using the 6328 Å He–Ne line) equipped with a variable-temperature Raman cell.

Ir Spectra. Ir spectra were recorded on a Beckman IR-10 spectrophotometer.

Preparation of the Solutions of the 1,2-Dimethylnorbornyl Cations. A saturated solution of freshly distilled SbF_5 (Allied Chemical Corp.) in SO_2 was prepared and cooled to $-78°$. To this solution was added with continuous vigorous stirring 1,2-dimethylnorbornyl chloride to give *ca.* 10 mol % solution.

1-Methylnorcamphor.[16] Concentrated sulfuric acid (270 g) was added to a solution of 112.5 g of sodium dichromate dihydrate in 840 ml of water in a 2-l. three-necked flask fitted with a mechanical stirrer, a reflux condenser, and dropping funnel. After the resulting mixture was heated to 90°, a solution of 50 g of 2-methyl-*endo*-2-norbornanol in 12 ml of absolute ether was added slowly with vigorous stirring. Stirring was continued for 2 hr more at 90° and the product was then isolated by steam distillation (*ca.* 500 ml of distillate). The distillate was extracted with four 35-ml portions of ether and dried; the solvent was removed by a rotary evaporator at room temperature. About 34 g of the crude product was obtained. The mixture of the crude product and 4.4 g of boric anhydride (prepared by heating 5.1 g of boric acid in a drying pistol under toluene reflux) was heated with stirring at 100° for 2 hr. Fractional distillation through a 25-cm Vigreux column yielded fractions boiling at 58–62° (15 mm) and at 62–63° (15 mm): 28 g (55% yield), 99% pure by vpc. Ir showed a five-membered ring C=O at *ca.* 5.70 μ, and pmr showed a singlet for CH_3 at τ 8.9.

1,2-Dimethyl-2-*endo*-norbornanol.[17] A solution of 1-methylnorcamphor (25 g, 0.20 mol) in ether was added slowly at 0° with stirring to a solution of freshly prepared CH_3MgI (5.4 g, 0.22 mol), Mg turnings (29.5 g, 0.20 g-atom), and CH_3I. The resultant mixture was stirred overnight at room temperature, and then cooled to 0°. The subsequent procedure was the same as that for preparing 2-methyl-*endo*-norborneol. The ether solution of the product was dried over anhydrous magnesium sulfate and Drierite and was decolorized. The solvent was removed *in vacuo* and distillation of the crude product at 60° (0.5 mm) afforded 28 g of 1,2-dimethyl-*endo*-norborneol (92%), mp 32–34° (lit.[15] 34.5–36°). Pmr showed two singlets for CH_3 groups at δ 1.03 and 1.18.

1,2-Dimethyl-2-*endo*-chloronorbornane. A solution of 8 g (0.057 mol) of 1,2-dimethyl-*endo*-2-norbornanol in 14 ml of methanol was added to 68 ml of concentrated hydrochloric acid contained in a separatory funnel. A white flocculent precipitate was formed immediately. The contents in the funnel were shaken for 15 min and then allowed to stand for an additional 2 hr with occasional shaking. The aqueous solution was extracted with petroleum ether and the combined extracts were washed twice with saturated solution of $CaCl_2$ and dried over $CaCl_2$. The solvent was removed *in vacuo* to yield 8.6 g (95.4%) of white flaky solid, mp 122–123° (lit.[18] 120–122°). Infrared yielded no OH absorption. Nmr showed two singlets of CH_3 groups at δ 1.23 and 1.56.

Acknowledgment. Professor Harlan Goering is thanked for a sample of 1,2-dimethylnorbornan-2-ol. The support of the National Science Foundation and the Petroleum Research Fund administered by the American Chemical Society is gratefully acknowledged.

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[16] Prepared by modification of the method of Liu.[15]

[17] H. Toivonen, *Suom. Kemistilehti B*, 33, 66 (1960).

[18] H. C. Brown and M. H. Rei, *J. Org. Chem.*, 31, 1090 (1966).

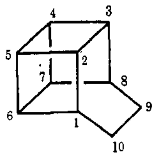
The Synthesis and Rearrangement of Strained Cage Molecules[1]

William G. Dauben,* Charles H. Schallhorn,[2] and Dale L. Whalen

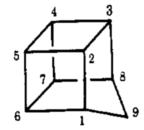
Contribution from the Department of Chemistry,
University of California, Berkeley, California 94720. *Received June 22, 1970*

Abstract: The preparation of *cis*-9,10-dicarbomethoxypentacyclo[$4.4.0.0^{2,5}.0^{3,8}.0^{4,7}$]decane (**5**, the 1,1′-bishomocubane structure) was effected by the sensitized irradiation of diene diester **4**. Photoproduct **5** was converted to bishomocubanedione **11** by a series of reactions involving saponification, bisoxidative decarboxylation, hydroboration, and two oxidations. The diketone **11**, *via* the diazo ketone **12**, was photochemically ring contracted to pentacyclo[$4.3.0.0^{2,5}.0^{3,8}.0^{4,7}$]nonane-9-carboxylic acid (**13**, the homocubyl structure). X-Ray analyses of both homocubyl and bishomocubyl derivatives were obtained. Oxidative cleavage of dione **11** also yielded *endo,endo*-tetracyclo[$4.2.0.0^{2,5}.0^{3,8}$]octane (secocubane) diester **19** which, upon treatment with dimsyl anion, was converted to the isomeric diesters **17** and **21**. The Dieckmann product **23** is postulated as an intermediate in the isomerization. The 1,1′-bishomocubyl system is isomerized to the pentacyclo[$4.4.0.0^{2,4}.0^{3,8}.0^{5,7}$]decane structure by silver ion. The analogous reaction occurs in the homocubane and secocubane series to yield the pentacyclo[$4.3.0.0^{2,4}.0^{3,8}.0^{5,7}$]nonyl and tetracyclo[$3.3.0.0^{2,8}.0^{4,6}$]octyl systems, respectively.

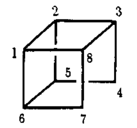
The syntheses of pentacyclo[$4.4.0.0^{2,5}.0^{3,8}.0^{4,7}$]decane (1,1′-bishomocubane, **1**)[3,4] and pentacyclo[$4.3.0.0^{2,5}.0^{3,8}.0^{4,7}$]nonane (homocubane, **2**)[3,5] have been described earlier. We wish to report in detail the studies undertaken with cage systems **1** and **2** and to describe the synthesis and reactions of the tetracyclo[$4.2.0.0^{2,5}.0^{3,8}$]octane (secocubane) series (**3**).



1



2



3

The photochemical reaction of **4**, in acetone solution, proceeded with intramolecular cycloaddition to yield pentacyclic diester **5**.[3,4] However, direct irradiation of **4** in pentane did not result in formation of photoproduct **5**, indicating that acetone acts as a sensitizer.

