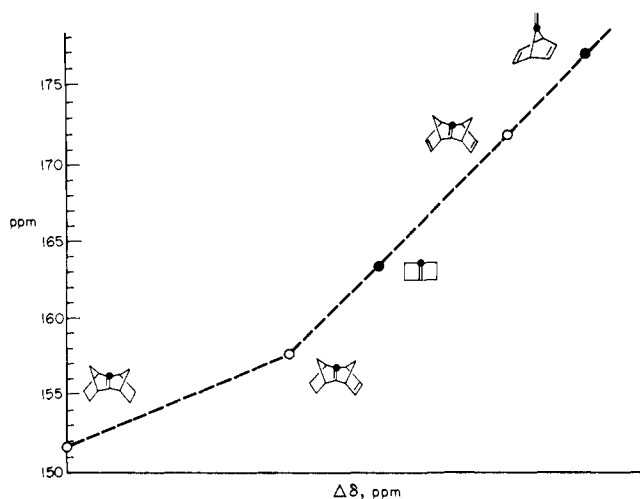
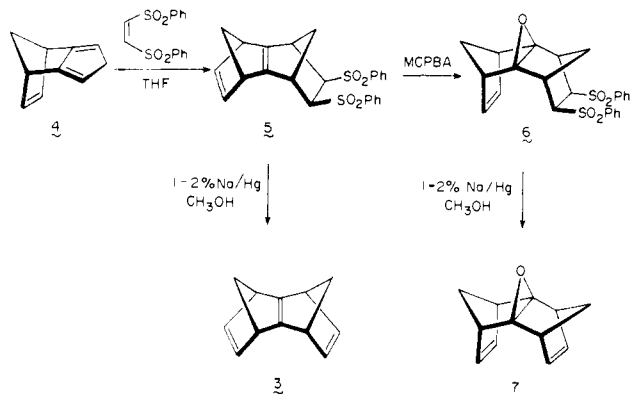


Figure 1. Plot showing ^{13}C chemical shift variation for carbon atoms comprising variously strained (and polarized) double bonds.

atoms (Figure 1) and a heightened sensitivity to triplet oxygen.⁶ As the maximally unsaturated member of this series, the title compound, **3**,⁷ commands special interest. This triene lacks sterically demanding endo substituents and likely will experience increased dihedral angle deformation about the central of its three parallel double bonds in an effort to accommodate the increased strain energy. Thus, **3** could represent the extreme example of π pyramidalization. This and the latent prospect of through-space interaction leads one to anticipate that **3** should exhibit unusual chemical and spectroscopic properties. The synthesis and characterization of this hydrocarbon are herein described.

The viable route took advantage of the known predilection of **4** for below-plane Diels–Alder capture.⁸ Condensation with (*Z*)-1,2-bis(phenylsulfonyl)ethylene⁹ in oxygen-free tetrahydrofuran solution (20 °C, 2 days, Ar atmosphere) led to the precipitation of **5**¹⁰ as an air-sensitive white solid, mp 222 °C dec (82%). Characterization of **5** as the syn isomer was achieved by peracid oxidation to epoxide **6**, mp 224 °C dec.¹¹ Since this



(6) Paquette, L. A.; Carr, R. V. C. *J. Am. Chem. Soc.* **1980**, *102*, 7228.

(7) *syn*-1,4,5,8-Tetrahydro-1,4,5,8-dimethanonaphthalene, which we herein trivialize to *syn*-sesquinorbornatriene in line with precedent (Bartlett, P. D.; Blakeney, A. J.; Kimura, M.; Watson, W. H. *J. Am. Chem. Soc.* **1980**, *102*, 1383). Following completion of this work, we have learned of the preparation of *anti*-sesquinorbornatriene (De Lucchi, O. University of Padova, Italy).

(8) (a) Paquette, L. A.; Carr, R. V. C.; Böhm, M. C.; Gleiter, R. *J. Am. Chem. Soc.* **1980**, *102*, 1186. (b) Böhm, M. C.; Carr, R. V. C.; Gleiter, R.; Paquette, L. A. *Ibid.* **1980**, *102*, 7218.

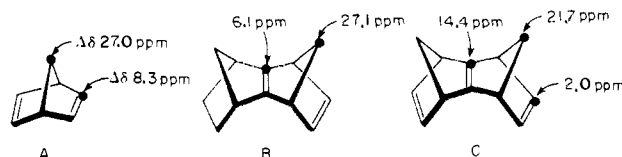
(9) De Lucchi, O.; Lucchini, V.; Pasquato, L.; Modena, G. *J. Org. Chem.* **1984**, *49*, 596.

(10) The structure assigned to each new compound was in accord with its infrared, 300-MHz ^1H NMR, ^{13}C NMR, and high-resolution mass spectra. Key intermediates have also given acceptable combustion analysis data. All recorded yields are based upon isolated material that was >97% pure and are not maximized.

(11) Air oxidation of **5** also gave **6**, but much less efficiently and with higher levels of byproduct contamination.

