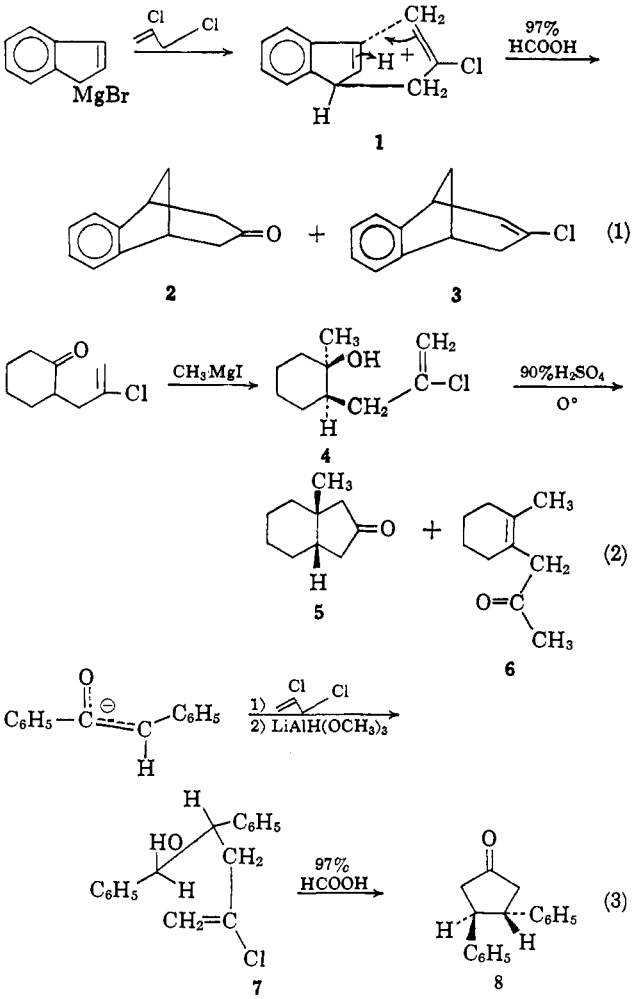


from indene.[2] The cyclization of **4** (presumably the alkyl groups are *trans*[3]) at 0° in 90% sulfuric acid for 1 hr produced *cis*-8-methyl-2-hydrindanone (15%), the stereochemistry being assigned by comparison with authentic *trans*-8-methyl-2-hydrindanone,[4] from which it differed. In particular, the nmr methyl signal in **5** had a half-height width only *ca.* one-half that of the corresponding angular methyl group in the *trans* isomer, in which long-range "*W*" coupling is more favorable stereoelectronically.[5] Sequence 2 thus suggests potential routes to 16-keto steroids with *cis* C/D ring fusions and A-nor steroids if one begins with appropriate precursors. In eq 3, the cyclization of an acyclic precursor is examined. Reduction of α-(β-chloroallyl)deoxybenzoin with lithium trimethoxyaluminohydride[6] produces a single racemic alcohol (**7**), presumably[7] *erythro*. Formolysis of **7** proceeded to give quite pure *trans*-3,4-diphenylcyclopentanone (30%); no *cis* isomer was found.[8]

(2) Ketone **2** was previously obtained in only 4–6% yield from benzonorbornene in several steps (P. T. Lansbury, R. E. MacLeay, and N. T. Boggs, unpublished results) involving dihalocarbene addition, ring expansion, etc., as in the preparation of bicyclo[3.2.1]octan-3-one from norbornene (W. Krauss, *Chem. Ber.*, 97, 2719 (1964).

(3) T. D. Nevitt and G. S. Hammond, *J. Am. Chem. Soc.*, 76, 4124 (1954).

(4) We thank Professor Carl Djerassi for an authentic sample.

(5) K. L. Williamson, T. Howell, and T. A. Spencer, *J. Am. Chem. Soc.*, 88, 325 (1966).

(6) H. C. Brown and C. J. Schoaf, *ibid.*, 86, 1079 (1964).

