ethanol in the presence of 10% palladium on carbon (0.5 g) for 5 hr. The catalyst was removed and the filtrate was evaporated to dryness. The residue was recrystallized from ethanol to give *cis*-α,β-diphenylbutyrolactone (1.5 g), mp 128–129°. The lactone showed an infrared band at 1760 cm^{-1}.

Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92; mol wt, 228. Found: C, 80.41; H, 5.88; mol wt, 227.

Conversion of the *cis* Lactone to the *trans* Lactone (IV). The *cis* lactone (1 g) was dissolved in 10 ml of ethanol, and the solution was added to a sodium ethoxide prepared from 0.5 g of sodium and 10 ml of ethanol. The mixed solution was stirred at room temperature for 3 hr. After acidification of the solution with hydrochloric acid, the solution was extracted with ether. The ethereal solution was washed with water and dried. The ether was removed and the residue was recrystallized from ethanol to give the *trans* lactone (IV), mp 94–95°.

Anal. Found: C, 80.46; H, 5.90; mol wt, 225.

An infrared spectrum showed a carbonyl band at 1775 cm^{-1}.

Reduction of the Lactone (I). Lithium aluminum hydride (0.5 g) was added to ether (80 ml). To the solution was added dropwise over a period of 20 min an ethereal solution of the lactone (I, 1.2 g in 180 ml). The solution was stirred for 2 hr at room temperature. After the usual work-up, the residue was recrystallized from carbon tetrachloride to give needles of 2,3-diphenyl-2-butene-1,4-diol, mp 86.5–87.5°. The diol showed the following nmr peaks: τ 3.07 (ring protons), 5.60 (singlet, CH_2), 6.20 (OH).

Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71; mol wt, 226. Found: C, 79.79; H, 6.69; mol wt, 225.

Reduction of Diphenylbutyrolactone. Lithium aluminum hydride (0.5 g) was dissolved in 80 ml of ether and an ethereal solution of the butyrolactone (III, 1.2 g in 180 ml) was added. After the usual work-up, *meso*-2,3-diphenyl-1,4-butanediol was obtained, mp 143–144° (different melting points had been reported for this compound, 137–138°,[8a] 143–144°,[8b] and 153–154°[8c]).

Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49; mol wt, 226. Found: C, 78.98; H, 7.35; mol wt, 224.

Formation of Diphenylmaleic Anhydride. Ethyl diphenylmaleate (1 g) was added to a solution of ethanolic sodium hydroxide (3 g) and the solution was refluxed for 25 hr. The solution was acidified and then extracted with ether. Evaporation of ether gave diphenylmaleic anhydride which was recrystallized from ethanol, mp 155–156° (lit.[11] mp 158°).

Reduction of Diphenylmaleic Anhydride. The anhydride (VII, 1 g) was reduced with 0.5 g of lithium aluminum hydride in ether (250 ml) at room temperature. After the usual work-up, 2,3-diphenyl-2-butene-1,4-diol was obtained and identified with the diol obtained above by mixture melting point determination and infrared spectra.

Chromic Anhydride Oxidation of the Diol (V). A pyridine solution of chromic anhydride (1.7 g) was prepared by the known method. To the solution was added a solution of the diol (1 g) in pyridine (12 ml) and the mixture was stirred at room temperature for 2 hr, and left overnight. The reaction mixture was poured into water and extracted with ether. After the usual work-up, the residue was recrystallized from ethanol, and *trans*-diphenylbutyrolactone (IV) was obtained and identified with the one obtained above.

(11) W. Metlescis and H. Zeiss, *J. Am. Chem. Soc.*, **81**, 4117 (1959).

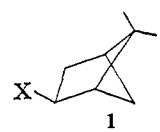
Highly Strained Bicyclic Systems. XI. Synthesis of 2-Bicyclo[2.1.1]hexanol and Tricyclo[2.2.0.0^{2,6}]hexane-1-carboxylic Acid[1,2]

J. Meinwald and J. K. Crandall[3]

Contribution from the Department of Chemistry, Cornell University, Ithaca, New York. *Received October 1, 1965*

Abstract: A convenient synthetic route from bicyclo[2.2.1]heptadiene (**3**) to nortricyclanone (**7**) and then to a number of simple, bifunctional bicyclo[2.1.1]hexanes is described. Decarboxylation of the readily available 2-acetoxybicyclo[2.1.1]hexane-5-carboxylic acids (**12** and **13**) leads to the preparation of bicyclo[2.1.1]hexan-2-ol (**23**). Base treatment of the tosyloxy ester **26** yields **28**, the first representative of the tricyclo[2.2.0.0^{2,6}]hexane ring system; a discussion of the nomenclature problems posed by polycyclic molecules of this type is presented in the Appendix. Hydrogenolytic and base-catalyzed cleavages of this tricyclic nucleus are described.

Earlier papers of this series have been concerned with the synthesis of a number of substituted bicyclo[2.1.1]hexanes and an exploration of the chemistry of these highly strained compounds.[4] Of particular concern is the behavior of the various cations derived from this carbon skeleton. The homologous bicyclo[2.2.1]heptanes have enjoyed extensive investigation for a number of years, and this work has produced a host of highly interesting and important results of practical and theoretical significance.[5] It appeared worthwhile to extend these investigations to smaller ring, bridged, bicyclic systems. In this connection, the solvolysis of 5,5-dimethylbicyclo[2.1.1]hex-2β-yl tosylate (**1**, X = OTs) and the nitrous acid deamination



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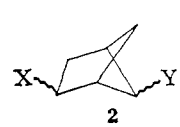

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of the corresponding amine (**1**, X = NH_2) have been discussed in prior publications.[6,7] To permit similar studies on the *parent* ring system, free of methyl substituents, simple bicyclo[2.1.1]hex-2-yl derivatives were required. Synthetic work leading to this objective is

(1) Presented in part at the 18th National Organic Chemistry Symposium, Columbus, Ohio, June 16–20, 1963, Abstracts, pp 37–44.

(2) The partial support of this research by National Science Foundation Research Grant G-22,541 is acknowledged with pleasure.

(3) National Institutes of Health Predoctoral Fellow, 1960–1963.

(4) For the previous paper in this series see J. Meinwald, C. B. Jensen, A. Lewis, and C. Swithenbank, *J. Org. Chem.*, **29**, 3469 (1964).

(5) J. A. Berson in "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963.

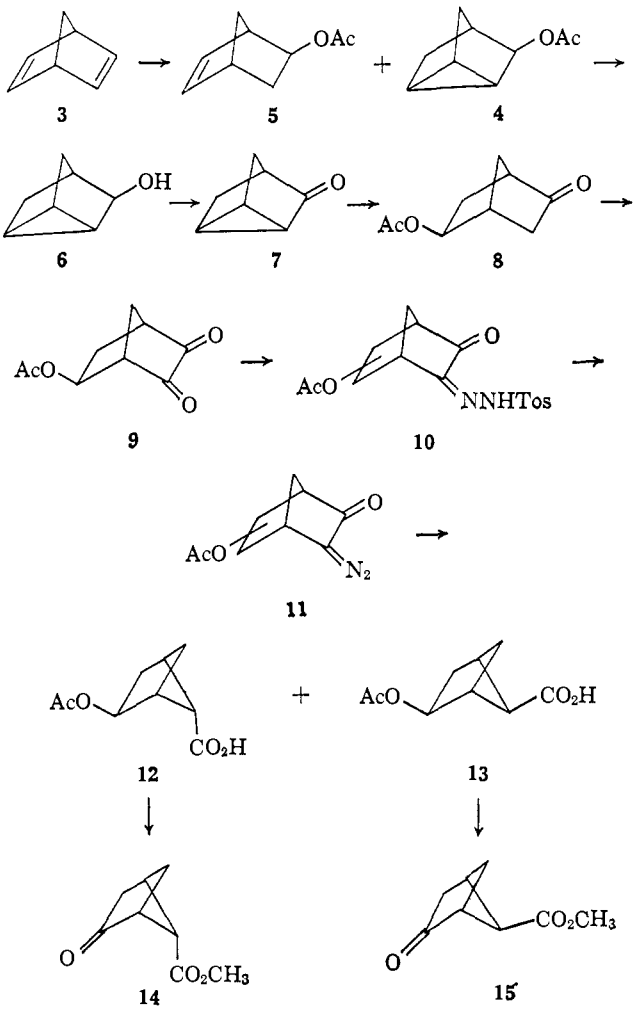
(6) J. Meinwald and P. G. Gassman, *J. Am. Chem. Soc.*, **85**, 57 (1963).

(7) J. Meinwald and P. G. Gassman, and J. J. Hurst, *ibid.*, **84**, 3722 (1962).

now described. In addition, attempts to prepare a bicyclo[2.1.1]hexene derivative are reported, along with the first synthesis of a tricyclo[2.2.0.0^{2,6}]hexane.[8,9]

Although several different syntheses of bicyclo[2.1.1]-hexanes have appeared in recent years, the only method of demonstrated general utility is the photochemical ring contraction of α-diazoketones, the reaction used in the first such synthesis by Horner and Spietschka.[10] This method constitutes the key step in the synthetic sequence described below (see Chart I). Our im-

Chart I



mediate goal was a 2,5-disubstituted bicyclo[2.1.1]-hexane of the type **2**, since this substitution pattern should allow conversion to bicyclo[2.1.1]hexanes having a functional group in either the 2 or 5 position, and possibly to 5-substituted bicyclo[2.1.1]hexenes. A readily available starting material was required, since a long synthetic sequence was envisaged.