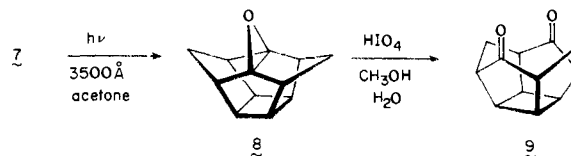
transformation is accompanied by shielding of both apical methylene bridge carbons in **6** (44.43 and 43.99 ppm) relative to **5** (48.24 and 46.94 ppm), these centers must simultaneously experience the magnetic anisotropy effects of a proximate oxirane oxygen.¹²

With the structure and stereochemistry of **5** secure, suitable desulfonylation conditions were sought. Whereas use of 6% sodium amalgam induced destruction of this substrate, recourse to a less concentrated reagent (1–2% Na) proved satisfactory. Rigorous exclusion of oxygen during reaction and in all subsequent operations resulted in smooth conversion to **3** (48%), an extremely sensitive clear oil. Its ^{13}C NMR spectrum in CDCl_3 (172.14, 140.32, 69.12, 50.02) proved particularly informative. For reference purposes, introduction of a second double bond into norbornene produces *downfield* shifts in both the olefinic and apical carbon atoms (see A).¹³ Comparable effects have been noted



when progressing from **1** to **2** (B).⁶ Upon insertion of the third double bond, shifts are induced in the same direction, but these are of appreciably different magnitude (C). Since the extent of electron transfer from the σ orbitals of the methano bridge to the antibonding orbitals of the π bonds is nonregular (Figure 1), **3** is very likely more pyramidal than **2**. Relevantly, the signal for its central olefinic carbons is significantly downfield of that observed for $\Delta^{1,4}$ -bicyclo[2.2.0]hexene,¹⁴ the level of deshielding surpassing that reported for any simple olefinic resonance. It is exceeded only by that of C7 in methylenenorbornadiene whose external double bond is known to be strongly polarized¹⁵ and therefore perturbed by a different mechanism.

Whereas simple air oxidation of **3** gives rise to several products, access to epoxy diene **7** (mp 75 °C) can be gained instead by reductive desulfonylation of **6** (46%). In actuality, purification of **7** is not required prior to its conversion to **8** (mp 126 °C) via photocyclization (Rayonet, 3500-Å lamps, acetone). This highly strained cage molecule is readily cleaved with periodic acid in aqueous methanol to the known diketone **9**.¹⁶ This five-step



sequence constitutes a particularly expedient route to [4]-peristylane-2,4-dione.

Along different lines, sensitized irradiation of **5** in dichloromethane solution (PhCOCH_3 , 450-W Hanovia lamp) successfully produced the air-stable quadricyclane disulfone **10** (57%). This substance is a colorless solid, which melts with decomposition at 216 °C. Treatment of **10** with 1–2% sodium amalgam afforded the structurally unusual olefin **11** (36%), a thermally sensitive and highly volatile oil that solidifies below room temperature. The ^{13}C chemical shifts of the cyclopropyl carbon atoms in **11** (35.9 and 15.12 ppm) appear normal for a quadricyclane.¹³ This seems

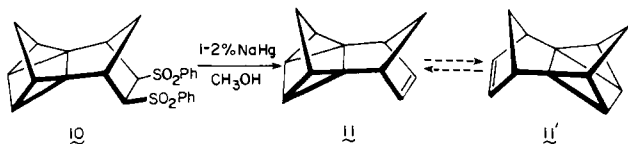
(12) (a) Paquette, L. A.; Carr, R. V. C.; Arnold, E.; Clardy, J. *J. Org. Chem.* **1980**, *45*, 4907. (b) Paquette, L. A.; Kravetz, T. M.; Hsu, L.-Y., submitted for publication and relevant references cited in these papers.

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to fit quite well with the absence of any obvious reason to deform additionally the hybridization of these atomic centers, quite unlike the situation in **3**. The interesting question of whether **11** and the corresponding anti isomer are capable of unprecedented degenerate quadricyclane-quadricyclane rearrangement is currently under active investigation.

Acknowledgment. We are grateful to the National Institutes of Health for the financial support of this work (Grant CA-12115) and Prof. Harald Günther for a helpful exchange relating to ^{13}C NMR shift theory.

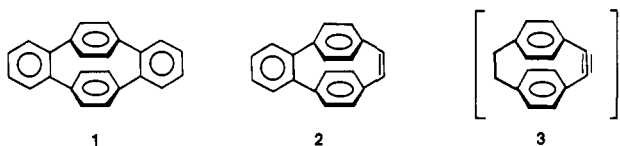
Synthesis of 1,2:7,8-Dibenzo[2.2]paracyclophane and 1,2-Benzo-7,8-naphtho[2.2]paracyclophane¹

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1,2:7,8-Dibenzo[2.2]paracyclophane (**1**) has attracted attention



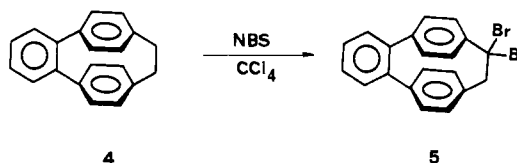
as a theoretically interesting but unknown substance.³ Structurally, cyclophane **1** possesses orthogonal benzene rings and therefore is expected to exhibit interesting chemical as well as physical properties. Moreover, it may serve as a novel ligand for metal complexation and it is also possible that it may behave as a host molecule in clathrate inclusion phenomenon.⁴

In 1978, Jacobson and Boekelheide reported the isolation and characterization of **2**,⁵ and in 1982, Psiorz and Hopf reported the identification of an elusive intermediate **3**.⁶ On the basis of their strategies, we here report the successful synthesis of **1** as well as 1,2-benzo-7,8-naphtho[2.2]paracyclophane (**11**).