(7) D. J. Cram and F. A. Abd Elhafez, *ibid.*, 74, 5828 (1952).

(8) Whether the cyclization **7** → **8** is a stereospecific or a stereoselective process requires study of (±)-*threo*-**7** also. Synthesis and cyclization of the *threo* alcohol is presently underway.

A typical experimental procedure for preparation of 3,5-(*o*-phenylene)cyclohexanone (**2**) is described below. A solution of 1-indenylmagnesium bromide (*ca.* 0.5 mole) was prepared in tetrahydrofuran by adding indene to ethylmagnesium bromide. This was slowly added to an equimolar amount of 2,3-dichloropropene in THF at −10°. After stirring for 1 hr at 0°, the reaction mixture was hydrolyzed and worked up in a typical manner. Distillation afforded 48% of 1-(2-chloroallyl)indene (**1**), bp 79–80° (2.0 mm), whose nmr spectrum was consistent with the 1-alkylindene structure[9] and verified the absence of the isomeric 3-substituted indene. Fifteen grams of **1** was gradually added (5 min) to 900 ml of stirred, refluxing 97% formic acid, and the mixture was then refluxed for 1 hr. Hydrolysis with 1 l. of ice water and extraction with ether, followed by washing with bicarbonate, drying, and solvent removal, resulted in 14 g of oily product. Alumina chromatography gave 29% of **3** (eluted with petroleum ether) and 59% of **2** (eluted with 15:85 ether–petroleum ether), mp 64–66°, characterized by elemental analysis, spectroscopy, and comparison with independently prepared material.[2] A similar formolysis procedure was employed for cyclizing **7** to **8**. However, this technique did not work well with **4**, necessitating the use of cold 90% sulfuric acid.

The above examples[10] show how the three-carbon segment of 2,3-dichloropropene can be built into cyclic ketones. We hope that further studies, which include the incorporation of heteroatoms into the ring, will demonstrate versatility of this ring-forming sequence comparable to the well-known Robinson[11] and Wichterle[12] annelation schemes.

(9) A. Bosch and R. K. Brown, *Can. J. Chem.*, 42, 1718 (1964).

(10) Reported yields are from pioneering experiments and hopefully will be improved when various conditions, *e.g.*, cyclization medium and reaction temperature, are checked.

(11) (a) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, New York, N. Y., 1965, pp 210–213; (b) E. D. Bergmann, D. Ginsburg, and R. Pappo, *Org. Reactions*, 10, 179 (1959).

(12) J. A. Marshall and D. J. Schaeffer, *J. Org. Chem.*, 30, 3642 (1965), and references cited therein.

(13) Alfred P. Sloan Foundation Fellow, 1963–1967.

Peter T. Lansbury,[13] Everett J. Nienhouse
Department of Chemistry
State University of New York at Buffalo, Buffalo, New York
Received July 18, 1966

A New Fragmentation Reaction. The Synthesis of 1-Methyl-*trans,trans*-1,6-cyclodecadiene

Sir:

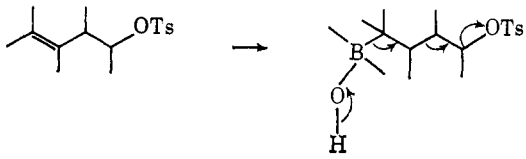
Medium-ring compounds provide a class of chemically interesting and synthetically challenging structures.[1] Widespread interest in these substances has stimulated the development of new methods for their efficient synthesis.[2] In this connection, we decided to examine the sequence depicted by **5** → **6** → **7** as a

(1) Reviews: J. Sicher, *Progr. Stereochem.*, 3, 202 (1962); A. C. Cope, M. M. Martin, and M. A. McKervey, *Quart. Rev.* (London), 20, 119 (1966).