Treatment of bicyclo[2.2.1]hepta-2,5-diene (**3**)[11] with 1 equiv of acetic acid in the presence of boron trifluoride etherate served to convert **3** into nortricyclyl acetate (**4**) containing 10–15% of isomeric *exo*-bicyclo-[2.2.1]hept-5-en-2-yl acetate (**5**).[12] The olefinic impurity was conveniently removed from the mixture by treatment with nitrosyl chloride in cold chloroform. The olefin reacted preferentially, yielding a solid, dimeric nitroso chloride which was removed by filtration, giving pure **4** in over 60% yield. Transesterification of the tricyclic acetate with sodium methoxide in methanol produced the corresponding alcohol (**6**), Jones oxidation of which gave nortricyclanone (**7**) in good yield. Treatment of **7** with a mixture of acetic and perchloric acids gave a single acetoxy ketone shown in an earlier publication to have structure **8**.[13] Selenium dioxide oxidation of **8** under carefully controlled conditions produced the yellow, crystalline diketone **9** in about 50% yield.

Ordinarily, α-diketones are smoothly converted into α-diazoketones by formation of a mono-*p*-toluenesulfonylhydrazone and subsequent treatment with aqueous base.[14] A crude tosylhydrazone (**10**) was, in fact, prepared from **9** in the usual fashion, but this material appeared to decompose on standing or attempted purification. Furthermore, treatment of crude **10** with aqueous base did not produce any product which was extractable into organic solvents. This problem was circumvented by a convenient one-step conversion of **9** to the diazoketone **11**. The tosylhydrazone was generated *in situ* by dissolving the reactants in cold chloroform. The resulting solution was then poured through a column of basic alumina, giving in the chloroform eluate good yields of **11** of purity suitable for use in the next step.[15]

Photolysis of **11** in aqueous dioxane produced a 50% yield of acidic material. Glpc analysis of the esterified product showed that a mixture of two compounds in about a 9:1 ratio had been obtained. Chemical and spectroscopic examination confirmed the expected saturated nature of these materials, and supported the assignment of the bicyclo[2.1.1]hexane structures **12** and **13**, epimeric at C_5. The major acid could be obtained as a crystalline solid by fractional recrystallization of the mixture. Confirmatory evidence for the assigned structures was provided by conversion of the photolysis mixture to a mixture of keto esters, **14** and **15**. The three-step sequence used in this conversion consisted of (1) hydrolysis of the acetate group, (2) diazomethane esterification, and (3) chromic acid oxidation of the resulting hydroxy ester mixture. The two keto esters were separated by glpc. Both esters displayed two distinct carbonyl bands in their infrared spectra, one at the expected position for an ester and a second absorption at 5.67 μ. This band at short wavelengths is characteristic of a bicyclo[2.1.1]hexan-2-one, thus further substantiating the assigned structures.[16]

The nmr spectra of **14** and **15** establish their stereo-

(8) Subsequent to the completion of this work, a synthesis of the parent tricyclic hydrocarbon has been described by D. M. Lemal and K. S. Shim, *J. Am. Chem. Soc.*, **86**, 1550 (1964).

(9) See the Appendix at the end of the Experimental Section for a discussion of some relevant nomenclature problems connected with this and similar bridged systems.

(10) L. Horner and E. Spietschka, *Chem. Ber.*, **88**, 934 (1955).

(11) We are indebted to Shell Chemical Co. for a generous gift of this diene.

(12) For other examples of the addition of carboxylic acids to **3**, see (a) L. Schmerling, J. P. Luvisi, and R. W. Welch, *J. Am. Chem. Soc.*, **78**, 2819 (1956); (b) S. Winstein and M. Shatavsky, *Chem. Ind.* (London), 56 (1956); (c) H. K. Hall, Jr., *J. Am. Chem. Soc.*, **82**, 1209 (1960); (d) H. Krieger, *Suomen Kemistilehti*, B33, 183 (1960).

(13) J. Meinwald, J. K. Crandall, and P. G. Gassman, *Tetrahedron*, **18**, 815 (1962).

(14) M. P. Cava and R. L. Little, *Chem. Ind.* (London), 367 (1957).

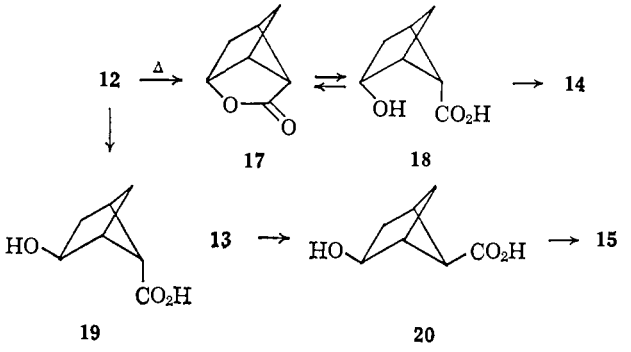
(15) It should be noted here that the position of the acetoxyl group in **10** and **11** (or their homogeneity) is not known, but this element of uncertainty is removed in the subsequent ring-contraction step.

(16) G. Büchi and I. M. Goldman, *J. Am. Chem. Soc.*, **79**, 4741 (1957); J. Meinwald and P. G. Gassman *ibid.*, **82**, 2857 (1960).

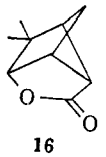
chemistry as the major and minor keto esters, respectively. Meinwald and Lewis[17] originally reported an unusual long-range coupling between the *endo* C_5 proton and the *endo* C_6 proton on the bicyclo[2.1.1]-hexane nucleus. Wiberg, Lowry, and Nist[18] have since tabulated data for a number of 5-substituted bicyclo[2.1.1]hexanes, demonstrating the generality of this long-range coupling. The *endo* C_6 proton is invariably found at highest fields in these spectra. In the absence of an *endo* proton at C_5, this high-field proton is a doublet due to coupling ($J \sim 7$ cps) with the geminal *exo* C_6 proton. With an *endo* proton at C_5, however, the long-range coupling described above appears, and the high-field signal becomes a triplet due to coupling with both the geminal *exo* C_6 proton and the *endo* C_5 proton. (The two coupling constants are similar ($J \sim 7$ cps), giving the observed triplet.) The multiplicity of the high-field resonance of the *endo* C_6 proton is thus useful in determining the stereochemistry about C_5. In fact, examination of the spectra of **14** and **15** shows a single proton at highest field in each case. The major ketone has a doublet at τ 8.63 (J = 7.0 cps) while the minor product has a triplet at 8.44 (J = 7.5 cps). This allows assignment of formula **14** to the major ketone and **15** to the minor one.

Several further conversions serve to confirm chemically the structures and configurations of these products (see Chart II). Attempted distillation of the

Chart II



crude photolysis acids produced a new, neutral material, and increased the proportion of the minor acid in the acidic portion of the distillate. The new material was also obtained in 72% yield by heating the pure major acetoxy acid in the presence of *p*-toluenesulfonic acid. The nmr spectrum of this compound shows no olefinic protons, and a distinctive carbonyl absorption appears at 5.63 μ in its infrared spectrum. The striking similarity of this carbonyl absorption to that of the known lactone **16**[6] suggested that the parent lactone (**17**)



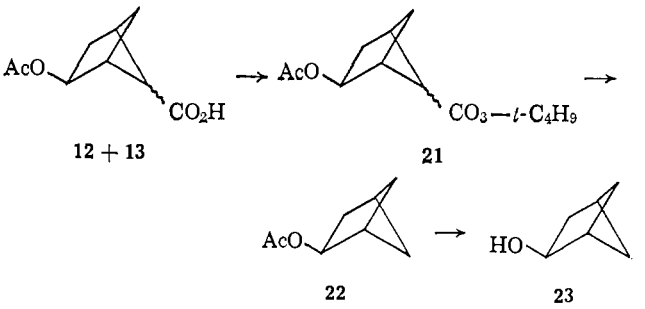
16

had been obtained. This was demonstrated by hydrolysis to the corresponding *syn*-2-hydroxy-*endo*-5-acid (**18**) which could be reconverted to **17** by heating in aqueous acid. Neither of the hydroxy acids (**19** and **20**), obtained by saponification of the original acetoxy acids, was affected by aqueous acid under comparable conditions. Diazomethane esterification and chromic acid oxidation of **18** gave a product identical with the major keto ester described above. Since the carboxyl group of **18** must be *endo*, that of the major keto ester must also be *endo*, and the major acetoxy acid must be **12**. The unanticipated lactonization is apparently a result of the rigid geometry of **12**, which holds the carboxyl group in a position appropriate for an internal displacement of the acetoxy group.

Finally, the hydroxy acid (**20**) derived from the minor photolysis acid gave the minor keto ester (**15**) when subjected to esterification and oxidation. The structures and configurations of all the compounds described above are thus uniquely determined and attention may now be directed toward our remaining synthetic objectives.

The first of these required removal of the carboxyl group from the bridged acids to give 2-substituted bicyclo[2.1.1]hexane derivatives suitable for a study of carbonium ion reactions. This was readily accomplished *via* the corresponding *t*-butyl peresters[19] (see Chart III). Thus, treatment of the acetoxy acid mix-

Chart III



ture with oxalyl chloride gave the expected acid chlorides, which were transformed to the *t*-butyl peresters (**21**) by treatment with *t*-butyl hydroperoxide. Thermal decomposition of **21** in phenylcyclohexane produced 2-acetoxybicyclo[2.1.1]hexane (**22**). The corresponding alcohol (**23**), a crystalline compound, mp 83–84°, was obtained by lithium aluminum hydride reduction of **22**. A solvolytic study of the *p*-toluenesulfonate of this alcohol has been carried out, and will be reported in a subsequent publication.