Evidence for the correctness of structure **5** was based on spectral data consistent with that expected for the pentacyclic structure and an X-ray analysis

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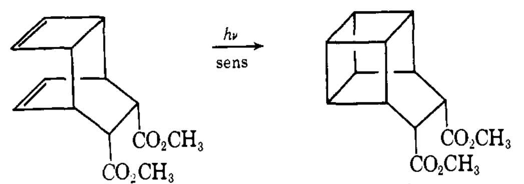
[1] This investigation was supported by Grant No. GP-8700, National Science Foundation.

[2] National Institutes of Health Predoctoral Fellow, 1967–1970.

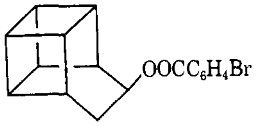
[3] W. G. Dauben and D. L. Whalen, *Tetrahedron Lett.*, 3743 (1966).

[4] S. Masamune, H. Cuts, and M. Hogben, *ibid.*, 1017 (1966).

[5] (a) C. G. Chin, H. Cuts, and S. Masamune, *Chem. Commun.*, 880 (1966); (b) G. L. Dunn, V. J. DiPasquo, and J. R. E. Hoover, *Tetrahedron Lett.*, 37 (1966); (c) K. V. Scherer, R. S. Lunt, and G. A. Ungefug, *ibid.*, 1199 (1965); (d) P. v. R. Schleyer, J. J. Harper, G. L. Dunn, V. J. DiPasquo, and J. R. E. Hoover, *J. Amer. Chem. Soc.*, 89, 698 (1967); (e) R. L. Cargill and T. Y. King, *Tetrahedron Lett.*, 411 (1970).



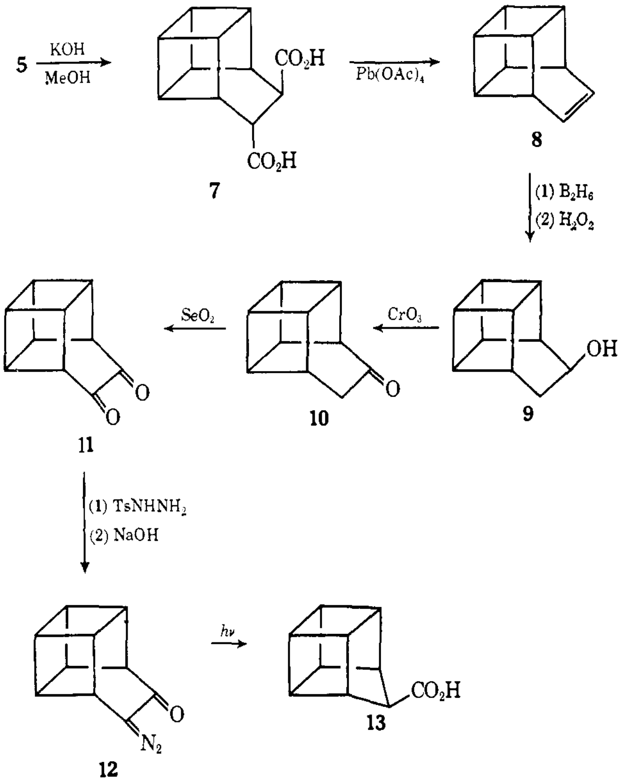
4 **5**



6

of the *p*-bromobenzoate **6**.[6] The chemical transformation of **5** to homocubyl-9-carboxylic acid **13** was accomplished by the series of reactions outlined in Scheme I.

Scheme I



Saponification of **5** occurred with concomitant cis → trans isomerization and gave *trans*-diacid **7**. Bisoxidative decarboxylation[7] of the diacid with lead tetraacetate afforded the new $(CH)_{10}$ isomer bishomocubene **8** which could be hydroborated to yield alcohol **9**.

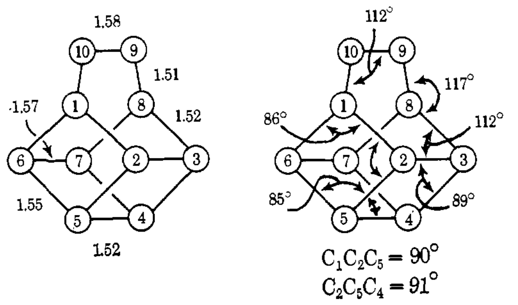
The nmr spectrum of olefin **8** contained resonances at τ 3.63, 6.39, 6.78 (quintet), and 7.40 which integrated for relative areas of 2:2:2:4, respectively. The absorption at 3.63 consisted of four intense lines (total separation 7.9 Hz equal to $J_{1,10} + J_{1,9}$) and two weak "wings" (total separation 18 Hz). The quintet at 6.78 was shown with a decoupling experiment to be due to the chemically equivalent protons H_4 and H_5 of **8**. The ^{13}CH satellite bands[8] of the vinylic proton resonance occurred as approximate triplets with a spacing of 15 Hz at 80 Hz on each side of the absorption at 3.63. The value of 160 Hz for the olefinic ^{13}CH coupling in **8** suggests[9] a normal CC=C angle of 120°. A first-order analysis[10] of these side bands yields approximate values for the coupling constants $J_{1,10}$, $J_{1,9}$, and $J_{9,10}$, of 7 ± 1, <1, and 8 ± 1 Hz, respectively. These estimates are derived from consideration of both the main olefinic absorption and the side bands.

Conversion of bishomocubanol **9** to diazo ketone **12** was accomplished by Jones oxidation[11] to the saturated ketone **10**, which upon selenium dioxide oxidation[12] afforded the diketone **11** which, in turn, was converted, *via* a monotosylhydrazone, to diazo ketone **12**. Irradiation of **12** produced the ring-contracted homocubyl-9-carboxylic acid **13**.[13] The structure of the homocubane ring system was verified by an X-ray analysis of the *p*-bromoanilide derivative of **13**.[14]

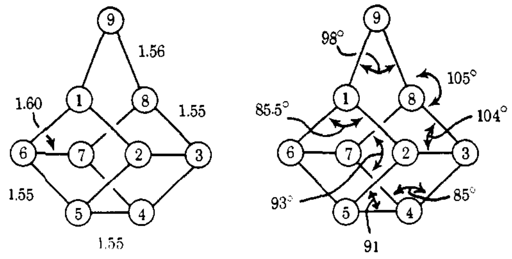
It is interesting to compare the bond angles and bond lengths of the homocubane structure with those of the bishomocubane nucleus. These data are given in Chart I. It is seen that in ring contracting from bis-

Chart I. Average Bond Angles and Lengths (Å)

Bishomocubane



Homocubane



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[6] D. H. Templeton and W. G. Quarles, private communication. The full details of this study are recorded in the Ph.D. Thesis of W. G. Quarles, University of California, Berkeley, and are available in Lawrence Radiation Laboratory Report, No. U.C.R.L. 19906. The *R* factor is 5%, and the standard deviation of bond length is 0.02 Å and of bond angle is 1°.