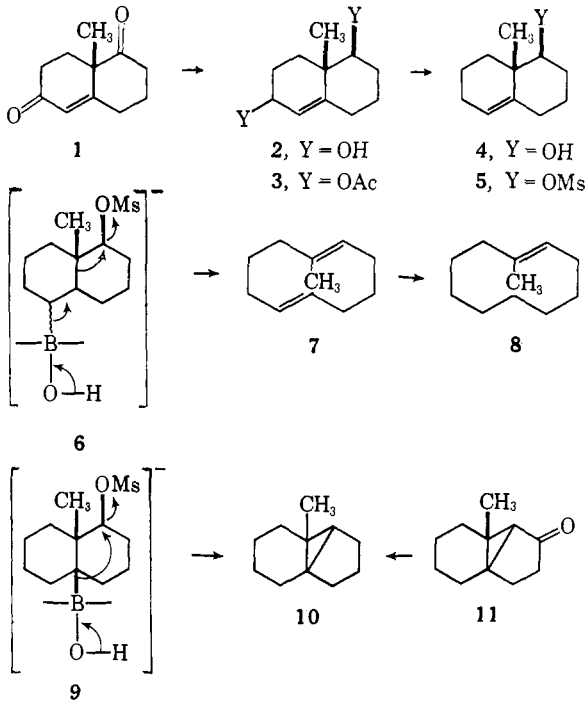
(2) (a) P. S. Wharton, *J. Org. Chem.*, 26, 4781 (1961); (b) P. S. Wharton and G. A. Hiegel, *ibid.*, 30, 3254 (1965); (c) E. J. Corey, R. B. Mitra, and H. Uda, *J. Am. Chem. Soc.*, 86, 485 (1964); (d) P. S. Wharton, Y. Sumi, and R. A. Kretchmer, *J. Org. Chem.*, 30, 234 (1965); (e) E. J. Corey and E. Hamanaka, *J. Am. Chem. Soc.*, 86, 1641 (1964); (f) E. J. Corey and A. G. Hortmann, *ibid.*, 87, 5736 (1965); (g) J. A. Marshall and C. J. V. Scanio, *J. Org. Chem.*, 30, 3019 (1965).

possible route to 1-methyl-*trans*,*trans*-1,6-cyclododecadiene (**7**) and related compounds.[3] The striking success of initial endeavors along these lines, plus the novelty and possible generality of the fragmentation sequence (Scheme I) to other homoallylic sulfonates (*e.g.*, cholesteryl tosylate), prompts this announcement of our preliminary findings.

Scheme I



Unsaturated dione **1**[4] was converted to the unsaturated alcohol **5** [bp 66–71° at 0.05 mm: λ_{max}^{film} 2.96 (OH), 9.45, 9.55, 10.00, and 10.62 μ; $\delta_{TMS}^{CCl_4}$ = 5.36 (C=CH), 3.45–3.05 (CHOH), and 0.97 ppm (angular CH_3)] *via* a three-step sequence involving reduction with lithium aluminum hydride, acetylation of the resulting diol **2**,[5] and hydrogenolysis of the diacetate **3** with lithium in ethylamine.[6] The methanesulfonate derivative **5** (mp 59–59.5°) was treated with an equi-



molar quantity of 0.4 *M* diborane in tetrahydrofuran, after 2 hr aqueous sodium hydroxide was added, and the mixture was heated to reflux for 1 hr. The hydrocarbons (*ca.* 90% yield after column chromatography) isolated by preparative gas chromatography consisted of an 85:15 mixture of the cyclodecadiene **7** [λ_{max}^{film} 6.94, 10.08, 10.38, 10.82, and 11.90 μ; $\delta_{TMS}^{CCl_4}$ = 5.35–4.85 (vinyl H, unresolved multiplet, 3 H) and 1.53 ppm (vinyl CH_3, 3 H)], and the tricyclodecane **10** [λ_{max}^{film} 9.90, 10.38, 10.60, and 10.95 μ; $\delta_{TMS}^{CCl_4}$ = 0.94 ppm (angular CH_3)].

(3) Several of the previously cited methods lead to medium rings containing *trans*, *trans*-1,5-dienes.[2d-f] However, no direct route to *trans*,*trans*-1,6-dienes has yet been reported.