A second synthetic objective of this investigation was the preparation of 5-substituted bicyclo[2.1.1]hexenes. A number of preliminary experiments designed to convert **24** into the olefin **25** were performed. For

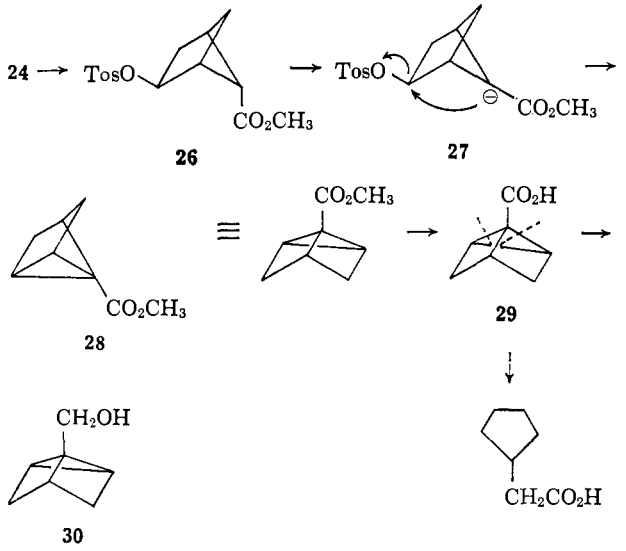
example, pyrolytic eliminations were attempted on the acetate, ethyl carbonate, and methyl xanthate esters of **24**. All of these compounds displayed a reluctance to undergo elimination at temperatures normally utilized for such reactions, probably due to the strained character of the double bond in the desired product. In the case of the latter two derivatives, reaction could be effected under forcing conditions. Cursory examination

(17) J. Meinwald and A. Lewis, *J. Am. Chem. Soc.*, **83**, 2769 (1961).
(18) K. B. Wiberg, B. Lowry, and B. Nist, *ibid.*, **84**, 1594 (1962).
(19) K. B. Wiberg, B. Lowry, and T. Colby, *ibid.*, **83**, 3998 (1961).

of the products by infrared and glpc techniques, however, indicated that **25** was not present in appreciable quantities (see the Experimental Section for details). The failure of these pyrolytic techniques may also reflect the thermal instability of **25**, since this bridged cyclobutane might be expected to undergo especially rapid ring opening at elevated temperatures.[20] Pyrolytic studies were therefore discontinued.

Base-promoted elimination reactions were examined next (see Chart IV). Hydroxy ester **24** was converted

Chart IV

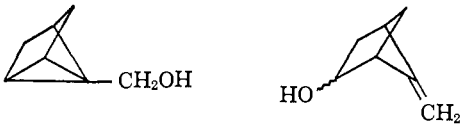


readily to its *p*-toluenesulfonate ester (**26**) in the usual manner. Treatment of **26** with potassium *t*-butoxide in a number of solvents resulted in a smooth elimination of *p*-toluenesulfonic acid at room temperature. Glpc analysis of the volatile products showed that a mixture of two compounds had been obtained. Although the nmr spectrum of this mixture no longer showed the presence of a tosyloxy group, it also lacked olefin hydrogens, and was therefore incompatible with the presence of **25**. The spectrum did suggest that a mixture of the *t*-butyl and methyl esters of a single acid had been obtained. This was confirmed by saponification to give a single, crystalline acid of molecular formula $C_7H_8O_2$, which could be esterified with diazomethane to regenerate one of the original esters ($C_8H_{10}O_2$).

The failure of **26** to form **25** was not entirely unexpected, since an alternative 1,3 elimination leading to the formation of a tricyclic product isomeric with the desired olefin is easily rationalized. Thus, attack of base on the acidic C_5 proton would generate carbanion **27**, which has the proper geometry for an intramolecular displacement of *p*-toluenesulfonate, giving methyl tricyclo[2.2.0.0^{2,6}]hexane-1-carboxylate (**28**).[22]

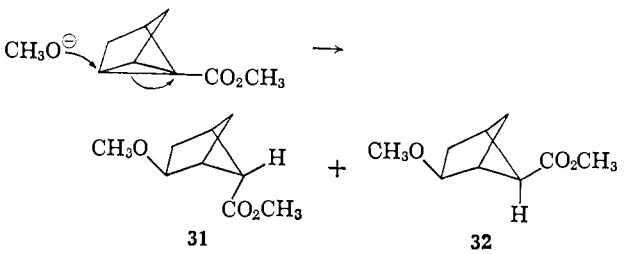
The infrared spectra of both **28** and the corresponding acid (**29**) show carbonyl bands at relatively long wavelengths (5.86 and 6.00 μ, respectively). The ester also has abnormally high end absorption in its ultraviolet spectrum (ϵ 6400 at 210 mμ). These spectral results support the assigned tricyclic structures with cyclopropyl conjugated carbonyl functions. The nmr spectrum of **28** shows a sharp three-proton singlet at τ 6.45 (OCH_3), a complex five-proton multiplet at 7.4, and a two-proton doublet at 8.34.

Lithium aluminum hydride reduction of **28** gave the alcohol **30**, whose nmr spectrum showed a sharp singlet for the two protons α to the hydroxyl group, confirming the attachment of this group to a tertiary carbon atom. In attempting to prepare an analytical sample of **30** by glpc, two rearranged alcohols were obtained. These both showed infrared absorption at 5.9 and 11.5 μ, typical of 5-methylenebicyclo[2.1.1]-hexanes,[23] and may represent the epimeric alcohols of structure **31**.[22c]



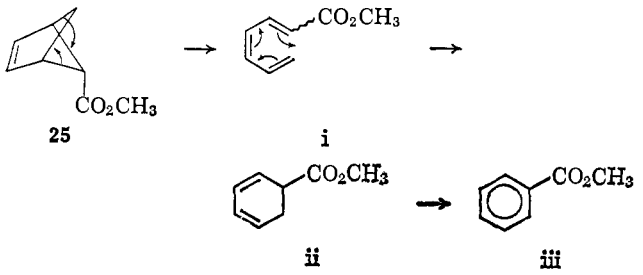
Catalytic hydrogenation of tricyclic acid **29** over Adams catalyst did not proceed at atmospheric pressure, but gave rise to a single, liquid acid identified as cyclopentylacetic acid in a Parr apparatus at 30 psi. The observed uptake of 2 moles of hydrogen is a characteristic feature of similar strained polycyclic ring systems.[8,24] Hydrogenolysis of the two cyclopropane bonds indicated in formula **29** would give rise to the observed product in a straightforward manner.

One further reaction of **28** deserves comment. Prolonged treatment with sodium methoxide in methanol at 100° in a sealed tube results in the addition of methanol to the tricyclic species producing two new compounds in a 3:1 ratio. This unusual reaction is formulated as a nucleophilic addition to the cyclopropyl-conjugated carbonyl system as shown below leading to structures **31** and **32**. This assignment was



confirmed by the alternate preparation of **31** from

(20) Pyrolysis of the ethyl carbonate at 450° gave methyl benzoate as the predominant product. Since conjugating groups attached to cyclobutanes are known to facilitate ring cleavage,[21] this interesting transformation is probably best formulated by the following sequence involving **25** as the initial intermediate.



(21) L. Daignault and W. Walters, *J. Am. Chem. Soc.*, **80**, 541 (1958).

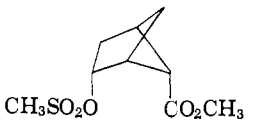
(22) *Cf.* (a) H. Toivonen, *Suomen Kemishtilehti*, B**31**, 354 (1958); (b) H. Krieger, *ibid.*, B34, 24 (1961); (c) H. Hart and R. Martin, *J. Org. Chem.*, 24, 1267 (1959).

(23) J. Meinwald, C. B. Jensen, A. Lewis, and C. Swithenbank, *ibid.*, **29**, 3469 (1964); J. Meinwald, A. Lewis, and P. Gassman, *J. Am. Chem. Soc.*, **84**, 977 (1962).

(24) K. Wiberg and R. Ciula, *ibid.*, **81**, 2561 (1959); W. Moore, H. Ward, and R. Merritt, *ibid.*, **83**, 2019 (1961); J. Meinwald, C. Swithenbank, and A. Lewis, *ibid.*, **85**, 1880 (1963).

hydroxy acid **19** by consecutive treatment with sodium hydride and methyl iodide in dimethylformamide. The two materials had identical infrared spectra and glpc retention times. The nmr spectrum of **31** is very similar to that of **24**, as expected. The ready attack of methoxide on **28** is presumably due to relief of ring strain in going from **28** to **31**[25] and suggests the possibility of similar reactions with other nucleophiles.

Since the failure of the elimination reaction to give olefinic product appeared to be due to the availability of a more favored reaction pathway, a sulfonate ester was prepared which has an unfavorable stereochemistry for similar internal displacement. Treatment of the methyl ester of **18** with methanesulfonyl chloride gave the corresponding methanesulfonate, **33**. However, several attempts to carry out an elimination reaction on this material were unsuccessful, only starting material being recovered.



33

Although the desired bicyclo[2.1.1]hexene system has not yet been obtained, the present efforts have resulted in the synthesis of the first representative of the tricyclo[2.2.0.0^{2,6}]hexane ring system, and a brief study of the chemistry of this novel nucleus. In addition, a number of doubly functionalized bicyclo[2.1.1]hexanes suitable for further attempts at introducing a double bond into this carbon skeleton have been prepared and characterized.