[7] C. A. Grob and A. Weiss, *Helv. Chim. Acta*, **86**, 1171 (1964).

[8] The $J(^{13}CH)$ value was obtained with the aid of a Varian time-average computer attached to a Varian A-60 nmr spectrometer.

[9] P. Laszlo and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 1171 (1964).

[10] The nmr spectra of symmetrical molecules are often complicated by the presence of chemically equivalent protons. However, the ^{13}CH satellite bands can usually be given a first-order analysis. For additional information, see ref 9 and J. I. Musher and E. J. Corey, *Tetrahedron*, **18**, 791 (1962).

[11] K. Bowen, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

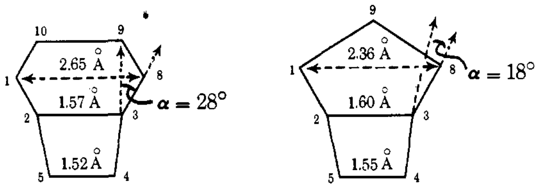
[12] N. Rabjohn in "Organic Reactions," Vol. V, Wiley, New York, N. Y., 1949, Chapter 8.

[13] (a) J. Meinwald and P. G. Gassman, *J. Amer. Chem. Soc.*, **82**, 2857 (1960); (b) K. Wiberg, B. Lowry, and T. Colby, *ibid.*, **83**, 3998 (1961).

[14] D. H. Templeton and R. C. Petterson, private communication. The full details of this study are recorded in the Ph.D. Thesis of R. C. Petterson, University of California, Berkeley [*Diss. Abstr. B*, **27** (11), 3894 (1967), University Microfilms (Ann Arbor, Mich.)], and are also available in Lawrence Radiation Laboratory Report, No. 19975. The *R* factor is 6%; the standard deviation of bond length is 0.03 Å and of bond angle is 3°.

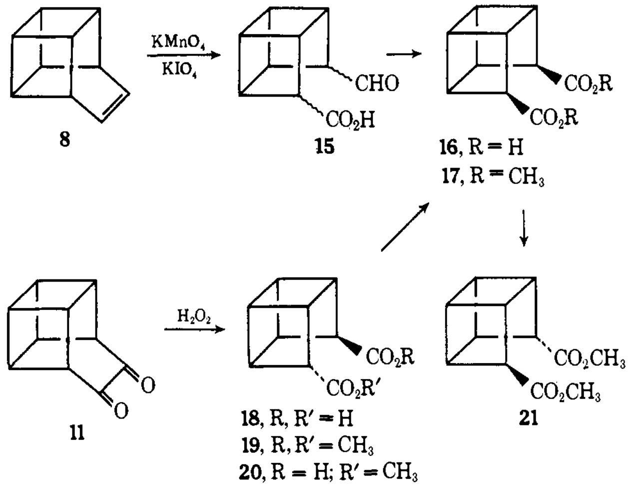
homocubane to homocubane, the C_4–C_5 bond is slightly lengthened from 1.52 to the normal 1.55 Å. The two cyclobutane rings, $C_2C_3C_4C_5$ and $C_4C_5C_6C_7$, are flat, the dihedral angle between any three contiguous carbons being 0°. The other two cyclobutane rings, $C_1C_2C_5C_6$ and $C_3C_4C_7C_8$, are both nonplanar. The presence of the two carbon bridge in the bishomocubyl skeleton changes the puckering to 28° (Chart II) as compared to the similar rings in the homocubane structure which are puckered only 18°. Calculations by Wiberg[15] show that the minimum energy for cyclobutane is found when the ring has been bent out of planarity by about 34°. However, the difference between an angle of 18 and 28° is of the order of only 0.4 kcal/mol for cyclobutane. This change in dihedral angle of the cyclobutane ring correlates with the change in the C_1–C_8 distance, 2.36 Å in homocubane *vs.* 2.65 Å in bishomocubane.

Chart II. Comparison of Bond Angles and Lengths

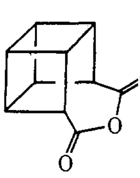


Bishomocubane Homocubane

Reactions in the Secocubane System. Two synthetic routes for preparing compounds having the secocubane structure 3 were utilized. Oxidation of olefin 8 with potassium permanganate periodate[16] did not yield the expected dicarboxylic acid **18**; instead the reaction gave a poor yield of aldehyde acid **15**. This material, when oxidized with basic permanganate solution, afforded **16**, characterized as its dimethyl ester. This diester **17** contained two methyl absorptions in its nmr spectrum, suggesting the exo,endo configuration.



A second, more successful route to the secocubane system involved diketone **11** as an intermediate. Treatment of **11** with basic hydrogen peroxide produced a good yield of **18**. The endo,endo configuration of the diacid was substantiated by its facile conversion to anhydride **22** by treatment with oxalyl chloride under mild conditions.



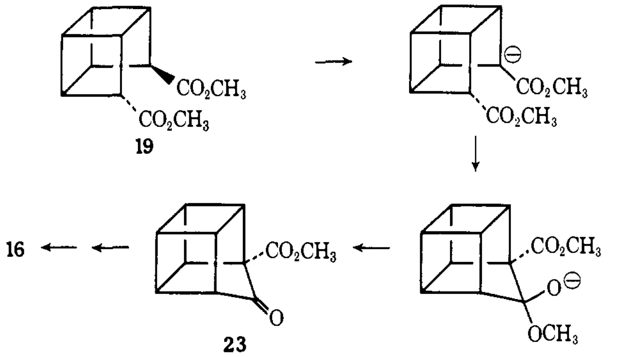
22

Esterification of **18** with diazomethane yielded the corresponding diester. The nmr spectrum of diester **19** contained a single methyl absorption consistent with the equivalency of the ester groups in the endo, endo isomer. The half-ester **20** could be obtained when diketone **11** was cleaved with 90% hydrogen peroxide in methanol.

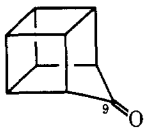
Isomerization of **19** to **17** was accomplished by reaction of **19** with excess potassium *tert*-butoxide in anhydrous dimethyl sulfoxide for 1 hr. The acidic material obtained after work-up was esterified with diazomethane to give almost exclusively the endo,exo diester **17**. Substitution of sodium hydride in place of potassium *tert*-butoxide did not change the results.

