with those noted above. The intensities of the 1755- and 1710-cm^{-1} bands were approximately equal.

Registry No.—**2**, 22482-52-6; **3**, 16957-72-5; **4**, 22482-54-8; **6**, 2568-17-4; **7**, 22482-56-0; **7** semicarbazone, 22482-57-1; **8**, 22482-58-2; **8** semicarbazone, 22482-59-3; diethyl 2-(3-cyclohexen-1-yl)ethane-1,1-dicarboxylate, 22482-60-6; 2-(3-cyclohexen-1-yl)ethane-1,1-dicarboxylic acid, 22482-61-7; 3-(3-cyclohexen-1-yl)propionic acid, 22482-62-8.

Transannular Reactions during Solvolyses of *exo*-2,3-Epoxybicyclo[3.3.1]nonane[1]

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Solvolysis of *exo*-2,3-epoxybicyclo[3.3.1]nonane (**1**) at 0° in trifluoroacetic acid gave (50–60%) a mixture of 7-bicyclo[3.3.1]nonen-*exo*-2-ol (**3**) and 6-bicyclo[3.3.1]nonen-*exo*-2-ol (**4**). Acetolysis of **1** gave (95%) a mixture containing 53% diols and 47% enols. Glpc analysis of the total mixture showed 46% *exo*-2-*endo*-3-bicyclo[3.3.1]-nonadiol (**9**), 23% a mixture of **3** and **4**, 21% 3-bicyclo[3.3.1]nonen-*exo*-2-ol (**7**), 5% *exo*-2-*exo*-7-bicyclo-[3.3.1]nonadiol (**10**), 3% a compound tentatively identified as 7-bicyclo[3.3.1]nonen-*exo*-3-ol (**8**), and 2% a diol tentatively assigned the structure *endo*-2-*exo*-3-bicyclo[3.3.1]nonadiol (**11**). The results are compared with similar solvolyses of *cis*-cyclooctene oxide.

In 1944 the classic and elegant experiments of Bartlett, Condon, and Schneider[3] showed that hydride transfer from a nonactivated CH group to a carbonium ion can occur with great rapidity. With the exception of such special reactions as 1,2-hydride shifts and cases where the product of reaction with the solvent regenerates the carbonium ion,[4] this hydride shift was not found to compete successfully with reaction between the carbonium ion and a nucleophilic solvent. Thus the discovery that a transannular hydride shift will compete quite effectively with a nucleophilic solvent for the carbonium ions of medium rings[5] evoked considerable interest. Despite a great deal of effort by a number of investigators,[6] the relative importance of such factors as proximity of the CH group to the cation, strain in the ring, and hindrance to reaction with the solvent is not yet clear, and questions of whether sequential ion formation, rearrangement, and solvent reaction is required or whether partial or fully concerted processes are possible have not been unequivocally answered. The conformational mobility of the medium rings has served to complex the investigative problem and has prevented a better understanding of the role which conformation must play in the transannular hydride transfer.

Hoping to be able to answer some of these questions about transannular processes, we began a comprehensive study of the chemistry of medium rings conformationally restricted by bridging. Our first efforts were directed at the symmetrically bridged cyclooctane ring, *viz.*, bicyclo[3.3.1]nonane. For molecules having only hydrogen on the *endo* sides of carbons 3 and 7, this ring is known[7] to have a double-chair conformation. Thus it should provide an ideal substrate for study of the mechanistic details of transannular processes. The present paper reports a comparison of the behavior of *exo*-2,3-epoxybicyclo[3.3.1]nonane (**1**) with that of *cis*-cyclooctene oxide[8] under comparable conditions.[9]

Solvolyses and Product Identification.—Epoxidation of 2-bicyclo[3.3.1]nonene was carried out by the method of Payne.[10] The product was shown to be *exo*-2,3-epoxybicyclo[3.3.1]nonane (**1**) by reduction to the known *exo*-2-bicyclo[3.3.1]nonanol (**2**).[11] Solvolysis of **1** was performed first in trifluoroacetic acid, and a modest yield (50–60%) of monomeric product was recovered after hydrolysis with dilute base. The crude product was purified chromatographically and a crystalline enol was recovered. This enol was reduced to **2**, which shows that ring opening occurred without loss of configuration at C_2.