Experimental Section

All boiling points and melting points are uncorrected. Petroleum ether refers to material with a 30–60° boiling range. Anhydrous magnesium sulfate was used as a drying agent. Nmr spectra were taken on a Varian A-60 instrument in carbon tetrachloride solution, unless otherwise noted. Microanalyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark, and Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Gas–Liquid Partition Chromatography (Glpc). Analytical determinations were run on an Aerograph Model 600 Hy-fl. Six-foot columns of the following liquid phases on Firebrick were used: Carbowax (15% Carbowax 20M), LAC-446 (20% LAC-446), NGS (3% neopentyl glycol sebacate), and TCEP (20% 1,2,3-tris(2-cyanoethoxy)propane).

A Beckman GC-2 gas chromatograph was used for preparative glpc. The following columns were used: Carbowax (10 ft of 10% Carbowax 20M), LAC-446 (5 ft of 20% LAC-446), and TCEP (5 ft of 20% 1,2,3-tris(2-cyanoethoxy)propane).

Nortricyclyl Acetate (4).[12] A mixture of 156 g (1.70 moles) of **3**, 105 g (100 ml, 1.67 moles) of glacial acetic acid, and 1 ml of boron trifluoride etherate was heated in a 500-ml flask equipped with a condenser and drying tube for 3 hr on a steam bath. The reaction mixture was cooled to room temperature and diluted with 250 ml of ether. The ethereal solution was washed with two 50-ml portions of aqueous ammonia (four parts of water to one part of concentrated NH_4OH) and 50 ml of water, and dried ($MgSO_4$). The solvent was removed by distillation through a short column of glass helices, and the dark residue was distilled under reduced pressure to give *ca.* 200 g of a mixture of nortricyclyl acetate and *exo*-5-acetoxybicyclo[2.2.1]hept-2-ene (**5**) as a colorless liquid, bp 85–95° (15 mm). (The exact proportion of unsaturated acetate varies slightly but is typically 10–15% as determined by glpc.)

The acetate mixture was dissolved in 500 ml of AR chloroform in a 2-l. erlenmeyer flask and cooled to −10° in an ice–salt bath. Nitrosyl chloride was bubbled into the solution with swirling until the color of the solution changed through a bright green to a brownish green (indicating excess nitrosyl chloride). A white precipitate formed at this point. Petroleum ether (500 ml) was added and the mixture was cooled for an additional 15 min. The precipitated nitrosyl chloride adduct was removed by suction filtration using a large Büchner funnel and a water aspirator. The filtrate was washed with two 200-ml portions of saturated sodium carbonate solution and 500 ml of saturated sodium chloride, and dried. The solvent was removed through a short column of glass helices and the dark residue was distilled under reduced pressure to give 158–167 g (62–66%) of nortricyclyl acetate (**4**) as a faintly green liquid, bp 83–85° (13 mm). (The hot distillation residue decomposes vigorously with the evolution of irritating gases when opened to the atmosphere. Consequently, the distillation flask should be cooled to room temperature before breaking the vacuum.)

The crude dimeric nitrosyl chloride adduct of **5** was recrystallized twice from chloroform to give the pure white crystalline adduct, mp 152–153°. This material was not investigated further.

Anal. Calcd for $(C_9H_{12}O_3NCl)_2$: C, 49.66; H, 5.56; Cl, 16.29; N, 6.44. Found: C, 49.74; H, 5.51; Cl, 16.57; N, 6.39.

Nortricyclanol (6). The nortricyclyl acetate obtained as described above was added to 500 ml of AR anhydrous methanol in which about 0.5 g of metallic sodium had been dissolved. The solvent was distilled off slowly through a short column of glass helices using a steam bath. The residue was cooled, diluted with 250 ml of petroleum ether, washed twice with 50-ml portions of water, and dried. The solvent was removed by distillation through a short column of glass helices, finally at reduced pressure. The crude product, which solidified on cooling, was sublimed at 80° (2 mm) to yield 101–107 g (89–94%) of nortricyclanol (**6**). After a second sublimation, the product melted at 108–109°.[26] Analysis by glpc showed no detectable impurities under conditions where <1% of isomeric material would have been easily visible.

Nortricyclanone (7). A solution of 110 g (1.0 mole) of **6** (the crude alcohol before sublimation is a satisfactory starting material for this reaction) in 600 ml of AR acetone was cooled (ice bath) in a 2-l. three-necked flask equipped with a high-speed stirrer, a thermometer, and a pressure-regulating dropping funnel. A cold solution of 70 g (0.7 mole) of chromium trioxide and 112 g (61 ml, 1.1 moles) of concentrated sulfuric acid in 300 ml of water was added at a rate to maintain the temperature at about 20°. The reaction mixture was stirred for 3 hr after the addition was completed. A small amount of sodium bisulfite was added until the brown color of chromic acid was gone from the upper layer of the two-phase mixture. The top layer was decanted and the dense green lower layer was extracted with 200 ml of petroleum ether. Combination of this extract with the original upper layer caused a separation into two phases. The lower phase was drawn off and added to the original lower phase, which was then extracted three times more with 200-ml portions of petroleum ether. The extracts were combined, washed twice with 50-ml portions of saturated sodium chloride solution, and dried. The solvent was removed by distillation through a short column of glass helices, and the residue was distilled under vacuum to give 87–95 g (81–88%) of **7**, bp 103–104° (75 mm), $n^{26}D$ 1.4873 (lit.[27] bp 78–79° (24 mm), $n^{25}D$ 1.4878). (This product contained <1% of the starting material and no other detectable impurity by glpc analysis.)

In large-scale preparative runs the nitrosyl chloride purification step was omitted and a sufficient excess of oxidizing solution was used to oxidize the olefinic impurity to acid.

***exo*-5-Acetoxybicyclo[2.2.1]heptan-2-one (8).** A mixture of 182 g (1.08 moles) of **7**, 25 ml of 70% perchloric acid, and 400 ml of glacial acetic acid was heated on the steam bath for 4 hr. Forty grams of potassium acetate was added and most of the acetic acid was removed under vacuum. The residue was dissolved in 250 ml of ether, washed twice with water, and then with saturated sodium carbonate solution until the washes were basic. The combined washes were extracted with ether and the combined extracts were dried. The solvent was removed and the residue was distilled to yield 241 g (85%) of **8**, bp 88–90° (1.2 mm), $n^{24}D$ 1.4742; infrared spectrum (neat) 5.75 and 8.07 μ.

Anal. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 63.91; H, 7.36.

(25) There are several reported cases of nucleophilic addition to cyclopropanes, but in all of these examples the situation is more obviously favorable for addition than that described above; for a summary see J. M. Stewart and H. H. Westberg, *J. Org. Chem.*, 30, 1951 (1965).

(26) J. D. Roberts, E. R. Trumbull, Jr., W. Bennett, and R. Armstrong, *J. Am. Chem. Soc.*, 72, 3116 (1950).

(27) H. K. Hall, Jr., *ibid.*, 82, 1209 (1960).

A semicarbazone was prepared in the usual way. Two recrystallizations from acetonitrile gave an analytical sample, mp 205–206° (lit.[28] mp 208.5–209.0°).

Anal. Calcd for $C_{10}H_{15}N_3O_3$: C, 53.32; H, 6.71; N, 18.66. Found: C, 53.39; H, 6.73; N, 18.61.

***exo*-5-Acetoxybicyclo[2.2.1]heptan-2,3-dione (9).** Compound **8** (150 g, 0.89 mole), 100 g (0.90 mole) of freshly sublimed selenium dioxide, and 150 ml of toluene were heated at 150° in an apparatus set up for azeotropic removal of water until the theoretical amount of water was collected (*ca.* 2 days). Most of the toluene was removed by distillation under vacuum. The cooled residue was diluted with ether and 67 g (95%) of metallic selenium was removed by suction filtration. The solvent was removed and the residue was distilled through a Podbielniak column at reduced pressure. After a forerun of 17 g of unreacted starting material, 95 g (58%) of yellow diketone **9**, bp 133–138° (1 mm), was obtained. The hygroscopic product, mp 70–74°, crystallized on standing. Fractional vacuum sublimation gave an analytical sample, mp 80–81°; infrared spectrum ($CHCl_3$) 5.61, 5.67, 5.73, and 8.01 μ.

Anal. Calcd for $C_9H_{10}O_4$: C, 59.33; H, 5.33. Found: C, 59.24; H, 5.68.

Diazoketone 11. To an ice-cold solution of 30.0 g of **9** in 150 ml of AR chloroform containing about 10 g of anhydrous magnesium sulfate was added 31.0 g of tosylhydrazine in small portions. The solution was allowed to stand for several hours in the refrigerator and was then chromatographed directly on an 8 × 15 cm column made up of 900 g of basic alumina (Merck 71707), using chloroform as eluent. The column was eluted until appreciable amounts of yellow diazoketone were no longer obtained. The chloroform solution of diazoketone was concentrated on a flash evaporator at 50° and finally by pumping under high vacuum for 10 min to give 25.4 g (79%) of crude diazoketone as a mobil yellow oil; infrared spectrum (neat) 4.80, 5.77, 5.94, and 8.06 μ (no N–H or aromatic absorption). This material was used for the next step without further purification. Appreciably better yields were obtained in smaller scale reactions.