Reaction of endo,exo diester **17** with dimsyl anion under the same conditions as above again yielded an acidic product. Esterification of this material yielded the exo,exo diester **21**. Why does the isomerization require two steps and why does saponification occur at each step? There must be some intermediate in the first step which allows one ester group to be epimerized and which also can lead to saponification. Such an intermediate could be the Dieckmann reaction product **23** (Scheme II).

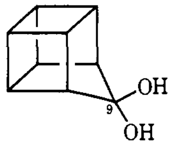
Scheme II



All of the reactions with dimsyl anion were worked up by dilution with water, acidification, and extraction. Thus the reaction mixture was a strongly basic (especially since a large excess of base was used) aqueous dimethyl sulfoxide solution for a few minutes before mineral acid was added. These are ideal conditions for both attack by hydroxide on the strained Dieckmann intermediate **23** and saponification. Some idea of the amount of strain present in intermediate **23** can be gauged from the fact that a pure sample of homocubanone **24** has been difficult to prepare.[17] The main



24



25

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[15] K. B. Wiberg and H. Lampman, *J. Amer. Chem. Soc.*, **88**, 4429 (1966).

[16] See ref 5a.

[17] E. Debus, Ph.D. Thesis, University of California, Berkeley, Calif., 1969.

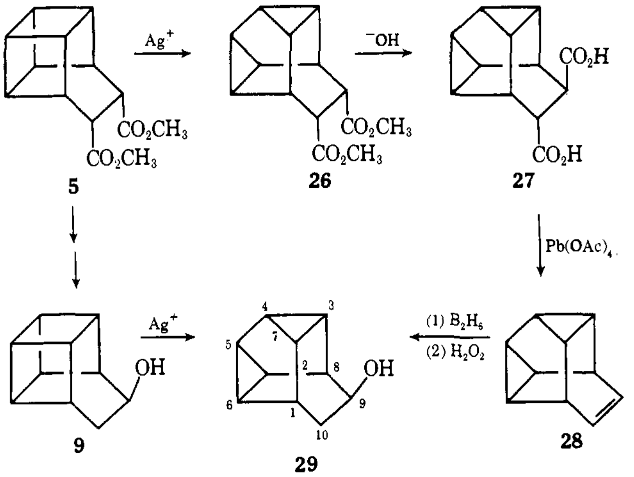
impurity was thought to be the hydrate **25**, which would indicate a willingness for the ring system to relieve strain by going from sp^2 to sp^3 hybridization at the 9 position.

The idea that rapid saponification could occur just before acidification is supported by the finding that sodium hydroxide hydrolyzed esters 10^3–10^4 faster in a 50% aqueous dimethyl sulfoxide than in water alone.[18]

Recently, Masamune found that treatment with methylsulfyl anion of endo,endo diester **19** yielded Dieckmann product **23** when the reaction was worked up under buffered conditions.[5a,19] It thus appears that a rapid ring opening and saponification has occurred under our more severe work-up procedure.

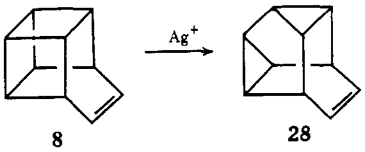
Silver(I) Catalyzed Rearrangements of Bishomocubane, Homocubane, and Secocubane Structures. We recently reported the silver(I) catalyzed isomerizations of two 1,1′-bishomocubane derivatives.[20] Both the diester **5** and the alcohol **9** rearranged to the pentacyclo$[4.4.0.0^{2,4}.0^{3,8}.0^{5,7}]$decane system (Scheme III).[21]

Scheme III

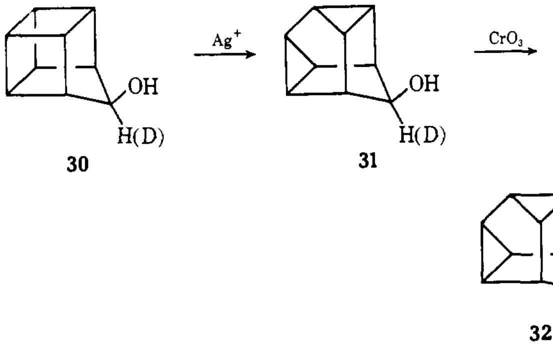


In analogy with the bishomocubane system, the cis diester **26** yielded a *trans* diacid **27**. Reaction of the diacid with lead tetraacetate[7] gave a new $(CH)_{10}$ isomer **28** which could be hydroborated to give alcohol **29**. The structure of the new pentacyclic ring system has been confirmed by X-ray analysis.[20]

The silver(I) catalyzed rearrangement now has been extended to bishomocubene **8**, the homocubane system, and the secocubane structure. Stirring olefin **8** in the homogenous medium of aqueous methanol and silver nitrate for 2 days produced the new $(CH)_{10}$ compound **28**; the rate of this reaction is approximately 100 times slower than the isomerization of bishomocubanol **9** or diester **5** under the same conditions.

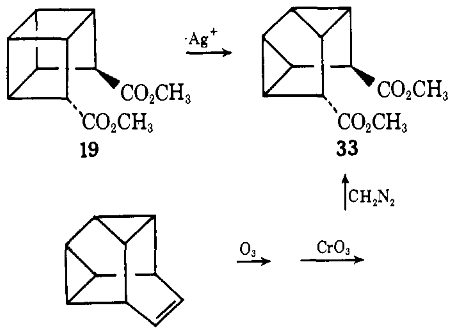


A mixture of homocubanol **30** and homocubanol deuterated at the carbinyl position (this mixture was used because of its easy availability)[22] completely isomerized when stirred for 4 days in an aqueous methanolic silver nitrate solution. The nmr spectrum of the isomeric product showed the carbinyl proton at τ 5.8 (a quartet!) with three multiplets between 7.5 and 8.4. Coates reported[23] that the nmr spectrum of **31** also had an unexpected quartet for the carbinyl proton (homocubanol has the normal triplet for this hydrogen).[17] The rest of the spectrum is also consistent with Coates' reported spectrum of alcohol **31**.



Oxidation of the mixture of deuterated and nondeuterated product with chromium trioxide at 0° yielded a ketone with the expected mass spectrum (M^+ at m/e 132, M − CO at m/e 104, and with an infrared absorption at 1770 cm^{-1}). The infrared spectrum of the purified ketone was identical with that of the known ketone **32**.[23] Thus the product of this silver nitrate reaction is assigned structure **31** based on the spectral comparisons and analogy with the other silver(I) catalyzed rearrangements.

The endo,endo-secocubane diester **19** also is rearranged by silver nitrate, but the reaction is the most sluggish found yet. The diester must be refluxed for 2 days in aqueous methanolic silver nitrate solution for complete reaction. A single product is obtained: a white crystalline solid, mp 89°. Its nmr spectrum showed a sharp six-proton singlet at τ 6.4 (methyl esters), a two-proton quintet at 6.9 (protons α to the ester groups), and a six-proton multiplet centered at τ 8.1.