Based on the assumption that this enol must be derived from a C_7 carbonium ion, a mixture of 7-bicyclo[3.3.1]nonen-*exo*-2-ol (**3**) and 6-bicyclo[3.3.1]nonen-*exo*-2-ol (**4**) is expected. However, we were unable to separate the product either by glpc or thin layer chromatography. Therefore, the enol fraction was oxidized by Jones oxidant. It is assumed that under these conditions the position of the double bond is not altered, since this procedure is known to leave even sensitive β,γ double bonds unaltered.[12] The oxidation product, mp 55–68°, was again inseparable on thin layer chromatography or glpc. Both 7-bicyclo[3.3.1]-nonen-2-one (**5**)[13] and 6-bicyclo[3.3.1]nonen-2-one (**6**)[14] were synthesized, and known mixtures of the two

(1) The authors are pleased to make acknowledgment to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(2) Petroleum Research Fund Fellow, 1963–1964.

(3) P. D. Bartlett, F. E. Condon, and A. Schneider, *J. Amer. Chem. Soc.*, **66**, 1531 (1944).

(4) See, *e.g.*, P. D. Bartlett and J. D. McCollum, *ibid.*, **78**, 1441 (1956).

(5) V. Prelog and K. Schenker, *Helv. Chim. Acta*, **35**, 2044 (1952); A. C. Cope, S. W. Fenton, and C. F. Spencer *J. Amer. Chem. Soc.*, **74**, 5884 (1952).

(6) For a recent review, see V. Prelog and J. G. Traynham, "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp 593–615.

(7) M. Dobler and J. Dunitz, *Helv. Chim. Acta*, **47**, 695 (1964); W. A. C. Brown, J. Martin, and G. A. Sim, *J. Chem. Soc.*, 1844 (1965).

(8) (a) A. C. Cope, A. H. Keough, P. E. Peterson, H. E. Simmons, Jr., and G. W. Wood, *J. Amer. Chem. Soc.*, **79**, 3900 (1957); (b) A. C. Cope, J. M. Grisar, and P. E. Peterson, *ibid.*, **81**, 1640 (1959); (c) A. C. Cope, G. A. Berchtold, P. E. Peterson, and S. H. Sharman, *ibid.*, **82**, 6366 (1960).

(9) After this study was virtually complete, a report of a similar study was published: R. A. Appleton, J. R. Dixon, J. M. Evans, and S. H. Graham, *Tetrahedron*, **23**, 805 (1967). Fortunately, their work was confined to formolysis while ours was limited to trifluoroacetolysis and acetolysis.

(10) G. B. Payne, *ibid.*, **18**, 763 (1962).

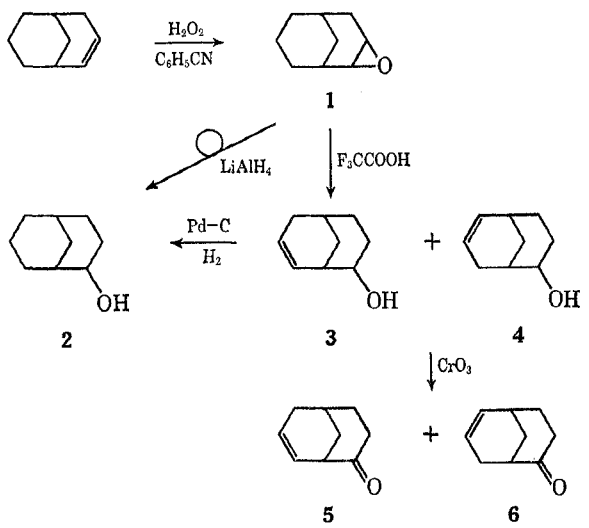
(11) J. P. Schaefer, J. C. Lark, C. A. Flegal, and L. M. Honig, *J. Org. Chem.*, **32**, 1372 (1967).

(12) C. Djerassi, R. R. Engle, and A. Bowers *ibid.* **21**, 1547 (1956).

(13) E. N. Marvell, G. J. Gleicher, D. Sturmer, and K. Salisbury, *ibid.*, **33**, 3393 (1968).