Irradiation of Diazoketone 11. A solution of 50.0 g of **11** in 700 ml of Spectrograde *p*-dioxane and 500 ml of water was irradiated under a nitrogen atmosphere with a 673A-36 Hanovia 550-w quartz mercury vapor lamp in a flask equipped to accommodate a water-cooled quartz immersion well. The course of the reaction was monitored by the disappearance of the diazo band at 4.80 μ in the infrared, and typically required about 4 hr. The reaction mixture was neutralized with sodium bicarbonate and concentrated to about 500 ml on a flash evaporator. The resulting dark solution was extracted with chloroform to remove neutral side products. (Addition of sodium chloride helps to break up emulsions formed at this point.) The aqueous phase then was cooled in an ice bath and carefully acidified with concentrated hydrochloric acid. This solution was saturated with sodium chloride and extracted thoroughly with ether. The combined extracts were dried and treated with Norit, and the solvent was removed to give 24.2 g (51%) of crude acidic product as a yellow oil. Glpc analysis of the methyl esters (diazomethane) on an NGS column demonstrated the presence of two components in a 9:1 ratio. (The ratio varies slightly with reaction conditions from this ratio to an 8:2 mixture.)

The major component could be isolated in a pure state by recrystallization from hexane (Norit), yielding crystalline *anti*-2-acetoxybicyclo[2.1.1]hexane-*endo*-5-carboxylic acid (**12**), mp 87–89°, which showed negative bromine and permanganate tests for unsaturation. Two sublimations gave an analytical sample, mp 89–90°; infrared spectrum (KBr) 2.94 (broad), 5.79, 5.90, and 8.01 μ. The nmr spectrum in $CDCl_3$ had a one-proton singlet at τ 1.36 (CO_2H), a one-proton doublet at 4.63 (C_2 hydrogen), a broad, two-proton singlet at 7.21 (bridgehead protons), a sharp singlet corresponding to three protons at 7.93 (CH_3CO_2–), and the rest of the spectrum consisted of a number of peaks between 7.5 and 9.2 representing the other five protons.

Anal. Calcd for $C_9H_{12}O_4$: C, 58.69; H, 6.57. Found: C, 58.63; H, 6.63.

The mother liquors from the above recrystallizations were concentrated, and the resulting oily mixture of acids was used where either a mixture of acids was desired or the stereochemistry at C_5 was destroyed in the subsequent reaction.

***endo*- and *exo*-5-Carbomethoxybicyclo[2.1.1]hexan-2-one (14 and 15).** A solution of 4.82 g (26 mmoles) of the photochemically prepared acid mixture and 4.5 g of potassium hydroxide in 40 ml of water was allowed to stand overnight. The reaction mixture was acidified with concentrated hydrochloric acid in the cold, saturated with sodium chloride, and extracted eight times with 50-ml portions of ether. After drying the combined extracts, the solvent was removed and the residual oil was esterified directly with ethereal diazomethane. The solvent was removed and the residual oil was distilled to give 3.15 g (77%) of the hydroxy ester mixture, bp 90–97° (2 mm).

A stirred solution of 1.5 g (1 mmole) of this mixture in 30 ml of AR acetone, cooled in an ice bath, was treated dropwise with 5 ml of 6 *N* chromic acid. After 1 hr the acetone solution was decanted from the inorganic precipitate and most of the solvent was removed. The residue was taken up in ether, washed with sodium carbonate solution, and dried. Removal of the solvent gave 1.13 g of incompletely oxidized product. Recycling with 2.5 ml of chromic acid gave 0.81 g of ketonic mixture. Preparative glpc on Carbowax gave pure samples of the two components.

The major component was *endo*-5-carbomethoxybicyclo[2.1.1]-hexan-2-one (**14**), $n^{18}D$ 1.4797; infrared spectrum (neat) 5.67 and 5.79 μ. The nmr spectrum had a sharp singlet corresponding to three protons at τ 6.59 (OCH_3), a complex, three-proton multiplet at 7.1, a broad, three-proton singlet at 8.05, and a well-defined one-proton doublet centered at 8.63 (J = 7 cps) (*endo* C_6 hydrogen).

Anal. Calcd for $C_8H_{10}O_3$: C, 62.32; H, 6.54. Found: C, 62.04; H, 6.67.

The minor component was *exo*-5-carbomethoxybicyclo[2.1.1]-hexan-2-one (**15**), $n^{20}D$ 1.4749, infrared spectrum (neat) 5.67 and 5.78 μ. The nmr spectrum had a sharp, three-proton singlet at τ 6.46 (OCH_3), broad, one-proton singlets at 7.09 and 7.14, a one-proton complex multiplet at 7.3, a one-proton doublet at 7.45 (J = 7.5 cps) (C_5 hydrogen), a complex, two-proton doublet at 7.9, and a well-defined, one-proton triplet centered at 8.44 (J = 7.5 cps) (*endo* C_6 proton).

Anal. Calcd for $C_8H_{10}O_3$: C, 62.32; H, 6.54. Found: C, 62.01; H, 6.72.

***syn*-2-Hydroxybicyclo[2.1.1]hexane-*endo*-5-carboxylic Acid Lactone (17).** A. A mixture of 1.81 g (98 mmoles) of **12** and 0.1 g of *p*-toluenesulfonic acid monohydrate was heated to 150–160° (2 mm) in a microdistillation apparatus. A colorless distillate, boiling at about 80°, was collected. This was taken up in ether, washed with sodium bicarbonate solution and water, and dried. Removal of the solvent gave 0.88 g (72%) of **17**, mp 50–61°. Recrystallization from petroleum ether followed by sublimation gave an analytical sample, mp 64–65°; infrared spectrum (CCl_4) 5.63 and 5.57 μ (shoulder). The nmr spectrum had a broad one-proton singlet at τ 5.21 (C_2 hydrogen), two extremely complex, three-proton multiplets at *ca.* 7 and 8, and a sharp, one-proton doublet centered at 8.79 (J = 7.5 cps) (*endo* C_6 hydrogen).

Anal. Calcd for $C_7H_8O_2$: C, 67.73; H, 6.50. Found: C, 67.92; H, 6.39.

B. Fifty milligrams (0.40 mmole) of **18** in 8 ml of an aqueous 5% sulfuric acid solution was heated on the steam bath for 0.5 hr. The reaction mixture was cooled, neutralized with sodium bicarbonate, and extracted several times with ether. The combined extracts were dried and the solvent was removed to give a semicrystalline residue which after sublimation at 50° (13 mm) gave 17 mg (39%) of **17**, mp 65–66°. The infrared spectrum was identical with that of the material obtained above, and a mixture melting point was undepressed.

The aqueous solution was acidified with concentrated hydrochloric acid, saturated with sodium chloride, and extracted thoroughly with ethyl acetate. The extracts were dried and the solvent was removed to give 15 mg (30%) of unchanged starting material, mp 139–141°.

Under more vigorous reaction conditions, excellent yields of starting material were recovered from aqueous acid treatment of **19** and **20**.

***syn*-2-Hydroxybicyclo[2.1.1]hexane-*endo*-5-carboxylic Acid (18).** A mixture of 0.88 g (7.1 mmoles) of **17**, 0.4 g of sodium hydroxide, 10 ml of water, and 15 ml of methanol was allowed to stand overnight. Most of the methanol was removed on the steam bath and the resulting solution was cooled in an ice bath, acidified carefully with concentrated hydrochloric acid, saturated with sodium chloride, and extracted several times with ethyl acetate. The combined extracts were dried and treated with Norit, and the solvent was removed to give 0.75 g (75%) of **18**, mp 139–141°. Recrystallization from ether gave an analytical sample, mp 141–142.5°.

Anal. Calcd for $C_7H_{10}O_3$: C, 59.14; H, 7.09. Found: C, 58.96; H, 7.14.

The methyl ester was prepared by treatment with ethereal diazo-

(28) H. Krieger, *Ann. Acad. Sci. Fennicae Ser. A. II*, No. 109 (1961).

methane, and the solvent was removed to give the liquid ester; infrared spectrum (neat) 2.94 and 5.82 μ. The nmr spectrum had a broad, one-proton doublet at τ 5.92 (C_2 hydrogen), one-proton singlet at 6.33 (OH), a sharp, three-proton singlet at 6.48 (OCH_3), a broad, two-proton singlet at 7.32 (bridgehead hydrogens), a broad, one-proton singlet at 7.50 (C_5 hydrogen), several broad peaks between 7.8 and 8.5 corresponding to two protons, a one-proton doublet split further into doublets at 8.63 (J_1 = 7 cps; J_2 = 3 cps) (*exo* C_6 hydrogen), and a one-proton doublet at 9.19 (J = 7 cps) (*endo* C_6 hydrogen).

Chromic Acid Oxidation of 18. A 204-mg sample of **18** (1.4 mmoles) was esterified with ethereal diazomethane as usual. Removal of the solvent gave a light yellow oil; infrared spectrum (neat) 3.00 and 5.80 μ. This was dissolved in 25 ml of AR acetone and 0.7 ml of 6 *N* chromic acid solution was added dropwise to the cooled, stirred solution. After 0.5 hr most of the acetone was removed and the residue was taken up in a small amount of water and extracted several times with ether. The combined extracts were washed with sodium carbonate solution and water, and dried. Removal of the solvent gave 162 mg (73%) of crude **14** which was shown by its infrared spectrum and glpc retention time on an NGS column to be identical with the major component in the mixture obtained directly from the mixture of photochemically produced acids.

***anti*-2-Hydroxybicyclo[2.1.1]hexane-*exo*-5-carboxylic Acid (20).** A sample of the photochemically obtained acid mixture (11.8 g) was saponified as described above. The crude product was fractionally recrystallized from ether–petroleum ether. The initial crop of crystals was a new acid. Recrystallization from ether and sublimation gave a pure sample of **20**, mp 132–133.5°; infrared spectrum (Nujol) 3.02 and 5.89 μ.