Ozonolysis of olefin **28** followed by chromium trioxide oxidation[24] and diazomethane treatment gave

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(18) D. D. Roberts, *J. Org. Chem.*, **31**, 4037 (1966).

(19) Professor S. Masamune, private communication.

(20) W. G. Dauben, M. G. Buzzolini, C. H. Schallhorn, D. L. Whalen, and K. Palmer, *Tetrahedron Lett.*, 787 (1970). The details of the X-ray crystal study are available from Dr. K. Palmer, Western Regional Research Laboratory, U. S. Department of Agriculture, Albany, Calif., and the data have an *R* factor of 8%. After publication of our study, L. A. Paquette and J. C. Stowell [*J. Amer. Chem. Soc.*, **92**, 2585 (1970)] reported similar chemical results using silver fluoroborate.

(21) In the earlier paper, ref 20, the numbering of this new polycyclic structure was incorrect.

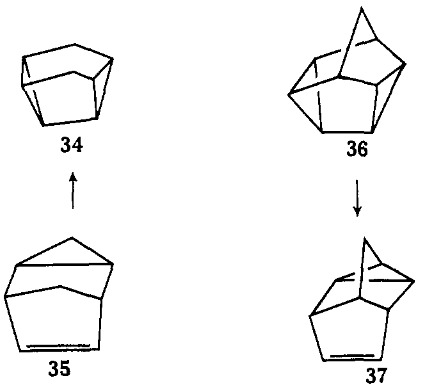
(22) Prepared by Debus according to ref 17.

(23) R. M. Coates and J. L. Kirkpatrick, *J. Amer. Chem. Soc.*, **90**, 4162 (1968).

(24) A. S. Narula and S. Dev, *Tetrahedron Lett.*, 1733 (1969).

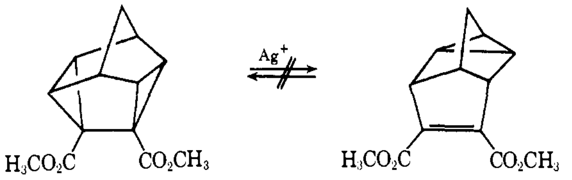
one volatile product in 30% yield. A small amount was purified by preparative glpc and found to have the same glpc retention time, infrared spectrum, and mass spectrum as the silver nitrate product. Thus structure **33** is assigned to the rearrangement product.

Certain rhodium compounds catalyze the isomerization of hydrocarbon **35** to **34**, the same tetracyclic ring system as in diester **33**. Introduction of a methylene bridge into this ring system reverses the reaction, *i.e.*, **36** goes to **37**. These interconversions were discussed in terms of relative thermodynamic stability.[25]



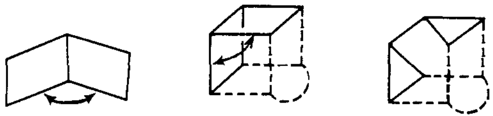
34 **36** **35** **37**

The new diester **26** is the same ring system as **36** except that it has a two-carbon bridge in place of a methylene bridge. Various rhodium compounds or silver nitrate did not cause **26** to rearrange further. Thus, in line with the discussion of Katz,[25] diester **26** may be thermodynamically stable relative to its ring-opened isomer. However, the analogy between silver and rhodium catalysis seems to be poor for the cage compounds in this study. The bishomocubyl diester **5** did not rearrange upon treatment with tris(triphenylphosphine)rhodium chloride[26] (or with mineral acid or mercuric, cuprous, zinc, and iron salts). Also we have observed that the ring system **36** (in the form of the diester derivative **38**)[27] did not ring open nor did diester **39** close upon extended treatment with silver ion in aqueous methanol.



38 **39**

All of the ring structures undergoing silver-catalyzed rearrangements contain the bicyclo[2.2.0]hexane moiety which has its normal dihedral angle contracted. The relative rates of these rearrangements can be rationalized in terms of differences in strain release in going to product. The contraction of this dihedral angle must cause the dicyclopropane structure (C) to be thermodynamically favored over the bicyclo[2.2.0]hexane system. The amount of energy by which it is favored determines the reaction rate.



Normal A Contracted B Product C

Experimental Section

Unless otherwise noted, the reactions were all worked up by dilution with water and extraction with ether. The ether extracts were shaken with saturated sodium chloride and dried with anhydrous magnesium sulfate. All the tlc analyses were done with silica gel PF_{254} (E.Merck A.G.) on microscope slides, and glpc analyses and preparations were carried out with a Wilkins Aerograph, Model A-90-P, with a 10% SE-30 column.

Combustion analyses were performed by the Microanalytical Laboratory, College of Chemistry, University of California, Berkeley.

Dimethyl *cis*-Pentacyclo[4.4.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]decane-9,10-dicarboxylate (5). A solution of 50 g (0.2 mol) of **4**[28] in 2 l. of acetone was irradiated under helium with a G.E. Alt-6 lamp for 6 hr. The solvent was evaporated and the oily residue was distilled at 0.1 mm pressure at a pot temperature of 170° until all volatile material had been collected. The distillate was recrystallized from methanol: yield 12.3 g (25%) of **5**; mp 81–82°; ir (CCl_4) 1736 cm^{-1}; nmr (τ, CCl_4) 6.36 (6 H, s, methyl ester), 6.80 (8 H, m), 7.18 (2 H, m).

Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.69; H, 6.53.

***trans*-Pentacyclo[4.4.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]decane-9,10-dicarboxylic Acid (7).** A solution of 220 g (0.87 mol) of diester **5**, 240 g (3.64 mol) of 85% potassium hydroxide, and 1 l. of methanol was allowed to reflux under nitrogen for 3 hr. The solution was cooled, diluted with water, and extracted with ether. The aqueous phase was acidified, and the work-up finished in the usual way to yield 193 g (99%) of *trans*-diacid **7**, mp 218–221° dec. Recrystallization from water–methanol raised the melting point to 226–228° dec; ir (KBr) 1698 cm^{-1}.

Anal. Calcd for $C_{12}H_{12}O_4$: C, 65.44; H, 5.49. Found: C, 65.20; H, 5.43.