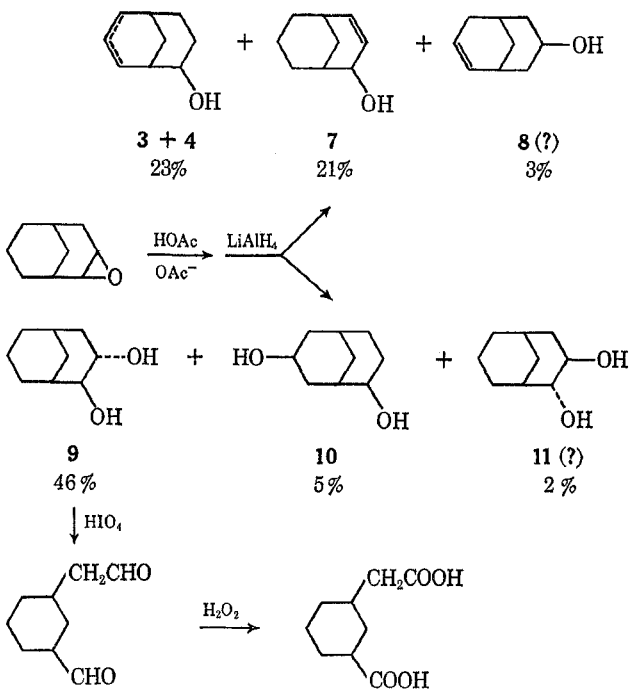
(14) E. N. Marvell, R. S. Knutson, T. McEwen, D. Sturmer, W. Federici, and K. Salisbury, *ibid.*, **35**, 391 (1970).

could not be separated under the same conditions. However, **5** shows λ_{max} 297 mμ (ε 184) and **6** has λ_{max} 297 mμ (ε 77). The oxidation product has λ_{max} 297 mμ (ε 100), which would correspond to a mixture of 79% **6** and 21% **5**. Similarly, **5** has a single-proton resonance (multiplet at 2.82 ppm) in its nmr spectrum in a region where **6** has no absorption. Integration of this region as compared with the two-proton olefinic region as a standard indicated that the oxidation product consisted of *ca.* 80% **6** and 20% **5**. Thus we consider that the enol from trifluoroacetolysis of **1** is a mixture containing 20 ± 5% **3** and 80 ± 5% **4**. Small amounts of a diol fraction were obtained (*ca.* 5–10%) from the trifluoroacetolysis but were not identified.



Acetolysis of **1** was carried out in the presence of sodium acetate at 100°. The reaction proceeded slowly and required *ca.* 72 hr. The crude reaction product was treated with lithium aluminum hydride and this product was analyzed by glpc. Enol and diol fractions were present in about equal amounts and each contained three components. The enol fraction contained 23% **3** + **4**, 21% 3-bicyclo[3.3.1]nonen-*exo*-2-ol (**7**), and 3% of a fourth enol. A crude sample of the 21% component of the enol fraction was isolated by preparative glpc. This was oxidized to the known 3-bicyclo[3.3.1]nonen-2-one.[11] Since reduction of the entire enol fraction gave **2** as the only important product, this second enol was assigned the structure **7**. Partial confirmation of this assignment was obtained by carrying out a formolysis of **1** under the published conditions[9] and showing by glpc comparison that the constituent that the previous workers had assigned structure **7** was identical with ours. Owing to the difficulty of the separation, we were not able to prepare a pure sample for comparison with the physical properties published for this substance.[11] Thus the structural assignment is based purely on the chemical data.

The minor constituent has not been fully identified, but it is not identical with either of the alcohols obtained from reduction of 6-bicyclo[3.3.1]nonen-2-one. Assuming that the configuration at C_2 or C_3 must be retained, this eliminates all possible enols except 6-bicyclo[3.3.1]nonen-*exo*-3-ol (**8**). Thus this structure is tentatively assigned to the minor enol.



The diol fraction was separated into three components by preparative thin layer chromatography. The main constituent (46%) in the diol fraction was shown to be a vicinal diol by oxidation with periodic acid. The ring-cleavage product was separated and oxidized to the known[15] *cis*-3-carboxymethylcyclohexanecarboxylic acid. This diol was not identical with *exo*-2-*exo*-3-bicyclo[3.3.1]nonadiol prepared by osmium tetroxide oxidation of 2-bicyclo[3.3.1]nonene. If the configuration is retained at either C_2 or C_3, then this must be either *exo*-2-*endo*-3-bicyclo[3.3.1]nonadiol (**9**) or *endo*-2-*exo*-3-bicyclo[3.3.1]nonadiol (**11**). Since **11** is expected to exist predominantly as a double-chair conformer, it should exhibit abnormally high frequency C–H stretching and bending modes in the infrared.[16] The major diol has no such abnormal bands and is therefore assigned the structure **9**, which should exist preferentially as a chair–boat conformer.