Anal. Calcd for $C_7H_{10}O_3$: C, 59.14; H, 7.09. Found: C, 59.09; H, 7.18.

The later crops of crystals consisted of **19**.

The methyl ester of **20** was prepared by treatment with ethereal diazomethane. Removal of the solvent gave the liquid methyl ester; infrared spectrum (neat) 2.90 and 5.78 μ. The nmr spectrum had a broad, one-proton doublet at τ 5.77 (C_2 hydrogen), a sharp, three-proton peak at 6.45 (OCH_3), a one-proton peak at 5.57 (OH), a broad, two-proton singlet at 7.43 (bridgehead hydrogens), a complex multiplet at 8.0 corresponding to four protons, and a one-proton triplet centered at 8.53 (J = 7 cps) (*endo* C_6 hydrogen) partially obscured by a broad doublet centered at 8.7 (probably one of the C_3 hydrogens).

Chromic Acid Oxidation of 20. A 200-mg sample of **20** was treated as described above for **18** to give its liquid methyl ester; infrared spectrum (neat) 2.90 and 5.80 μ. Oxidation of 67 mg (0.43 mmole) as described above gave 40 mg (60%) of **15**, identified by its infrared spectrum and glpc retention time on an NGS column.

***anti*-2-Hydroxybicyclo[2.1.1]hexane-*endo*-5-carboxylic Acid (19).** A solution of 8.00 g (0.43 mole) of **12** and 4.0 g of sodium hydroxide in 80 ml of water was heated on the steam bath for 5.5 hr. The reaction mixture was cooled in an ice bath and carefully acidified by dropwise addition of concentrated hydrochloric acid. This solution was saturated with sodium chloride and extracted several times with ethyl acetate. The combined extracts were dried and treated with Norit, and the solvent was removed. The resulting oil was pumped under high vacuum to remove acetic acid. The residual oil was recrystallized from ether–petroleum ether, several crops being taken. The total combined yield of **19**, mp 100–104°, was 5.07 g (82%). One further recrystallization followed by vacuum sublimation gave an analytical sample, mp 101–102.5°; infrared spectrum (KBr) 2.94 and 5.90 μ.

Anal. Calcd for $C_7H_{10}O_3$: C, 59.14; H, 7.09. Found: C, 59.11; H, 7.04.

Methyl *anti*-2-Hydroxybicyclo[2.1.1]hexane-*endo*-5-carboxylate (24). A 1.5-g sample (96 mmoles) of **19** was esterified with ethereal diazomethane in the normal fashion. The solution was dried, and the solvent was removed. Distillation of the residual oil gave 1.46 g (89%) of **24**, bp 87–93° (2 mm), n^{19}D 1.4803; infrared spectrum (neat) 2.96 and 5.76 μ. This product was homogeneous by glpc analysis on NGS. The nmr spectrum had a one-proton doublet (J = 7 cps) at τ 5.75 (C_2 hydrogen), a sharp, one-proton singlet at 5.93 (OH), a sharp, three-proton singlet at 6.52 (OCH_3), a broad, three-proton singlet at 7.44 (bridgehead hydrogens plus the C_5 hydrogen), a one-proton doublet of doublets centered at 7.98 (J_1 = 11, J_2 = 7 cps), and a two-proton singlet at 8.62 obscuring half of a broad one-proton doublet centered at 8.7.

Anal. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.75. Found: C, 61.42; H, 7.78.

2-Acetoxybicyclo[2.1.1]hexane (22). To a solution of 9.5 g (52 mmoles) of the photochemically prepared acid mixture in 100 ml of benzene was added 4.6 ml of oxalyl chloride. After standing for 6 hr protected from moisture, the solvent and excess reagent were removed on the flash evaporator to give 10.5 g of crude acid chloride; infrared spectrum (neat) 5.56, 5.77, and 8.00 μ. This was dissolved in 50 ml of dry ether and added dropwise to a stirred, cooled solution of 8 ml of *t*-butyl hydroperoxide and 5 ml of dry pyridine in 50 ml of dry ether over a period of 0.5 hr. After standing overnight in the refrigerator, the reaction mixture was washed twice with cold portions of 10% sulfuric acid, once with sodium carbonate solution, and thrice with water. The solution was dried and the solvent was removed under vacuum at room temperature to give 9.3 g (70%) of crude **21**; infrared spectrum (neat) 5.68, 5.78, and 8.05 μ.

The crude perester was dissolved in 50 ml of phenylcyclohexane and heated to 150° for 1 hr under a nitrogen atmosphere. The crude reaction mixture was distilled through a Podbielniak column at atmospheric pressure to give 1.55 g (30%) of **22**, bp 170–180°; infrared spectrum (neat) 5.78 and 8.00 μ. An analytical sample was prepared by preparative glpc on Carbowax, n^{25}D 1.4477. The nmr spectrum showed a broad, one-proton doublet at τ 4.97 (C_2 hydrogen), a broad, two-proton peak at 7.48 (bridgehead protons), and a sharp, three-proton singlet at 8.04 (CH_3CO_2–). The remainder of the spectrum was a complex series of sharp peaks between 7.6 and 9.2.

Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.43; H, 8.61.

Bicyclo[2.1.1]hexan-2-ol (23). A solution of 1.55 g (11.1 mmoles) of **22** in 20 ml of dry ether was added to an ice-cold, stirred slurry of 0.5 g of lithium aluminum hydride in 50 ml of dry ether. After stirring for 2 hr, the complex was decomposed by adding 2.0 ml of water and working up in the usual fashion. The solvent was removed by distillation through a column of glass helices, and the residue was purified by preparative glpc on Carbowax to give 525 mg (48%) of highly volatile, crystalline **23**, mp 82.5–83.5°; infrared spectrum (Nujol) 3.04 μ. An analytical sample, mp 83–84°, was prepared by sublimation. The nmr spectrum had a one proton doublet at τ 5.68 (J = 6 cps) (C_2 hydrogen), a one-proton peak at 6.13 (OH), a broad, two-proton singlet at 7.58 (bridgehead protons), and a complex series of peaks between 7.8 and 9.3 similar to that observed for **22**, accounting for six additional protons.

Anal. Calcd for $C_6H_{10}O$: C, 73.43; H, 10.27. Found: C, 73.76; H, 10.38.

Pyrolysis of Methyl *anti*-2-Acetoxybicyclo[2.1.1]hexane-5-carboxylate. One-half gram of the acetoxy acid mixture was esterified with ethereal diazomethane. The solvent was removed to give a light yellow oil (infrared spectrum (neat) 5.77 and 8.00 μ), which was taken up in 10 ml of petroleum ether and slowly dropped through an 18-in. glass tube packed with carborundum chips in a stream of nitrogen. The temperature of the tube was held at 450°. Examination of the product by analytical glpc showed several products as well as a large amount of unreacted starting material.

Preparation and Pyrolysis of the Ethyl Carbonate of 24. To a solution of 0.50 g of **24** in 10 ml of cold, dry pyridine was added 1.0 ml of ethyl chloroformate. After standing overnight in the refrigerator, the reaction mixture was poured into ice–water containing 10 ml of concentrated hydrochloric acid. The mixture was extracted with ether. The extracts were washed with sodium bicarbonate and water and dried. Removal of the solvent gave the liquid carbonate ester; infrared spectrum (neat) 5.77 μ.

Attempted pyrolysis at 360° under the conditions described for the acetate gave only recovered starting material. Raising the temperature to 450° resulted in complete reaction of the starting material. Analytical glpc on Carbowax showed that two major products had been formed. (These were probably the same as the major products from the acetate pyrolysis). These materials were separated by preparative glpc. The major component was methyl benzoate as demonstrated by a comparison of infrared spectra. The other material was a colorless oil; infrared spectrum (neat) 5.89, 6.12, and 6.37 μ.

An attempt to decompose the corresponding methyl carbonate (prepared analogously using methyl chloroformate) by heating in dimethyl sulfoxide at 180° under nitrogen gave only recovered starting material.

Preparation and Pyrolysis of the Xanthate of 24. A mixture of 1.10 g (7 mmoles) of **24** and 0.35 g of sodium hydride in 25 ml of

dry ether was heated to reflux for 3 hr. Two grams of carbon disulfide was added and heating was continued for 4 hr. After adding 2.0 g of methyl iodide, the mixture was allowed to reflux for an additional 12 hr. The reaction mixture was diluted with ether and washed with water several times. Drying and removal of the solvent gave 1.13 g (65%) of the crude liquid xanthate; infrared spectrum (neat) 5.79 μ.

The crude xanthate was heated to 250–280° in a small distillation apparatus for 4 hr. The total crude product was analyzed by glpc which showed that a variety of products had been obtained. There was a great deal of high-boiling material, probably starting material. The major volatile component was isolated by preparative glpc. The infrared spectrum had a weak band at 5.78 and strong ones at 6.08 and 11.4 μ.

endo-**5-Carbomethoxybicyclo[2.1.1]hexan-*anti*-2-ol Tosylate (26).** To an ice-cold solution of 5.00 g (32 mmoles) of **24** in 30 ml of dry pyridine was added 6.10 g (32 mmoles) of tosyl chloride. The reaction mixture was allowed to stand overnight in the refrigerator and was then poured into 300 ml of an ice–water mixture containing 30 ml of concentrated hydrochloric acid. The resulting mixture was extracted several times with ether, and the combined extracts were washed with water, sodium carbonate solution, and water. Drying of the solution and removal of the solvent gave 8.80 g (89%) of **26** as a light yellow, viscous oil; infrared spectrum (neat) 5.78, 6.23, 7.33, 8.38, 8.46 μ. All attempts to crystallize this material failed. An analytical sample was prepared by treating an ethereal solution with Norit, filtering, and removing the solvent by pumping under high vacuum for several hours.

