retention times and nmr spectral comparison with authentic specimens.

The assignment of the *trans* configuration **1a** to this tricyclohexane follows from the method of synthesis and the fact that the precursor **7** has the C_8 carbon locked *trans* to the fused cyclopropyl ring.

In preliminary experiments we have observed that **1a** is recovered unchanged after 2 hr at 100°; however, it is converted to *ca.* 50% 1,4-cyclohexadiene in 3 hr at 165°. Highly strained bicyclo[2.1.0]pentane and bicyclo[1.1.0]butane[14] have thermal rearrangement 3-hr half-lives at *ca.* 270[15] and 214°,[16] respectively. This stability comparison indicates that the intrinsic strain of **1a** is very high.

Further investigation of the physical and chemical properties of **1a** is in progress. We also are investigating the possibility of converting **8** to the *cis* isomer **1b**.

Acknowledgments. We express appreciation to the National Science Foundation for support of this work with Grant GP-6923. We thank the University of Utah Research Fund for photolysis equipment and the National Institutes of Health for purchase of a gas chromatograph through Biomedical Sciences Support Grant No. 1805FR07092-01.

---

(14) R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, and M. Pomerantz, *J. Am. Chem. Soc.*, **90**, 4315 (1968).

(15) Estimated from the data of M. L. Halberstadt and J. P. Chesick, *ibid.*, **84**, 2688 (1962).

(16) Estimated from the data of H. M. Frey and I. R. D. Stevens, *Trans. Faraday Soc.*, **61**, 90 (1965).

Evan L. Allred, Jerald C. Hinshaw
Department of Chemistry, University of Utah
Salt Lake City, Utah 84112

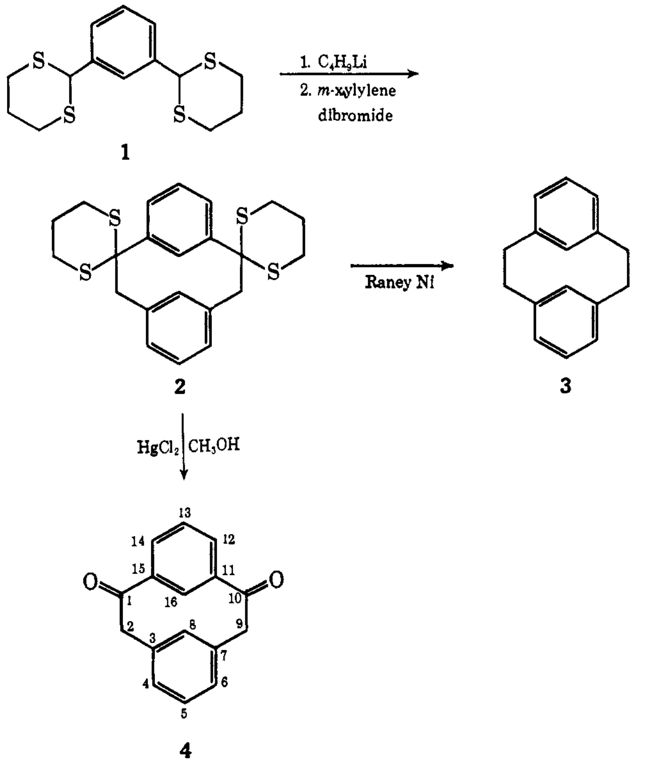
Received September 11, 1968

A New Method of Synthesis of Cyclophanes. [2.2]Metaparacyclophane-1,9-diene

Sir:

Of the methods investigated for preparing cyclophanes, the Wurtz reaction has proved to be the most general and useful procedure, especially for cyclophanes having a two-carbon bridge.[1,2] The yields in a Wurtz dimerization are modest, usually being about 30%, and the choice of compounds is very limited due to the severity of the reaction conditions.[3,4] Also, the Wurtz reaction has generally been limited to the synthesis of symmetrical cyclophanes.[5] In our studies on the synthesis of unusual aromatic molecules,[6–8] we have been concerned with the syntheses of [2.2]-metacyclophanes as intermediates and how to introduce unsaturation into the two-carbon bridges.[9] We now report a method that appears to be general for the synthesis of cyclophanes and which retains functionality in the bridges that can later be converted to olefinic unsaturation.

Corey and Seebach introduced the use of 1,3-dithianes for the synthesis of ketones,[10] and recently they have described the stepwise synthesis of diketones.[11] We have investigated the reaction of the dianion derived from isophthalaldehyde bis(1,3-propanedithioacetal) (**1**) with *m*-xylylene dibromide and have found that the corresponding [2.2]metacyclophane derivative (**2**) is formed in 28% yield. As proof of structure, **2** was treated with Raney nickel and converted in 68% yield to [2.2]metacyclophane (**3**), identical in all respects with an authentic sample.