The diol of intermediate abundance was shown to be identical with the formolysis product which Appleton, *et al.*,[9] assigned the structure **10**. A complete proof of structure for the diol has not been carried out, but the structure is assigned on the mode of formation. A single attempt to prepare the diol **10** by hydroboration of **3** + **4** was not successful. Compound **10** is expected to adopt a double-chair conformation, and in accord with our assignment the diol product has abnormal bands in the infrared at 2985 and 1485 cm^{-1}.[16] The third component of the diol fraction was isolated only in impure form and a complete spectral examination was not possible. However, it was oxidized by periodic acid, and on that basis was tentatively assigned the structure **11**.

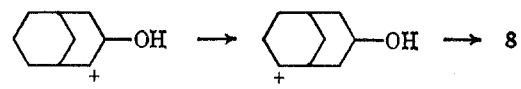
Discussion

The results of the present study are not particularly surprising, but they are revealing with respect to some aspects of the mechanism of transannular processes.

(15) V. N. Ipatieff, J. E. Germain, W. W. Thompson, and H. Pines, *J. Org. Chem.*, **17**, 272 (1952).

(16) G. Eglinton, J. Martin, and W. Parker, *J. Chem. Soc.*, 1243 (1965).

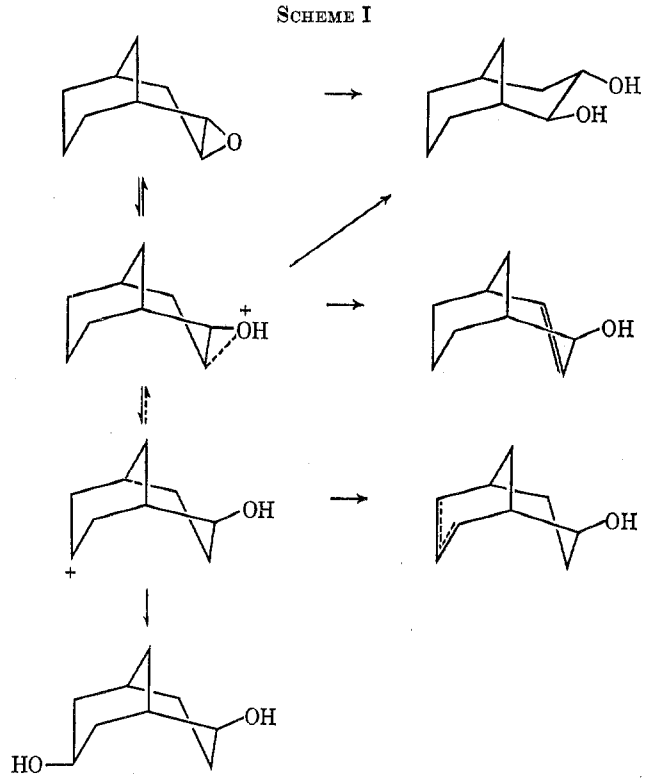
Consider first the probable routes to the products isolated from **1**. Clearly, ring opening of the epoxide occurs preferentially in the expected manner *via* cleavage of the equatoriallike C–O bond and retention of the axial. This is also favored by the formation of a carbonium ion at C_3 which eliminates the transannular C_8–C_7 hydrogen interactions. However, if our tentative structural assignments are correct, the presence of **8** and **11** indicates that cleavage in the reverse direction can occur, albeit much less readily. The formation of **8** would require a 1,3-hydrogen shift from C_8 to C_2. Schaefer and Honig[17] have found



evidence which points to this type of shift in a somewhat different case.

In view of the recent observation that solvolysis of *exo*-7-methyl-*exo*-3-bicyclo[3.3.1]nonyl tosylate shows no kinetic isotope effect when deuterium is substituted for the *endo* 7 hydrogen,[18] the route of Scheme I is suggested as the most likely for solvolysis

SCHEME I



of the bicyclic epoxide. Thus the initial protonated epoxide is converted into a carbonium ion which reacts either normally or transannularly. Complete absence of *cis*-1,2-diol in the product must mean that the hydroxyl at C_2 protects the carbonium ion from *exo* attack by the solvent, and that even in this relatively rigid molecule the protection is *complete*. Finally, the formation of the *exo*-2-*endo*-3-diol can be related to solvent attack from the *endo* side of the ion or to direct SN2 ring opening of the protonated epoxide by acetate ion. Either process requires an *endo* attack, which has no precedent in this ring system.

Comparison of these results with those of the solvolysis of *cis*-cycloocetene oxide (**12**) reveals several striking relations. As Table I shows, the bicyclic molecule shows an enhanced tendency to undergo elimination.