Anal. Calcd for $C_{15}H_{18}O_5S$: C, 58.05; H, 5.84; S, 10.33. Found: C, 58.08; H, 5.99; S, 9.68.

Treatment of 26 with Potassium *t*-Butoxide. A solution of 8.10 g (26 mmoles) of **26** in 50 ml of dry benzene was added to 300 ml of dry benzene containing 6 g of commercial, alcohol-free potassium *t*-butoxide, and the resulting solution was allowed to stand overnight, protected with a drying tube, under a nitrogen atmosphere. A gelatinous precipitate began to form almost immediately. The reaction mixture was poured into water and the benzene layer separated and washed twice with small portions of water. The benzene solution was dried, the solvent removed through a column of glass helices, and the residual oil distilled under vacuum to give 3.33 g of a volatile, sweet smelling oil, bp 100–113° (80 mm). Analytical glpc indicated approximately a 1:1 mixture of two components. The nmr spectrum of this material was identical with that of the tricyclic ester (**28**) prepared below, except that the τ 6.45 peak (OCH_3) was decreased in relative intensity and a new sharp singlet appeared at τ 8.65. This is attributed to the *t*-butyl ester of **29** formed by transesterification.

Similar results were obtained when ether or dimethyl sulfoxide was used as solvent.

Tricyclo[2.2.0.0^{2,6}]hexane-1-carboxylic Acid (29). One gram of the tricyclic ester mixture described above was added to 20 ml of anhydrous methanol in which 0.3 g of sodium had been dissolved, and the resulting solution was heated to reflux for 2 hr. Fifteen milliliters of water was added, and refluxing was continued for 3 hr longer. Some of the solvent was removed and water was added to the remainder. The resulting solution was extracted with ether, acidified with concentrated hydrochloric acid in the cold, and extracted several times with ether. These latter extracts were dried, and the solvent removed to give 0.74 g of **29**, mp 50–62°. After two fractional sublimations the melting point rose to 64–66°; infrared spectrum (CCl_4) 6.00 μ.

Anal. Calcd for $C_7H_8O_2$: C, 67.73; H, 6.50. Found: C, 67.75; H, 6.34.

A sample of this acid was esterified with ethereal diazomethane, and the resultant ester was purified by preparative glpc on Carbowax to give methyl tricyclo[2.2.0.0^{2,6}]hexane-1-carboxylate (**28**), n^{25}D 1.4757; ultraviolet spectrum (EtOH) 210 mμ (ϵ 6400); infrared spectrum (neat) 5.86 μ. The nmr spectrum had a sharp, three-proton singlet at τ 6.45 (OCH_3), a complex, five-proton multiplet at 7.4, and a two-proton doublet at 8.34 (J = 8 cps).

Anal. Calcd for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: C, 69.58; H, 7.45.

1-Hydroxymethylbicyclo[2.2.0.0^{2,6}]hexane (30). A solution of 0.48 g (4.4 mmoles) of **28** in 10 ml of dry ether was added dropwise to an ice-cold, stirred slurry of 0.3 g of lithium aluminum hydride in 30 ml of ether. After 2 hr, the reaction mixture was hydrolyzed by adding 1.2 ml of water dropwise with stirring and cooling. The inorganic salts were removed by suction filtration, and the solution was dried. Removal of the solvent, finally under high vacuum, gave 0.32 g (84%) of **30** as a colorless oil; infrared spectrum (neat) 3.04, 3.29, 3.45, and 3.51 μ. The nmr spectrum had a one-proton singlet at τ 6.12 (OH), a sharp, two-proton singlet at 6.35 ($-CH_2O-$), a seven-line multiplet centered at *ca.* 7.6, a two-proton pair of multiplets centered at 8.29 (cyclopropyl proton), and a sharp, two-proton doublet centered at 8.46 (J = 7.5 cps). (These τ values may be somewhat unreliable because of possible miscalibration of the instrument). The two cyclopropyl protons appear further up field compared to their position in the spectrum of **28**, presumably due to removal of the electron-withdrawing carbonyl function.

Attempted preparative glpc purification of **30** on Carbowax resulted in isomerization to two new alcohols. The major product was a colorless oil; infrared spectrum (neat) 3.01, 5.90, and 11.47 μ. The nmr spectrum had a three-proton singlet at τ 5.7 (OH + $=CH_2$), a one-proton singlet at 6.8 (—CH—O), a two-proton singlet at 7.1, a one-proton triplet at 7.9, a two-proton singlet at 8.3, and a one-proton doublet at 8.6. This material is tentatively considered to be 5-methylenebicyclo[2.1.1]hexan-2-ol (**31**). The minor rearranged alcohol was also an oil; infrared spectrum (neat) 2.97, 5.93, 11.50 μ, and is probably the epimer of the major product.

Hydrogenation of 29. One hundred milligrams of **29** in 25 ml of AR methanol was hydrogenated in a Parr apparatus at 30 psi for 12 hr using a platinum dioxide catalyst. The catalyst was filtered off, and 50 ml of water containing a small amount of sodium bicarbonate was added. Most of the methanol was removed on a flash evaporator and the basic solution was extracted with ether to remove any neutral material. The solution then was acidified with concentrated hydrochloric acid and extracted several times with ether. After drying these extracts and removing the solvent, there was obtained 89 mg (86%) of an oily acid whose infrared spectrum was identical with that of cyclopentylacetic acid. Conversion of the acid to its methyl ester with ethereal diazomethane and purification by preparative glpc gave methyl cyclopentylacetate, shown to be identical with an authentic sample by its infrared and nmr spectra, and by glpc retention times on two columns (Carbowax and LAC-446).

Addition of Methanol to 28. To a sodium methoxide solution prepared by dissolving 0.25 g of sodium in 5 ml of anhydrous methanol was added 287 mg of the tricyclic ester mixture. This solution was sealed in a glass bomb under nitrogen and heated at 100° for 4 days. The bomb was cooled down and the contents was poured into water. This solution was immediately extracted several times with ether. The extracts were washed several times with water and dried. The solvent was removed to give a crude product showing two components by glpc analysis on LAC-446 in the ratio of 77:23. These components were isolated by preparative glpc. The infrared spectra of the two materials were similar but differed in the fingerprint region; the major and minor components had carbonyl bands at 5.78 and 5.79 μ, respectively. The major component was identical with the synthetic material described below as shown by comparison of its infrared spectrum and glpc retention time on LAC-446.

Methyl *anti*-2-Methoxybicyclo[2.1.1]hexane-5-*endo*-carboxylate (31). A mixture of 200 mg (1.4 mmoles) of **19** and 200 mg of sodium hydride in 20 ml of dry dimethylformamide was heated on a steam bath for 1.5 hr under a nitrogen atmosphere and protected by a drying tube. One-half milliliter of methyl iodide was added, and the reaction mixture was heated overnight on the steam bath and then poured into 150 ml of water. The aqueous solution was extracted several times with a total of 200 ml of pentane, and the extracts were washed several times with water and dried. The solvent was removed and the residue was purified by preparative glpc on LAC-446 to give 77 mg (32%) of **31**. The infrared spectrum was the same as that of the major ether obtained by adding methanol to **28**, and these products had identical retention times on a LAC-446 analytical column. The nmr spectrum had a broad, two-proton doublet at τ 6.05 (C_2 hydrogen), a sharp, three-proton singlet at 6.42 (CO_2CH_3), a sharp, three-proton singlet at 6.71 (OCH_3), a broad, two-proton peak at 7.3 (bridgehead protons), a one-proton triplet centered at 7.43 (J = 2.5 cps) (C_5 hydrogen), a very broad, one-proton multiplet at ~8, and a three-proton multiplet at 8.7.

Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.20; H, 8.28.

There was a minor product (*ca.* 2–3%) of longer glpc retention time also formed which probably corresponds to the minor product obtained by methanol addition to **28**.

endo-**5-Carbomethoxybicyclo[2.1.1]hexan-*syn*-2-ol Mesylate (33).** To an ice-cold solution of 0.67 g (4.3 mmoles) of the methyl ester of **18** in 6 ml of dry pyridine was added 1.0 ml of methanesulfonyl

cnloride. The reaction was allowed to proceed for 4 days in the refrigerator. The dark mixture was cooled in an ice bath, and a small piece of ice was added. After standing for a few minutes, the reaction mixture was poured into ice–water containing 6 ml of concentrated hydrochloric acid and extracted several times with ether. The extracts were washed with water, sodium bicarbonate solution, and water again. The solution was dried and the solvent was removed to give 0.96 g (96%) of the crude mesylate, as a bright yellow liquid; infrared spectrum (neat) 5.78 μ.

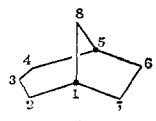
Treatment of 33 with Potassium *t*-Butoxide. The crude **33** was dissolved in 10 ml of dry dimethyl sulfoxide and added to a solution of 2.0 g of alcohol-free potassium *t*-butoxide in 20 ml of dimethyl sulfoxide under a nitrogen atmosphere. The reaction mixture turned dark immediately. After 3 hr at room temperature, it was poured into 150 ml of ice–water containing 2 ml of concentrated hydrochloric acid. The aqueous solution was extracted several times with ether and the combined extracts were washed several times with water and dried. Removal of the solvent gave an acidic oil which was esterified with diazomethane to give 0.4 g of crude starting material.