The preparation of **1** was readily accomplished in quantitative yield by heating isophthalaldehyde with 1,3-propanedithiol in benzene containing a small quantity of *p*-toluenesulfonic acid. After recrystallization from a benzene–hexane mixture, **1** separated as white needles, mp 129.0–129.5°.[12] Formation of the metacyclophane **2** was carried out by treating **1** in tetrahydrofuran at −30° under a nitrogen atmosphere with 2 mol of *n*-butyllithium followed by dropwise addition of a solution of *m*-xylylene dibromide in tetrahydrofuran. After isolation and chromatography over silica gel, **2** was recrystallized from a benzene–hexane mixture to give white rhombic crystals, mp 242.0–243.5°. In addition to its conversion to [2.2]metacyclophane, **2** was hydrolyzed by heating with mercuric chloride in a methanol–tetrahydrofuran mixture in a sealed tube at 130° for 7 hr, followed by boiling the resulting dimethyl ketal in a solution of acidic aqueous acetone. This gave the diketone **4** in 42% yield as white needles, mp 144.0–144.5°. With regard to the spectral properties of **4**, the carbonyl frequency in the infrared is normal, appearing at 5.90 μ; the signals for the protons at the

---

(1) R. W. Griffin, Jr., *Chem. Rev.*, **63**, 45 (1963).

(2) B. H. Smith, "Bridged Aromatic Compounds," Academic Press Inc., New York, N. Y., 1964.

(3) S. Akabori, T. Sato, and K. Hata, *J. Org. Chem.*, **33**, 3277 (1968).

(4) V. Boekelheide and R. W. Griffin, Jr., *ibid.*, in press.

(5) For an exception, though, see V. Boekelheide, C. Ramey, E. Sturm, T. Miyasaka, and B. A. Hess, Jr., *ibid.*, in press.

(6) W. S. Lindsay, P. Stokes, L. G. Humber, and V. Boekelheide, *J. Am. Chem. Soc.*, **83**, 943 (1961).

(7) V. Boekelheide and J. B. Phillips, *ibid.*, **89**, 1695 (1967).

(8) V. Boekelheide and T. Miyasaka, *ibid.*, **89**, 1709 (1967).

(9) H. Blaschke and V. Boekelheide, *ibid.*, **89**, 2747 (1967).

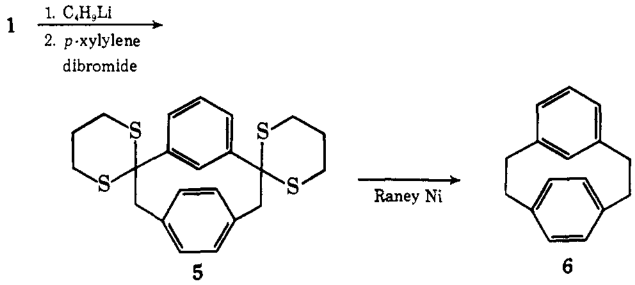
(10) E. J. Corey and D. Seebach, *Angew. Chem.*, **77**, 1134, 1135 (1965).

(11) D. Seebach, N. R. Jones, and E. J. Corey, *J. Org. Chem.*, **33**, 300 (1968).

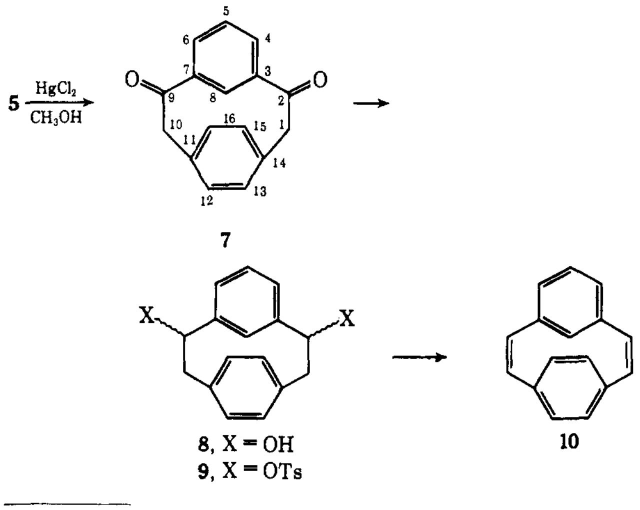
(12) Satisfactory elemental analyses have been obtained for all new compounds.

8 and 16 positions in the nmr spectrum appear as broad singlets at τ 5.79 and 4.10.