Pentacyclo[4.4.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]dec-9-ene (8). To a rapidly stirred suspension of 193 g (0.87 mol) of *trans*-diacid **7**, 145 ml (1.84 mol) of pyridine, and 840 ml of acetonitrile was added 430 g (0.97 mol) of lead tetraacetate (Arapahoe Chemicals, Inc., dried *in vacuo* at 50° before use). The reaction was conducted in a 2-l. round-bottom flask equipped with a mechanical stirrer, a condenser, and a nitrogen bubbler. The flask was placed in a water bath and the temperature slowly raised to 55° and maintained there for 2.5 hr. The reaction mixture was diluted with 4 l. of 5% nitric acid and extracted with pentane. The pentane solution was washed with water, dried, and carefully concentrated to 200 ml by aspirator pressure at room temperature. The pentane was carefully evaporated from a small aliquot, and the residue was carefully sublimed at 80° to give olefin **8**, mp 61–62°, in approximately 25% yield: ir (CCl_4) 1616 cm^{-1}; nmr, see text.

Anal. Calcd for $C_{10}H_{10}$; C, 92.26; H, 7.74. Found: C, 92.20; H, 8.10.

The concentrated solution of **8** was used directly for hydroboration to alcohol **9**.

Pentacyclo[4.4.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]decan-9-ol (9). The solution of the crude olefin **8**, obtained from decarboxylation of diacid **7** above, was cooled in an ice bath. Then 900 ml of a 1.0 *M* solution of diborane in tetrahydrofuran (Metal Hydrides, Inc.) was slowly added to the cooled solution under nitrogen atmosphere. The reaction mixture was stirred for 20 min at 0–5° and for 18 hr at room temperature. The excess borane was destroyed by slow addition of water until the violent reaction had ceased. Then 250 ml of 3 *N* sodium hydroxide was added followed by the slow addition of 250 ml of 30% aqueous hydrogen peroxide. The mixture was stirred for 4 hr at room temperature and diluted with ether. The aqueous layer was drawn off and the organic phase was washed with water, a 5% ferrous sulfate solution containing a trace of sulfuric acid, and again with water. The ether solution was dried and the solvent removed by evaporation to yield 81 g of viscous oil which was filtered through 500 g of alumina (Activity III) with benzene. Re-

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[25] T. J. Katz and S. Cerefice, *Tetrahedron Lett.*, 2509 (1969).

[26] Using $[Rh(NOR)Cl]_2$ as the catalyst, J. Halpern (private communication) has found a slow isomerization. A similar high specificity of the exact rhodium complex used has been found in the isomerization of cubane derivatives.

[27] C. F. Hueber, E. Donoghue, L. Dorfman, E. Wenkert, W. Streth, and S. Donehy, *Chem. Commun.*, 419 (1966).

[28] W. Reppe, O. Schlichting, K. Klager, and T. Toepel, *Justus Liebigs Ann. Chem.*, **560**, 1 (1948).

crystallization from pentane gave 57.9 g of alcohol **9**, mp 131–134°; yield from diacid **7** wás 40%.

A second recrystallization from pentane raised the melting point to 136–137°: ir (CCl_4) 3610 cm^{-1}; nmr (τ CCl_4) 6.22 (1 H, doublet of triplets, J = 3.5, 9.0 Hz), 7.0 (8 H, broad m), 8.2 (1 H, m), 8.6 (1 H, m).

Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 81.28; H, 8.05.

Pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decan-9-one (10). The alcohol **9** (36.7 g, 0.25 mol) was oxidized at 0° according to the Jones procedure[11] to yield 36.1 g of oily crystals which recrystallized from methanol: yield 28.6 g (79%); mp 85–87°; ir (CCl_4) 1727, 1709 cm^{-1}; nmr (τ, CCl_4) 6.3–7.1 (8 H, m), 7.95 (2 H, m).

Anal. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.90. Found: C, 81.88; H, 6.97.

Pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decane-9,10-dione (11). A mixture of 7.0 g (48 mmol) of ketone **10**, 5.55 g (50 mmol) of selenium dioxide (Fairmont Chemical Co.), and 350 ml of xylene in an open round-bottom flask was heated and stirred at 135° for 4 hr. The water–xylene azeotrope formed was allowed to distil from the reaction mixture. The hot reaction mixture was filtered and the filtrate cooled to 0°. The orange crystals of diketone **11** were collected and allowed to air dry. This filtrate was concentrated at reduced pressure to one-fourth its original volume and again cooled. A second crop of crystals was collected and dried to give a total yield of crude **11** of 6.74 g (87%). The product was purified by sublimation to yield pure **11**: mp 243–244°; ir ($CHCl_3$) 1739, 1718 cm^{-1}; nmr (τ, $CDCl_3$) 6.0–6.5 (m).

Anal. Calcd for $C_{10}H_8O_2$: C, 74.99; H, 5.03. Found: C, 74.77; H, 4.97.

9-Diazopentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decan-10-one (12). To a solution of 7.0 g (44 mmol) of diketone **11** in 100 ml of chloroform was added 8.97 g (48.1 mmol) of *p*-toluenesulfonylhydrazine,[29] and the mixture was stirred for 24 hr. The solution was filtered through a column of Woelm basic alumina (Activity I) and eluted with chloroform until the yellow color was completely removed from the column. The solvent was evaporated to yield a yellow oil, ir ($CHCl_3$) 2083 cm^{-1}. The crude product **12** was used for irradiation without further purification.

Pentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane-9-carboxylic Acid (13). A solution of the crude diazo ketone **12** in 225 ml of tetrahydrofuran and 100 ml of water was irradiated under a helium atmosphere with a 450-W Hanovia lamp (Corex filter) for 10 hr. The irradiated solution was concentrated under aspirator pressure and diluted with ether. The ethereal solution was extracted with 5% sodium bicarbonate solution, the bicarbonate solution was acidified with 10% hydrochloric acid, and the work-up finished as usual to yield, after sublimation, 3.1 g (44% from diketone **11**) of acid **13**: mp 156–157°; ir ($CHCl_3$) 1695 cm^{-1}; nmr (τ, $CDCl_3$) 6.4–6.9 (8 H, m), 7.12 (1 H, m).

Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.05; H, 6.22. Found: C, 74.21; H, 6.33.

***endo,endo*-Tetracyclo[4.2.0.0^{2,5}.0^{3,8}]octane-4,7-dicarboxylic Acid (16).** A solution of 12.5 ml of 30% hydrogen peroxide was added to a mixture of 1.0 g (6.3 mmol) of diketone **11**, 2.0 g (50 mmol) of rhodium hydroxide, and 40 ml of water.[28] The reaction mixture was stirred at room temperature for 3.5 hr, and filtered. The filtrate was acidified, and the precipitate was collected and dried: yield 1.07 g (88%) of diacid **18**, mp 240–242° dec; ir (KBr) 3500–2500, 1701 cm^{-1}.

Anal. Calcd for $C_{10}H_{10}O_4$: C, 61.85; H, 5.19. Found C, 62.05; H, 5.11.

Treatment of **18** with diazomethane gáve diester **19**: mp 93°; ir (CCl_4) 1733 cm^{-1}; nmr (τ, CCl_4) 6.45 (6 H, s, methyl ester).

Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 65.04; H, 6.10.

***endo*-4-Carbomethoxy-*endo*-7-carboxytetracyclo[4.2.0.0^{2,5}.0^{3,8}]-octane (20).** A suspension of 1.45 g (9.1 mmol) of diketone **11**, 2.2 ml of 90% hydrogen peroxide, and 75 ml of methanol was stirred at room temperature for 24 hr. The reaction mixture was worked up in the normal manner to yield 1.67 g of a mixture of half-ester **20** and diacid **18**. The half-ester was isolated by sublimation to yield 1.0 g (53%) of **20**: mp 186–188°; ir ($CHCl_3$) 3400–2500, 1724 cm^{-1}; nmr (τ, $CDCl_3$) 0.62 (1 H, m, acid), 6.26 (3 H, s, methyl ester), 6.23 (4 H, m), 6.80 (4 H, m).

Anal. Calcd for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81; Found: C, 63.19; H, 5.67.

The sublimation residue was esterified with diazomethane to yield 0.40 g (20%) of endo,endo diester **19**.

***endo,exo*-4,7-Dicarbomethoxytetracyclo[4.2.0.0^{2,5}.0^{3,8}]octane (17).** A solution of 700 mg (3.14 mmol) of endo,endo diester **19** in 5 ml of dimethyl sulfoxide (distilled from sodium hydride and stored over molecular sieves) was added to a stirred mixture of 3.5 g (31.2 mmol) of potassium *tert*-butoxide (MSA Research Corp.) in 20 ml of dimethyl sulfoxide under a dry nitrogen atmosphere. The mixture was stirred at room temperature for 1 hr and then diluted with water. The solution was acidified with 10% hydrochloric acid and the work-up finished in the normal way to yield 480 mg of crude diacid **16**. Treatment of **16** with diazomethane gave 520 mg (74%) of endo,exo diester **17**: mp 72–73° after recrystallization from pentane; ir (CCl_4) 1727 cm^{-1}; nmr (τ, CCl_4) 6.36 (3 H, s, methyl ester), 6.40 (3 H, s, methyl ester).

Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 64.56; H, 6.17.

***exo,exo*-4,7-Dicarbomethoxytetracyclo[4.2.0.0^{2,5}.0^{3,8}]octane (21).** The diester **17** was treated as described for endo,endo diester **19** above. This yielded 70% of exo,exo diester **21**: mp 81°; nmr (τ, CCl_4), 6.36 (6 H, s), 6.5 (8 H, m).

Anal. Calcd for $C_{10}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 64.63; H, 6.50.

***endo,endo*-Tetracyclo[4.2.0.0^{2,5}.0^{3,8}]octane-4,7-dicarboxylic Anhydride (22).** A mixture of 315 mg (1.62 mmol) of endo,endo diacid **18**, 1.5 ml of oxalyl chloride, a trace of pyridine, and 1.5 ml of benzene was heated under nitrogen at 70° for 1 hr. The solvent and excess oxalyl chloride were removed by a stream of nitrogen, and the residue was sublimed to yield 220 mg (77%) of anhydride **22**: mp 191°; ir ($CHCl_3$) 1799, 1736 cm^{-1}; nmr (τ, $CDCl_3$) 6.20 (6 H, m), 6.54 (2, H, m).

Anal. Calcd for $C_{10}H_8O_3$: C, 68.18; H, 4.58. Found: C, 68.28; H, 4.38.

***cis*-9,10-Dicarbomethoxypentacyclo[4.4.0.0^{2,4}.0^{3,8}.0^{5,7}]decane (26).** A solution of 500 mg of bishomocubyl diester **5**, 5 g of silver nitrate, 60 ml of water, and 80 ml of methanol was stirred at room temperature in the dark for 2 hr. The reaction mixture was worked up in the normal way to yield 480 mg (96%) of diester **26**: mp 104°; ir ($CHCl_3$) 1735 cm^{-1}; nmr (τ, CCl_4) 6.43 (6 H, s), 7.04 (2 H, broad s), 7.37 (2 H, m), 8.39 (6 H, m); mass spectrum, *m/e* 248.

Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.93; H, 6.31.

***trans*-Pentacyclo[4.4.0.0^{2,4}.0^{3,8}.0^{5,7}]decane-9,10-dicarboxylic Acid (27).** The same procedure as in preparation of diacid **7** was used. A 98% yield of **27** was obtained from diester **26**: mp 217–218°; ir (KBr) 3100–2850, 1685 cm^{-1}.

Anal. Calcd for $C_{12}H_{12}O_4$: C, 65.44; H, 5.49. Found: C, 65.17; H, 5.37.

Pentacyclo[4.4.0.0^{2,4}.0^{3,8}.0^{5,7}]dec-9-ene (28). (a) The same procedure as in the preparation of olefin **8** was used. A 40% yield of **28** was obtained from diacid **27**: mp 59–60° after recrystallization in methanol; ir ($CHCl_3$) 3049, 2959, 1595 cm^{-1}; nmr (τ, CCl_4) 3.75 (2 H, q), 6.87 (2 H, m), 7.92 (2 H, m), 8.47 (4 H, m); mass spectrum *m/e* 130.

Anal. Calcd for $C_{10}H_{10}$: C, 92.26; H, 7.74. Found: C, 92.20; H, 7.70.

(**b**) The same procedure as in the preparation of diester **26** was used except that the reaction time was 2 days. A 98% yield of olefin **28** was obtained from olefin **8**.

Pentacyclo[4.4.0.0^{2,4}.0^{3,8}.0^{5,7}]decan-9-ol (29). (a) The same procedure as in the preparation of alcohol **9** was used. A 35% yield (from diacid **27**) of alcohol **29** was obtained: mp 129°; ir ($CHCl_3$) 3597, 3436 cm^{-1}; nmr (τ, CCl_4) 5.98 (1 H, m), 6.89 (1 H, s), 7.69 (2 H, m), 8.1–9.0 (8 H, m); mass spectrum, *m/e* 148, 130.

Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 80.89; H, 8.31.

(**b**) The same procedure as in the preparation of diester **26** was used. A 99% yield of alcohol **29** was obtained from alcohol **9**.