TABLE I

RESULTS OF SOLVOLYSIS OF *cis*-CYCLOOCTENE OXIDE (12) AND 1

Reactant	Solvent	Vicinal diol	Vicinal enol	Transannular diol	Transannular enol
12[a]	F_3COOH	...	...	56	43
1	F_3COOH	...	...	...	~100
12[a]	HCOOH	13	1	53	33
1[b]	HCOOH	24	2	36	36
12[a]	HOAc–OAc^-	77	...	9	11
1	HOAc–OAc^-	46	21	5	23

[a] Data from ref 8b. [b] Data from ref 9.

If, however, the ratio of vicinal to transannular product is considered, the two systems are very much alike, although the monocyclic reactant has a slightly greater tendency to undergo transannular reactions. This is quite different from the results with solvolysis of the tosylates, where the bicyclic molecule shows a dramatically reduced transannular reactivity.[19] Although this has been attributed[19] to the strain in the 3,7 hydrogen bridged transition state, the epoxide results suggest that the ratio of rates of transannular hydride shift *vs.* the collapse to normal products also plays an important role. Thus the strain relief in the transition state for elimination may increase this rate in the bicyclic system as compared with the cyclooctane case enough to reduce the competition by transannular shifts.

The results of acetolysis in the two systems shows that the rear side of the carbon atom at which displacement occurs is more available in the *cis*-cyclooctene oxide as compared with **1**. Also the absence of *cis*-1,2-diol in both systems indicates effective protection of the carbonium ion by the hydroxyl group in both cases. Finally, the analysis below indicates that the hydroxyl group may also play a further role in the transannular process.

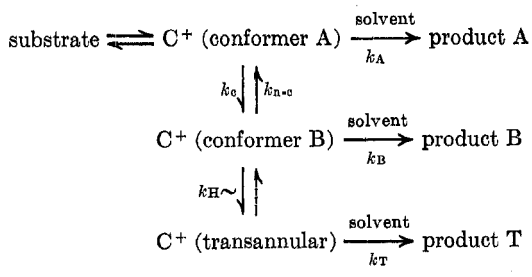
At present it is not possible to make an accurate conformational analysis of the *cis*-cycloocetene oxide solvolysis without making some assumptions. If we assume that **12** has a geometry only slightly distorted from one of the minima on the conformational surface described by Hendrickson,[20] it is possible to utilize his data for the analysis. Thus, if the geometry resembles the CC conformation, there would be four different positions for the epoxide. Ring opening of any one of these at an equatoriallike bond would lead to a carbonium ion which could pseudorotate in the TCC/CC system without loss of stereospecificity for transannular processes of 1,3 or 1,5 types. For all other pseudorotational systems, *i.e.*, BC/TBC, TC/C, and BB/S_4/B, a similar ring opening would give an ion whose pseudorotation would destroy the stereospecificity required (usually for the 1,3-hydride

(17) J. P. Schaefer and L. M. Honig, *J. Org. Chem.*, **33**, 2655 (1968).
(18) M. A. Eakin, J. Martin, W. Parker, C. Egan, and S. H. Graham, *Chem. Commun.*, 337 (1968).
(19) M. A. Eakin, J. Martin, and W. Parker, *ibid.*, 298 (1968).
(20) J. B. Hendrickson, *J. Amer. Chem. Soc.*, **89**, 7047 (1967).

shift).[21] It has been found[18] that *exo*-7-methyl-*endo*-3-bicyclo[3.3.1]nonyl tosylate undergoes transannular reactions to a moderate extent. This means that the initial carbonium ion, which is presumably a chair–boat conformer, must convert into the chair–chair conformer fast enough to permit the transannular hydride shift to compete with normal solvent reactions. If the transition state for this interconversion is assumed to lie at about the same energy level as that for the chair–boat interconversion in cyclohexane, then the finding[22] that the chair–boat form lies about 6.5 kcal/mol above the chair form of cyclohexane leads to a barrier of *ca.* 4–5 kcal for the bicyclic interconversion.