The alkylation of **1** was then investigated using *p*-xylylene dibromide. When the reaction was carried out as before, the yield of the desired [2.2]metaparacyclophane (**5**) was only 1.9%. However, when solutions of the dianion of **1** and of *p*-xylylene dibromide in tetrahydrofuran were added separately, but simultaneously, to a large volume of boiling tetrahydrofuran stirred vigorously in a Morton flask, **5** was isolated, after recrystallization from a benzene-hexane mixture, as white rhombic crystals, mp 244–246°, in 36% yield. Desulfurization with Raney nickel was carried out to give [2.2]metaparacyclophane (**6**), whose melting point (79–81°) and other physical properties are in accord with those described by Cram, *et al.*[13]



Dewhirst and Cram have described a synthesis of [2.2]paracyclophane-1,9-diene, an extreme example of inhibition of resonance resulting from the geometry of the molecule.[14] It was of interest, therefore, to see whether we could utilize the dithiane functions of **5** to introduce unsaturation and prepare the analogous diene **10**. Treatment of **5** with mercuric chloride and methanol, as before, led to the diketone **7** as white crystals, mp 129.5–129.8°, in 91% yield. As with **4**, the carbonyl frequency in the infrared was not unusual, appearing at 5.90 μ, and the signal in the nmr spectrum for the internal proton at the 8 position was at τ 4.36. Reduction of **7** with sodium borohydride gave a mixture of diastereoisomers (**8**) as fine white needles, mp 186–191°, in 97% yield. This was converted to the corresponding ditosylate **9**, isolated as white needles, mp 178–184°, in 95% yield. Treatment of **9** with potassium *t*-butoxide in *t*-butyl alcohol then gave [2.2]-metaparacyclophane-1,9-diene (**10**) as white crystals, mp 58–59°, in 68% yield.



As proof of structure, **10** readily absorbed 2 mol of hydrogen on reduction over palladium to give **6**, identical in all respects with the sample prepared previously. The mass spectrum of **10** showed the parent molecular ion at *m/e* 204, as expected. The ultraviolet absorption spectrum of **10** in hexane showed a maximum at 232.5 mμ (log ϵ 4.40) with a shoulder at 260 mμ (log ϵ 4.02) but with no absorption above 300 mμ. In the nmr (CCl_4), **10** showed doublets at τ 2.83 (2 H, J = 10.0 cps) and 3.40 (2 H, J = 10.0), a multiplet at τ 3.00–3.40 (7 H), and a broad singlet at τ 5.71 (1 H). Although the ultraviolet absorption bands of **10** are of high intensity, they occur at shorter wavelength than for either [2.2]paracyclophane-1,9-diene[14] or 8,16-dimethyl-[2.2]metacyclophane-1,9-diene.[15] A detailed interpretation of the nmr spectrum of **10** is best made when the precise geometry of **10** is known from a single-crystal X-ray analysis.

The synthesis of cyclophanes by this method appears to proceed in equal or better yields than the Wurtz reaction and has the advantage of allowing the synthesis of unsymmetrical cyclophanes containing functionality for later transformations. The use of this procedure for the synthesis of a variety of interesting molecules seems possible, and exploratory work along these lines is being continued.

Thomas Hylton, V. Boekelheide[16]
Department of Chemistry
University of Oregon, Eugene, Oregon 97403

Received September 23, 1968

---

[13] D. J. Cram, R. C. Helgeson, D. Lock, and L. A. Singer, *J. Am. Chem. Soc.*, **88**, 1324 (1966).

[14] K. C Dewhirst and D. J. Cram, *ibid.*, **80**, 3115 (1958).

[15] H.-R. Blattmann, Ph.D. Dissertation, Federal Institute of Technology, Zurich, Switzerland, 1967.

[16] We express our gratitude to the National Science Foundation for their support of this investigation.

Strain Energy in Bicyclo[3.3.1]non-1-ene[1]

Sir:

Recent syntheses of bicyclo[3.3.1]non-1-ene (**1**),[2,3] of interest in connection with limitations in the applicability of Bredt's rule, have prompted us to measure the strain energy present in this molecule. A sample of the substance was prepared by Wiseman's procedure,[4] purified by vapor chromatography on a Carbowax on Chromosorb P column, and flash distilled under vacuum prior to use. The material showed all of the spectral properties that have been reported for this compound.[2,3]

Bicyclo[3.3.1]non-1-ene (**1**) reacts rapidly with acetic acid in the absence of catalysts to furnish 1-acetoxy-bicyclo[3.3.1]nonane (**2**).[5] The quantitative nature of the reaction was demonstrated by comparison of the vapor chromatographic behavior and the infrared and

---

[1] Support of this work through National Science Foundation Grant GP 203 is gratefully acknowledged.

[2] J. A. Marshall and H. Faubl, *J. Amer. Chem. Soc.*, **89**, 5965 (1967).

[3] J. R. Wiseman, *ibid.*, **89**, 5966 (1967).

[4] We are indebted to Dr. Wiseman for supplying details of his experimental work in advance of publication.

[5] Product recovered from calorimetric runs by distillation of the acetic acid solvent and vapor chromatography of the resulting residue showed infrared and nmr absorption identical with that of an authentic sample. It is a pleasure to acknowledge the assistance of Professor W. G. Dauben in furnishing reference spectra.