Conversion of 9-Homocubanol (30) to Pentacyclo[4.3.0.0^{2,4}.0^{3,8}.-0^{5,7}]nonan-9-ol (31). A solution of 17 mg of homocubanol **30** (partially deuterated at the carbinyl position because the sample was readily available),[20] 300 mg of silver nitrate, 3 ml of water, and 6 ml of methanol was stirred for 4 days at room temperature in the dark. The reaction mixture was worked up as in the preparation of diester **26** to yield 16 mg (94%) of an oily solid, a mixture of alcohol **31**, and **31** deuterated at the carbinyl position (see text). The mixture

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[29] M. P. Cava, R. L. Litle, and D. R. Napier, *J. Amer. Chem. Soc.*, 80, 2257 (1958); M. Cava and R. Litle, *Chem. Ind.* (*London*), 367 (1957); J. Meinwald, personal communication.

of alcohols was oxidized with chromium trioxide as in the preparation of ketone **10** to yield 11 mg (69%) of crude ketone **32**. Analysis of the crude compound by glpc showed it to be 90% of one ketone. A small amount of the ketone was purified by preparative glpc; ir (CCl_4) 1770 cm^{-1}; mass spectrum, *m/e* 132 (M^+), 104 (M − CO).

***endo,endo*-3,7-Dicarbomethoxytetracyclo[3.3.0.0^{2,8}.0^{4,6}]octane (33).** (a) A solution of *endo,endo*-secocubane dimethyl ester **19** (290 mg, 1.3 mmol), 3.0 g of silver nitrate, 20 ml of water, and 25 ml of methanol were refluxed under nitrogen for 2 days. The reaction mixture was cooled and diluted with 100 ml of ether. The water layer was drawn off and the ether solution dried. The solvent was removed by evaporation to give 194 mg (66%) of diester **33**: mp 87–88°; ir (CCl_4) 2935, 1735 cm^{-1}; nmr (τ, CCl_4) 6.40 (6 H, s), 6.90 (2 H, quintet, J = 2.2 Hz), 8.15 (6 H, m); mass spectrum, *m/e* 222.

Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 64.84; H, 6.16.

(b) A solution of pentacyclo[4.4.0.0^{2,4}.0^{3,8}.0^{5,7}]deca-9-ene (**28**, 100 mg, 0.77 mmol) in 30 ml of ethyl acetate was treated with a 20% excess of ozone at −70°. The crude ozonide, after removal of the ethyl acetate by evaporation, was oxidized at 0° with Jones reagent.[11] The crude reaction mixture was diluted with 3 *N* sodium hydroxide and extracted with ether. The aqueous solution was acidified with 10% hydrochloric acid and extracted three times with ether. The acidic ether extracts were dried, concentrated by aspirator pressure, and treated with excess diazomethane. The 120 mg of yellow oil obtained was examined by glpc and found to contain one volatile product (30% yield from olefin **28** according to glpc estimates). A sample of this product was purified by preparative glpc and found to have the same infrared spectrum, mass spectrum, and glpc retention time as the material from part a.

Aliphatic Semidiones. XV. 2,3-Semidiones Derived from the Bicyclo[*n*.1.0]alkanes[1]

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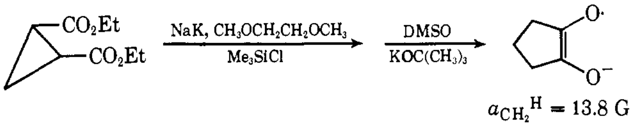
Contribution from the Department of Chemistry, Iowa State University, Ames, Iowa 50010. *Received May 29, 1970*

Abstract: The synthesis of bicyclo[2.1.0]pentane-, bicyclo[3.1.0]hexane-, bicyclo[4.1.0]heptane-, bicyclo[5.1.0]octane-, and bicyclo[6.1.0]nonane-2,3-semidiones has been investigated. Acyloin condensations of *cis*-1,2-cyclopropanedicarboxylic esters failed to yield bicyclopentane semidiones. Instead, the ring-opened cyclopentanesemidiones were formed. Acyloin condensation or oxidation of the 2- or 3-ketones in basic solution produced the bicyclo[3.1.0]hexane-2,3-semidione. The hyperfine splittings observed in the esr spectrum were assigned to the six hydrogen atoms by examination of a number of deuterium and alkyl derivatives. Extended Hückel self-consistent field calculations are reported which are in excellent agreement with the experimentally observed values. During this investigation it was determined that the α-methylene group in bicyclo[3.1.0]hexanesemidione underwent a highly stereoselective hydrogen–deuterium exchange in basic dimethyl sulfoxide solution wherein the exo hydrogen exchanged much more rapidly than the endo hydrogen. It was also observed that *syn*-6-alkylbicyclo[3.1.0]hexane-2,3-semidiones rearranged to the anti isomers with base catalysis. An electrocyclic mechanism is suggested in which the bicyclo[3.1.0]hexane ring opens to a cyclohexadienyl intermediate which undergoes competing ring closure and aromatization. Overoxidation of the bicyclo[3.1.0]hexanesemidione leads to an *o*-semiquinone with molecular rearrangement in which C-6 of the bicyclic semidione is converted to C-3 in the semiquinone. A sigmatropic 1,4 migration followed by a cyclopropanol ring opening is suggested. A variety of tricyclic derivatives containing the bicyclo[3.1.0]hexanesemidione nucleus and showing interesting long-range esr splittings have been synthesized. Bicyclo[4.1.0]heptane-2,3-semidione appears to exist in two conformations depending upon the substitution pattern. The importance of long-range interactions is greatly reduced in the bicyclo[4.1.0]heptane system and inconsequential in the bicyclo[5.1.0]octane- and bicyclo[6.1.0]nonane-2,3-semidiones.

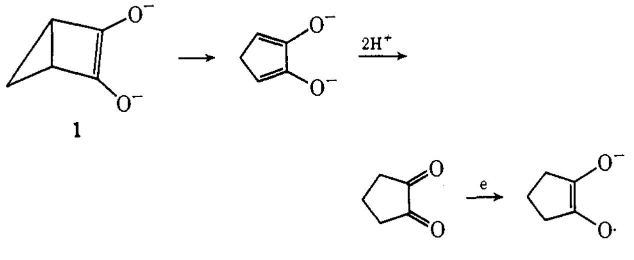
Attempts to prepare bicyclopentanesemidione (**1**) by acyloin condensation of the *cis*-cyclopropanedicarboxylic ester in the presence or absence of trimethylchlorosilane led instead to cyclopentanesemidione, detected by esr spectroscopy (Scheme I).

Scheme I



Ring opening is not surprising since the enediol derivative resulting from the acyloin condensation would be a bicyclopentene derivative. Ring opening could occur by hydrogenation with hydrogen released from traces of hydroxylic impurities. Alternately disymmetric ring opening (not allowed by orbital symmetry considerations) might precede the gain of the two hydrogen atoms (Scheme II). Ring opening also oc-

Scheme II



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[1] Application of Electron Spin Resonance Spectroscopy to Problems of Structure and Conformation. XX. Supported by the Army Office of Research (Durham) and by the National Science Foundation.

[2] National Aeronautics and Space Agency Predoctoral Fellow, 1965–1968; Petroleum Research Fund Fellow, 1968–1969.

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