Among the general mechanistic schemes which must be considered for transannular reactions, one (Scheme II), which finds the substrate converted into a carbonium ion which can react with solvent directly but must undergo a conformational change before a transannular reaction can occur, is of considerable importance. For this mechanism the height of the energy barrier for conformational interconversion is of crucial importance. If it were too high, then $k_c < k_A$ and the transannular reaction would be excluded. The data above suggest that a barrier much in excess of 5 kcal/mol would exclude the transannular reaction. Thus in accounting for stereospecificity in a transannular reaction, conformational interconversions requiring energies above 5 kcal/mol might be ignored while those of lower activation energy would necessarily have to be taken into account. For cyclooctane chemistry Hendrickson's calculations[20] indicate that all pseudorotation processes would have to be considered but all symmetrical interconversion modes could safely be ignored. As a result the stereospecificity of the transannular reactions can be accounted for only if (a) the carbonium ion formed by ring opening falls into the TCC/CC conformational system, (b) the ion falls into another conformational system and the hydroxyl group restricts the pseudorotation, or (c) the conformations involved do not belong to any of the symmetrical ones studied by Hendrickson. Investigation of the alternative b is underway at present.

SCHEME II



Experimental Section

***exo*-2-*exo*-3-Epoxybicyclo[3.3.1]nonane (1).**—This compound was prepared by the method of Payne[10] using the directions of Marvell and Knutson.[22] The product, mp 182–183°, was purified by preparative layer chromatography and was obtained in *ca.* 30% yield.

***exo*-2-Bicyclo[3.3.1]nonanol (2).**—A mixture of 0.53 g (3.8 mmol) of **1** and 1.1 g (3 mmol) of lithium aluminum hydride in 45 ml of tetrahydrofuran was heated at 50° for 24 hr. A crude alcohol, mp 150–170°, was obtained from the mixture after hydrolysis of excess hydride and removal of the solvent. Glpc purification (silicone SF-96 at 148°) gave a single alcohol, mp 174–176° (lit.[11] mp 176–177°).

Trifluoroacetolysis of 1.—A cold solution of 3.6 g (26 mmol) of **1** in 25 ml of pentane was added to 36 ml of trifluoroacetic acid at 0°. The solution was stirred at 0° for 4 hr, after which a solution containing 28 g of sodium hydroxide in 125 ml of water was added. This mixture was stirred for 15 hr. The organic materials were extracted with ether, and the ether extracts were washed with saturated sodium sulfate solution. The ether layer was dried (K_2CO_3) and the ether was evaporated. The crude product was chromatographed over activity II/III alumina. Elution with benzene–ether gave an alcohol, mp 142–149°, which was further purified by sublimation: mp 150–151°; ir (CS_2) 3385 (br), 3040, 1096, 1060, 1040, 968, 955, and 715 cm^{-1}; nmr (CCl_4) δ 5.73 (m, 2 H), 3.77 (broad s, 1 H), 2.22 (s, 1 H), 2.20 (m, 2 H), 1.96 (m, 4 H), and 1.63 (br m, 6 H).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 77.99; H, 10.23.

Acetolysis of 1.—A solution of 93 mg (0.067 mmol) of **1** and 145 mg (1.7 mmol) of sodium acetate in 2.9 ml of glacial acetic acid was heated in a sealed tube for 73 hr at 100°. Water was added to the cooled reaction mixture, and the solution was extracted with ether. The dried ($MgSO_4$) extracts were treated with an excess of lithium aluminum hydride at 25° for 24 hr. Excess hydride was destroyed and the solution was treated with 0.1 *N* hydrochloric acid. The organic products were taken up in ether. The solution was concentrated *in vacuo* and analysis *via* glpc (12 ft × 0.125 in. 5% FFAP column at 193°) showed 47% enol and 53% diol. The diols separate in three peaks, **11** (2%), **9** (46%), and **10** (5%). Analysis of the enols on the same column showed three peaks, **7** (21%), **3** + **4** (23%), and **8** (3%).

Identification of Trifluoroacetolysis Product.—The enol mixture was obtained as a solid, mp 150–151°, as was described above. A sample of the enol (53 mg, 0.38 mmol) was hydrogenated over palladium on charcoal. The product was purified by sublimation, mp 176–179°, and was identical by both glpc analysis and spectral examination with an authentic sample of **2**.[23]

A further sample of enol, mp 134–141°, isolated from chromatography on alumina and sublimed once (79 mg), was dissolved in 20 ml of acetone. An aqueous solution containing 2.67 g of chromic anhydride and 2.3 ml of sulfuric acid in 10 ml of solution was added dropwise to the acetone solution cooled to −8° in an ice–salt bath. When the orange color persisted (*ca.* 0.25 ml of oxidant), the solution was stirred for 20 min and a few drops of methanol were added. The solution was diluted with water and neutralized with sodium bicarbonate. Organic products were taken up in ether and the solution was dried ($MgSO_4$). Evaporation of the ether gave 80 mg of solid which showed a single peak on glpc (5% SE-30 on Chromosorb W). After sublimation, 49 mg of white solid, mp 55–68°, was obtained: λ_{max} 297 nm (ϵ *ca.* 100); nmr (CCl_4) δ 5.8 (d, 2 H), 2.8 (m, 0.2 H), and 2.6–1.0 (m, *ca.* 10 H).

