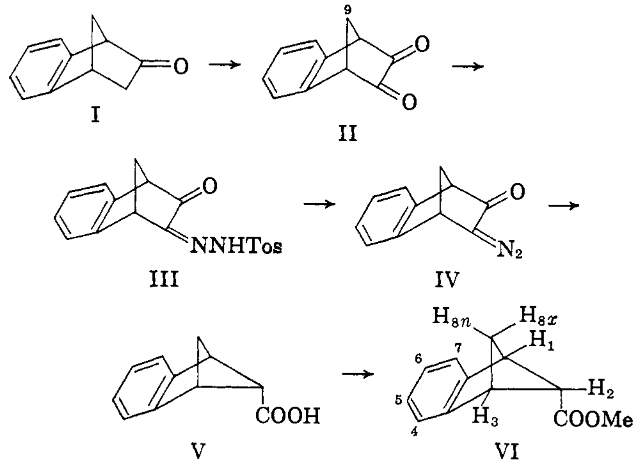
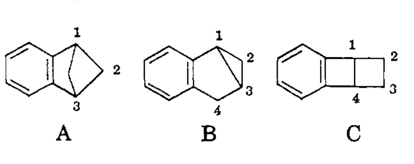
dioxide in boiling xylene for 16 hr produced in about 15% yield the yellow, crystalline diketone II, isolated by distillation at 120–122° (1 mm); mp 85° (cyclohexane); $\nu_{C=O}^{CCl_4}$ 1765 (s) and 1783 (sh) cm^{-1}; nmr in CCl_4[4]:



four Ar–H at τ 2.7 (A_2B_2 system), two C_9–H at τ 6.96 (dt) and 7.36 (dt), and two bridgehead H at τ 6.25 (t). *Anal.* Calcd for $C_{11}H_8O_2$: C, 76.73; H, 4.68. Found: C, 76.83; H, 4.87. The monotosylhydrazone III was generated *in situ* by dissolving II and tosylhydrazine in cold chloroform. The resulting solution was poured through a column of basic alumina, giving in the ether eluate good yields of the α-diazo ketone IV of purity suitable for use in the next step.[5]

An aqueous dioxane solution of IV made weakly alkaline by $NaHCO_3$ was irradiated at room temperature under nitrogen atmosphere for about 25 hr (when evolution of nitrogen ceased) using a 300-w high-pressure mercury vapor lamp, giving an acidic material together with a neutral polymer. After esterification with diazomethane, the material was indicated by vpc to be a mixture of four compounds. The main compound VI was isolated by preparative vpc, followed by distillation, as colorless crystals, mp 58°, $\lambda_{max}^{n\text{-heptane}}$ 260.5 mμ (ε 630), 267 (850), and 274 (930) (no double bond conjugated with benzene ring), in about 10% yield from II. *Anal.* Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43; mol wt, 188. Found: C, 76.28; H, 6.64; mol wt, 186 (vapor phase osmometry, in chloroform). Catalytic hydrogenation of VI over PtO_2 in ethanol did not proceed.

In view of the chemical, nmr, and ultraviolet observation that VI is saturated, it must be derived from one of the three ring systems shown below. The method of preparation suggests that the system A is most probable.



Confirmatory evidence for the indicated structure VI was provided by the nmr spectrum, which showed in CCl_4 four Ar–H at τ 3.0 (A_2B_2 system), one H_2 at τ 6.38 (t), two H_1, H_3 at τ 6.62 (t), one H_{8x} at τ 7.44 (A part of AB system, dt), and one H_{8n} at τ 7.82 (B part of AB system, d), $J_{H_1,H_2} = 2.5$, $J_{H_1,H_{8x}} = 2.5$, $J_{H_1,H_{8n}} \cong 0$, and $J_{H_{8n},H_{8x}} = 6$ cps. The presence of two protons at the bridgeheads, with the symmetrical signal pattern of aromatic protons, excludes the structures substituted at the bridgehead positions in all the systems. Because cyclopropane and its alkyl-substituted derivatives invariably have methylene nmr bands above τ 9.5, the lack of such a band in VI eliminates the system B, unless substituted in the 2 position. Completely symmetrical pattern of the triplet due to the bridgehead protons rules out the 2-substituted B and the 2- or 3-substituted C systems. Wiberg, *et al.*,[6] have reported the spectrum of methyl bicyclo[2.1.1]hexane-*endo*-5-carboxylate (VII). Although the spectrum of VI is considerably shifted to a lower field due to the effect of benzene ring, the shapes of signals and coupling constants of H_1, H_2, H_3, H_{8n}, and H_{8x} correspond well to those of VII. Thus, having eliminated all other possible structures, we must conclude that the compound VI is methyl benzobicyclo[2.1.1]hexene-2-carboxylate. The absence of a long-range coupling between H_{8n} and the C_2 *endo* proton,[1,6] with the vicinal coupling constant $J_{H_1,H_2} = 2.5$ cps, suggests predominantly *endo* configuration of the methoxycarbonyl group.