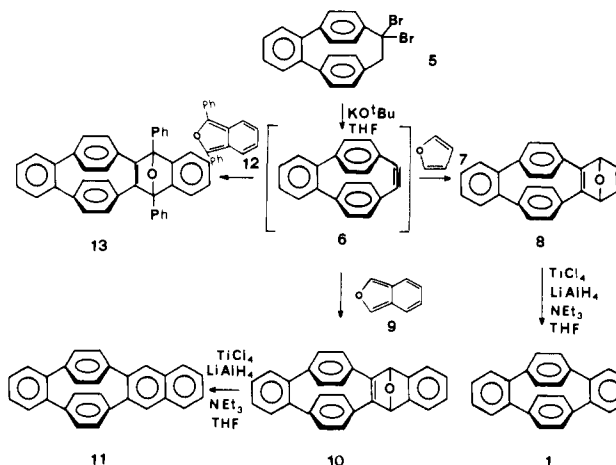
Treatment of the known cyclophane **4**⁵⁻⁸ with a large excess of *N*-bromosuccinimide gave the dibromide **5** in 30% yield (Scheme I), isolated as white crystals,⁹ mp 223–225 °C; ^1H NMR δ 4.71 (s, 2 H), 6.50–6.70 (m, 4 H), 6.70–7.30 centered at 7.00 (AA'XX', 4 H), 7.30–7.70 (A₂B₂, 4 H).

Dehydrobromination of **5** with KO-*t*-Bu in THF led presumably to the fugitive cyclophene **6** which was trapped in situ with furan (**7**) to yield the endoxide **8** in 15% yield (Scheme II): mp 203–205 °C, ^1H NMR δ 5.83 (s, 2 H), 6.10–6.60 centered at 6.36

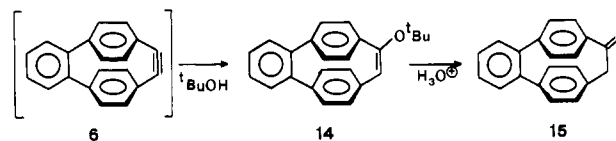
Scheme I



Scheme II



Scheme III



(AA'XX', 4 H), 6.55 (AA'XX', 4 H), 7.40–7.60 (A₂B₂, 4 H), 7.49 (s, 2 H).⁹ Similarly, cyclophene **6** underwent the Diels–Alder reaction with isobenzofuran (**9**)¹⁰ to provide the endoxide **10** in 70% yield: mp 247–249 °C; ^1H NMR δ 5.70–6.50 centered at 6.08 (AA'XX', 4 H), 6.10 (s, 2 H), 6.71 (s, 4 H), 7.05–7.55 (m, 8 H).⁹ Reaction of **6** with 2,5-diphenylisobenzofuran (**12**) yielded **13** in 47% yield: mp 270 °C dec; ^1H NMR δ 6.61–6.80 (m, 8 H), 7.20–7.80 (m, 18 H).⁹ Ketone **15** was isolated as a side product in every dehydrobromination reaction (Scheme III). We anticipated that the strained cyclophene **6** would react with *t*-BuOH during the dehydrobromination step and provide the enol–ether **14**, which was hydrolyzed to the ketone **15** during acidic workup of the reaction mixture.¹¹

The intermediacy of **6** is indirectly confirmed by the fact that **2** gave no Diels–Alder adduct with furan (**7**) at room temperature. Thus the alternative mechanism which involves the initial cycloaddition between furan (**7**) and the vinyl bromide (generated by eliminating one molecule of HBr from **5**) and the subsequent elimination of the second HBr to give **8** is rather unlikely, although further confirmation is necessary.

Deoxygenation of **8** by low valent titanium generated by reducing TiCl₄ with LiAlH₄¹²⁻¹⁴ gave a 15% yield of **1**, which sublimed at 275 °C: ^1H NMR δ 6.69 (s, 8 H), 7.42–7.70 (A₂B₂, 8 H).⁹ Similarly, **10** was converted to **11** in 17% yield: mp 278 °C dec; ^1H NMR δ 6.65–6.80 (A₂X₂, 8 H), 7.45–7.62 (A₂B₂, 4 H), 7.65–8.00 (A₂B₂, 4 H), 8.10 (s, 2 H).⁹ The endoxide **13** resists deoxygenation; hence no reasonable product has been isolated.

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