(4) Obtained from Aldrich Chemical Co., Inc., Milwaukee, Wis.

(5) C. B. C. Boyce and J. S. Whithurst, *J. Chem. Soc.*, 2680 (1960).

(6) *Cf.* A. S. Hallsworth, H. B. Henbest, and T. I. Wrigley, *ibid.*, 1969 (1957).

The strong absorption band at 10.4 μ in the infrared spectrum of diene **7** confirms the *trans* stereochemistry assigned to the disubstituted double bond.[2a] Partial hydrogenation of this diene over platinum in ethanol afforded *trans*-1-methylcyclodecene (**8**),[7] thus establishing the nature of the trisubstituted double bond. The stereochemistry and the location of both double bonds follows from mechanistic considerations. Additional support for the latter assignment was provided by the isolation of methyl 5-oxohexanoate and dimethyl glutarate as the sole products from oxidation of diene **7** ($KMnO_4$–KIO_4)[8] followed by treatment of the acidic material with ethereal diazomethane.

An authentic sample of the minor hydrocarbon product, tricyclodecane **10**, was prepared *via* Wolff–Kishner reduction of the related ketone **11**.[9] Hydrocarbons **7** and **10** gave very similar mass spectra with prominent peaks at *m/e* = 150 (parent), P − 15, P − 57, P − 71, P − 83, and P − 109.

Scheme I depicts one possible mechanism for cleavage of the carbon–boron bond leading to the observed products. Alternatively the tetracoordinated boron species (*e.g.*, **6** and **9**) could undergo displacement on boron by hydroxide. Undoubtedly the driving force for both processes comes from partial ionization of the carbon–oxygen bond of the sulfonic ester.

Judging from analogous cases, the hydroboration of olefin **5** should not be stereoselective.[10] However, this factor would not be expected to influence the conversion of **6** to **7** since both the *cis*- and *trans*-fused isomers of **6** can meet the geometric requirements for β fragmentation.[11] Assuming inversion of configuration at the carbon attached to boron, the *cis*-decalylborane **9** should lead to hydrocarbon **10**.[12] The formation of this particular alkylborane isomer from olefin **5** finds close precedent in a related system.[13]

Acknowledgment. Support of this work through a research grant (GP-4174) from the National Science Foundation is gratefully acknowledged.

(7) *Cf.* J. G. Traynham and W. C. Baird, Jr., *J. Org. Chem.*, 27, 3189 (1962).

(8) *Cf.* R. U. Lemieux and E. von Rudloff, *Can. J. Chem.*, 33, 1701 (1955).

(9) H. E. Zimmerman, R. G. Lewis, J. J. McCullough, A. Padwa, S. W. Staley, and M. Semmelhack, *J. Am. Chem. Soc.*, 88, 1965 (1966).

(10) *Cf.* F. Sondheimer and S. Wolfe, *Can. J. Chem.*, 37, 1870 (1959).

(11) *Cf.* C. A. Grob, IUPAC Kekule Symposium, London, Sept 1958, Butterworth and Co., Ltd., London, 1959, p 114 ff.

(12) For an analogous synthesis of cyclopropanes, see M. F. Hawthorne, *J. Am. Chem. Soc.*, 82, 1886 (1960).

(13) J. A. Marshall, M. T. Pike, and R. D. Carroll, *J. Org. Chem.*, in press. For a possible explanation of the relatively high percentage of anti-Markovnikov hydroboration product obtained from these olefins, see P. Binger and R. Köster, *Tetrahedron Letters*, No. 4, 156 (1961).

(14) Public Health Service Fellow of the National Institute of General Medical Sciences, 1964–present.

James A. Marshall, Gordon L. Bundy[14]
Department of Chemistry, Northwestern University
Evanston, Illinois 60201
Received August 1, 1966

Nucleoside Phosphorothioates

Sir:

A great number of nucleotides with modifications in the sugar or base residue have been synthesized. So far, the only nucleotides modified at the phosphate residue