Stability of 7 in Trifluoroacetic Acid.—An impure sample of **7**, mp 127–131°, isolated from the acetolysis product by preparative gas chromatography, was stirred with trifluoroacetic acid at 0° for 4 hr. The reaction mixture was worked up as described under the solvolysis and the product was purified by sublimation. The infrared and nmr spectra were identical with those of the starting material.

Identification of Acetolysis Products.—The acetolysis product was separated into diol and enol fractions either by column chromatography (alumina activity II/III, benzene–ether followed by methanol) or preparative layer chromatography [alumina Merck PF_{254}, methylene chloride–methanol (95:5)].

Diol Fraction.—The diol fraction was separated into three components by preparative layer chromatography. One component (5%) separated on the alumina plate with methylene chloride–methanol (95:5). The other two (2% and 46%) were separated using alumina with methanol as eluent.

The 5% component (10) was a white crystalline solid: mp 215–216° after sublimation and recrystallization from ethanol (lit.[9] mp 204°); ir (CCl_4) 2985, 2920, 2885, 2875, 2854, 1485, 1466, and 1446 cm^{-1}; ir (KBr) 3350, 1355, 1280, 1265, 1090 (s),

(21) It should be noted that **12** gives only *cis*-1,4-cyclooctanediol, and that this is formed by both 1,5- (61%) and 1,3-hydride shifts (39%)[8c]

(22) E. N. Marvell and R. S. Knutson, *J. Org. Chem.*, **35**, 388 (1970).

(23) We are indebted to Dr. Jack Martin, The University, Glascow, for furnishing us with spectral data on this compound for comparison purposes.

1062 (s), 998, 973 (s), 956 (s), and 902 (s) cm^{-1}; nmr ($CHCl_3$) δ 3.9 (br s, 2 H), 3.5 (br unresolved m, 2 H), 2.0 (m, 5 H), and 1.61 (br s, 7 H). A sample of **10** was prepared according to the directions of Appleton, *et al.*,[9] and spectral comparison showed it to be identical with the 5% diol above.

The 2% component (11) was not isolated in pure form, being contaminated with stopcock grease and traces of alumina. This crude material (84 mg) was stirred at 25° with 75 ml of 0.0125 *M* potassium periodate solution and 7.5 ml of 2.0 *N* sulfuric acid for 24 hr. Titration according to the directions given by Jackson[24] showed that periodate equivalent to 17.4 mg of diol was consumed.

The 46% component (9) was isolated as a crystalline solid and was purified by sublimation: mp 118–121°; ir (KBr) 3320, 1150 (w), 1074, 1052 (s), 1034, 1008 (s), 996, 906, and 720 cm^{-1}; ir (CCl_4) 2930, 2872, 2856, 1468, and 1466 cm^{-1}; nmr ($CHCl_3$) δ 4.05 (br s, 2 H), 3.49 (m, 2 H), 2.16 (m), 1.93 (br s), 1.58 (br s), and 1.0–2.4 (12 H).

Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 69.48; H, 10.38.

A sample (118 mg, 0.76 mmol) of this diol was oxidized with periodate as described above. In 24 hr at 25°, 113% of the theoretical amount of periodate was consumed. The reaction mixture was concentrated *in vacuo*, saturated with sodium chloride, and extracted with chloroform. The extracts were dried ($MgSO_4$) and the solvent was evaporated to give 130 mg of solid, mp 154–156°, which reacted with dinitrophenylhydrazine and showed bands in the infrared at 2710 and 2810 cm^{-1}. Treatment of the crude material with 30% hydrogen peroxide gave a crystalline acid, mp 153–155° (lit.[15] mp 150–152°).

Enol Fraction.—Glpc examination of the enol fraction showed three components. The major component (23% of the solvolysis product or 50% of the enol fraction) was shown by glpc comparison (12 ft × 0.125 in. 5% FFAP column at 145°) to be identical with the main component of the trifluoroacetolysis, *i.e.*, **3** + **4**. The minor component (3% of the solvolysis product or 6% of the enol fraction) was not isolated, but was shown by glpc comparison to be different from the hydride reduction products of either **5** or **6**.