This was taken up in 20 ml of benzene, dried over Linde 4A molecular sieves, and 0.7 g of potassium *t*-butoxide was added. After refluxing overnight the dark gelatinous reaction mixture was diluted with ether and washed with dilute hydrochloric acid and water. After drying, the solvent was removed to give a small amount of crude starting material.

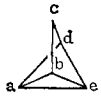
Appendix on Nomenclature

Although the many advances in the synthesis of small-ring, bridged molecules represent one of the dramatic recent developments in organic chemistry, the reporting of these advances is in danger of causing serious confusion, for the reason that a relatively simple problem in nomenclature has gone largely unrecognized. It would seem worthwhile to try to correct this situation before it leads to chaos.

In 1900, Adolph von Baeyer put forward the system of nomenclature which is essentially still standard for bridged bicyclic molecules.[29-31] According to this system, a bicyclic molecule is designated as a bicyclo-[*x.y.z*]alkane, where *x*, *y*, and *z* are the numbers of carbon atoms (given in decreasing order) in each of the three bridges joining the common, bridgehead atoms, and the alkane name is that of the hydrocarbon having the number of carbon atoms necessary to construct the ring system. In numbering the skeleton, one starts at one bridgehead, proceeds along the longest bridge to the other bridgehead, then back along the next smaller bridge to the starting point, and finally along the smallest bridge. Bicyclo[3.2.1]octane (I) provides a convenient example. This system is too well known to require further illustration.



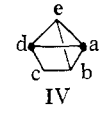
I



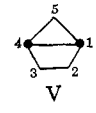
II

III

Although von Baeyer pointed out that the same principles could be extended to tricyclic compounds,[29] the need to do so in 1900 did not exist, and so the details were not worked out at that time. With the advent of powerful new synthetic techniques, many such polycyclic compounds have now been prepared. These have generally been designated by *informal* extensions of von Baeyer's rules. Unfortunately, many of the active workers in this area[32] have failed to realize the ambiguity of this procedure. To illustrate the problem, consider the tricyclopentane II. Probably the most obvious name for this compound would be "tricyclo[1.1.1.$0^{2,4}$]pentane," in which advantage is taken of the close relation to bicyclo[1.1.1]pentane (III), and in which the one additional zero-membered bridge between C_2 and C_4 of III is designated in a most simple way. However, this particular name is really arbitrarily based on the view that II is derived from III. Alternatively, it should be noted that II can also be regarded as a cyclopentane derivative to which two zero-membered bridges (a–d and b–e) have been added, as shown in formula IV. The name generated in



IV



V

this way would be "tricyclo[2.1.0.$0^{2,5}$]pentane." Clearly, in view of this apparent ambiguity, some authoritative rules are desirable. In fact, the IUPAC has provided such rules;[30,31] up to now, however, they have been more often violated than obeyed. Thus, there is a real danger of the literature in this area becoming badly confused. In the hope of preventing further misunderstanding, a summary and illustration of the relevant IUPAC rules seems appropriate.

(1) Select the *largest possible ring* as the "main ring."

(2) Choose as the "main bridge" the *largest bridge* spanning the "main ring." If there are two potential main bridges of equal length, choose the one that divides the main ring most symmetrically.

(3) The main ring and main bridge now form a bicyclic system which is numbered according to the rules given above.

(4) Designate the remaining bridges in the usual way by additional numbers in brackets, with the smallest possible superscripts to designate their points of attachment to the parent bicyclic nucleus.

Applying these rules to the tricyclopentane II, we find the largest ring to be five membered, the parent bicyclic nucleus to be bicyclo[2.1.0]pentane (V), and the IUPAC name to be *tricyclo[2.1.0.$0^{2,5}$]pentane*. Turning now to the chemical literature, we see that although three syntheses of this nucleus have been reported,[33-35] it has been consistently misnamed, and in fact that *the correct IUPAC designation has never been given.*

Many other ring systems which have been made for the first time in recent years are in need of rechristening. Illustrative examples are given in Chart V, in which some formulas have been redrawn to show the basis for the IUPAC designations.

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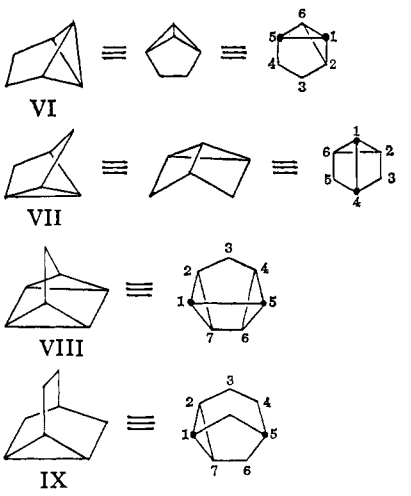
(31) A. M. Patterson, L. T. Capell, and D. F. Walker, "The Ring Index," 2nd ed, American Chemical Society, Washington, D. C., 1960.
(32) This list would include the present authors.
(33) S. Masamune, *J. Am. Chem. Soc.*, **86**, 735 (1964).
(34) W. von E. Doering and M. Pomerantz, *Tetrahedron Letters*, 961 (1964).
(35) G. L. Closs and R. B. Larrabee, *ibid.*, 287 (1965).

Chart V



Structure	IUPAC name	Name to be replaced
VI	tricyclo[3.1.0.0^{2,6}]hexane	tricyclo[2.1.1.0^{5,6}]-hexane[35-39]
VII	tricyclo[2.2.0.0^{2,6}]hexane[40]	tricyclo[2.1.1.0^{2,5}]-hexane[41]
VIII	tetracyclo[3.2.0.0^{2,7}.0^{4,6}]-heptane	quadricyclo[2.2.1.0^{2,6}.0^{3,5}]-heptane[42,43]
IX	tricyclo[3.2.1.0^{2,7}]octane[44]	tricyclo[2.2.2.0^{2,6}]octane[45]

It is to be hoped that the IUPAC and "Ring Index" suggestions, which are both unambiguous and easy to follow, will be used more uniformly in the future.

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(44) W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).
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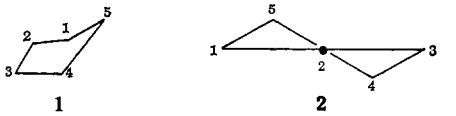
Fused Small-Ring Compounds. II. Solvolysis Reactions of Some *cis*- and *trans*-Bicyclo[3.2.0]heptane Derivatives[1,2]

Jerrold Meinwald, Paul Anderson,[3] and Joseph J. Tufariello[4]

Contribution from the Department of Chemistry, Cornell University, Ithaca, New York. *Received October 1, 1965*

Abstract: The *p*-toluenesulfonate esters of the *exo* and *endo* isomers of *cis*-bicyclo[3.2.0]heptan-3-ol, *cis*-bicyclo[3.2.0]hept-6-en-3-ol, and of *trans*-bicyclo[3.2.0]heptan-3-ol have been prepared and subjected to acetolysis at 75°. All five esters gave chiefly unrearranged products; the *cis* esters yielded acetates with predominant inversion at C_3. The bicyclic esters were generally less reactive than cyclopentyl *p*-toluenesulfonate by relatively small factors. *trans*-Bicyclo[3.2.0]heptan-3-ol *p*-toluenesulfonate proved to be the least reactive compound in this series, solvolyzing at a rate less than 2×10^{-2} times that of cyclopentyl *p*-toluenesulfonate. These results show what range of solvolysis reaction rate effects may be expected for rather extreme changes in cyclopentane conformations.

The contributions of conformational reasoning to the analysis of the chemistry of six-membered rings have been impressive.[5] Although a valuable start has also been made in the analogous analysis of five-membered rings, the impact of this reasoning has been relatively small to date, in part because of the great conformational mobility of simple cyclopentyl systems.[6] Two important conformations for the cyclopentane ring have come to be known as the *envelope* form (**1**) and the *half-chair* form (**2**).[7] In the first of these, four carbon atoms are coplanar (1, 2, 3, and 4 in formula **1**), with the fifth somewhat out of plane. In the second, only three carbon atoms are coplanar (1, 2, and 3 in formula **2**), and the remaining two are above and below this plane. Whereas it is difficult to specify the conformations of simply substituted cyclopentanes, because of the mobility characteristic of the five-membered ring, the fusion of a cyclopentane to a less flexible ring should serve to fix the geometry of the over-all system more firmly, thus providing an opportunity to examine the properties associated with specific cyclopentyl conformations.



The chemistry of a number of compounds of this general type (*i.e.*, a cyclopentane fused to a smaller ring) has already been studied. Outstanding examples are provided by the work of Winstein and his coworkers, who have investigated the reactions of the *exo*

(1) The partial support of this work by a research grant (GM 10090) provided by the National Institutes of Health is acknowledged with pleasure.
(2) For the initial publication in this series, see J. Meinwald, J. J. Tufariello, and J. J. Hurst, *J. Org. Chem.*, **29**, 2914 (1964).
(3) National Institutes of Health Postdoctoral Fellow, 1963–1964.
(4) National Institutes of Health Postdoctoral Fellow, 1962–1963.
(5) For an excellent recent summary, see E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.
(6) See ref 5, pp 248–252.
(7) F. V. Brutcher, T. Roberts, S. J. Barr, and N. Pearson, *J. Am. Chem. Soc.*, **81**, 4915 (1959).