We plan to prepare derivatives suitable for the study of carbonium ion reactions of this system.

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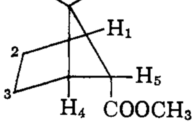
[4] For the description of nmr peaks, s = singlet, d = doublet, dt = doublet of triplets, etc.

[5] Substantially the same procedure was used by Meinwald[1] for the preparation of 3-diazonorcamphors.

[6] K. B. Wiberg, B. R. Lowry, and B. J. Nist, *J. Am. Chem. Soc.*, **84**, 1594 (1962). The shapes of signals and coupling constants in VII were reported: for H_5, a broad band at τ 7.68; for H_1, H_4, τ 7.30, t; for



VII

H_{6x}, a broad band at τ ~8.63; for H_{6n}, τ 9.25, d; $J_{H_1,H_{6x}} = 3.8$ cps; $J_{H_{6n},H_{6x}} = 6.6$ cps.

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A Versatile Synthesis of Cyclic Ketones

Sir:

We wish to report initial examples of a simple synthetic sequence leading to cyclohexanones and cyclopentanones, which may portend a general method for preparing cycloalkanones of various ring size. In essence, one allows 2,3-dichloropropene to react with a nucleophilic reagent to produce a β-chloroallyl derivative; an electrophilic center is subsequently generated in the latter, followed by its intramolecular attack on the vinyl chloride grouping and hydrolysis of the "masked" ketone. This is illustrated below in several examples,[1] wherein carbon nucleophiles are alkylated and a carbonium ion created for cyclization by treatment of derived alcohols or olefin with acid.

The solvolytic cyclization of **1** proceeded in *ca.* 65% yield to ketone **2**, and the 30% of **3** produced could itself be converted to **2** by treatment with 90% sulfuric acid. Thus **2** is obtainable in *ca.* 40% over-all yield

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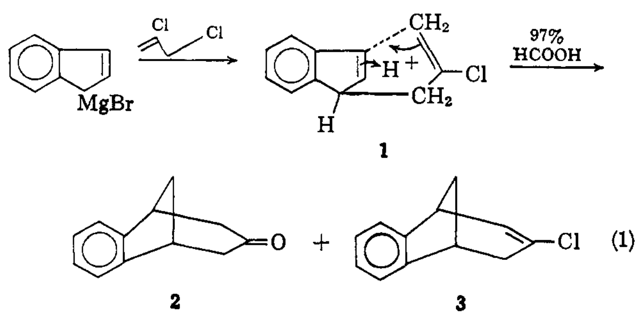
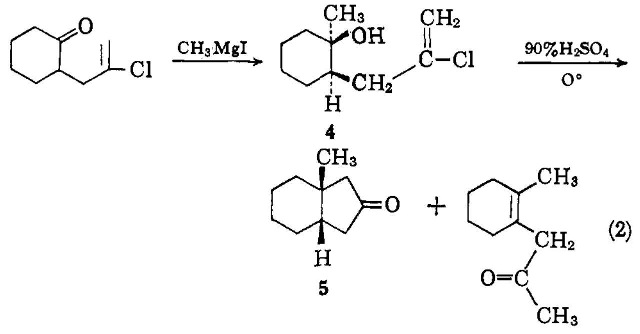
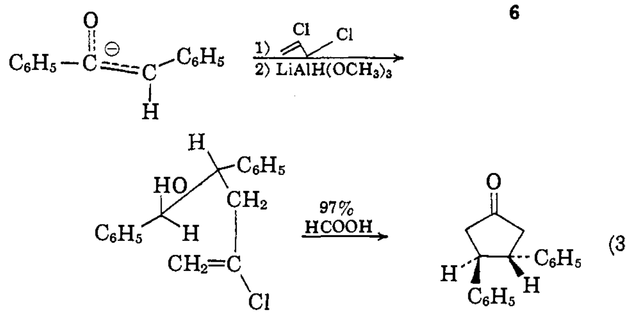
[1] All new compounds gave satisfactory elemental analysis and were further characterized by spectroscopic methods.



1, **2**, **3** (1)



4, **5**, **6** (2)



7, **8** (3)

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]

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 gradully 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.

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(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.

(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.

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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

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(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).