A sample of the enol fraction (110 mg) was hydrogenated over palladium on charcoal in methanol solution. The main product was collected from a preparative gas chromatographic run: mp 176–178°; ir 3400, 2980, 1480, 1040, 982, 963, and 910 cm^{-1}. The spectral data and melting point identify this as **2**.

Partial separation of the two main enol components was achieved in a preparative scale gas chromatography run on 5 ft × 0.25 in. 20% SE-30 on Chromosorb W column at 90°. A crude sample enriched in component **7** (21% of the solvolysis mixture) was obtained: mp 127–131°; ir (CCl_4) 3620, 3360 (br), 3020, 2920, 1458, 1446, 1250, 1220, 1067 (w), 1045 (m), and 985 cm^{-1} (s); nmr (CCl_4) δ 5.5–6.0 (m, 2 H), 3.82 (unresolved, 1 H), 2.23 (m), 2.08 (s, 1 H), 2.0 (m), 1.5 (br s), and 1.2–2.4 (11 H). Compound **7** is reported[11] to melt at 103–103.5°, but the overlap between the peaks for enols **3** + **4** and **7**, even on an analytical level, prevented isolation of pure **7** on a preparative scale.

A portion of this enol (125 mg) was treated with 200 mg of chromium trioxide in 5 ml of pyridine at 25° for 14 hr. The solution was diluted with ether and an excess of water was added. The ether layer was separated and passed through an activity IV alumina column. The ether eluate was concentrated and the ketonic products were separated by preparative gas chromatography (10% SF-96 on silanized Chromosorb at 114°). The main product was isolated as a white solid: mp 98–100° (lit.[11] mp 97.5–98.5°); ir (CCl_4) 1675 cm^{-1}; uv λ_{max} 235 nm; nmr (CCl_4) δ 6.89, 6.12 (modified AB, 2 H, J_{AB} = 9.8 Hz), and 1.5–2.8 (m, 10 H).

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The Lactonization of Camphene-8-carboxylic Acid

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Whereas lactonization of camphene-8-carboxylic acid with formic acid has been reported to give β lactone **2**, the initial product has been identified as the γ lactone **3**. The structure and configuration of bornane-1-carbo-2-*exo*-lactone (**3**) have been established by conversion with excess phenyllithium into the same glycol **10** as obtained from 10-benzoyl-2-*exo*-bornanol (**9**) with excess phenylmagnesium bromide. The configuration of **8**, previously reported as the *endo* alcohol, was proven by degradation to isoborneol (2-*exo*-bornanol). A second lactone, *exo*-2,3-dimethyl-*endo*-3-hydroxynorbornane-*endo*-2-acetic acid lactone (**4**), is produced from **1** and **3** on longer heating with formic acid or prolonged standing with trifluoroacetic acid. A third lactone, *endo*-2,3-dimethyl-*exo*-3-hydroxynorbornanane-*exo*-2-acetic acid lactone (**5**), is also formed in small quantity. Lactone **5** is the major or exclusive product when **1**, **3**, or **4** are treated with 10% sulfuric acid–formic acid for 6.5 hr, 50% sulfuric acid, or concentrated sulfuric acid, respectively. The structure and configuration of lactone **5** have been unequivocally established by degradation to 9-methylcamphene, which has been synthesized by a stereospecific reaction sequence. Convenient syntheses of optically active **1** from nopol (10-hydroxymethyl-α-pinene) and camphene *via* camphene-8-methanol are described, and it is noted that lactonization of optically active **1** is accompanied by complete racemization. Deuterium exchange reactions involving **1** and the lactones **3**, **4**, and **5** are described and a probable mechanistic pathway from **1** to the lactones is suggested. Finally, hydrochlorination of **1**, previously described by Langlois, is shown to produce *exo*-2-chlorocamphane-10-carboxylic acid rather than the reported 2-chloro-3,3-dimethylbornane-2-acetic acid.

For a number of years, studies in one of these laboratories have been concerned with the various types of rearrangements encountered in the camphane–isocamphane systems[3–5] with particular attention to camphene racemization,[4,5] while studies in the other laboratory have been concerned with devising simple synthetic routes to certain terpene intermediates.[6] In the course of these studies the attention of both groups of investigators was attracted independently to a paper

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