Stereoelectronic Effects in the Base-Catalyzed Decomposition of Stereoisomeric Norbornanediol Mesylates

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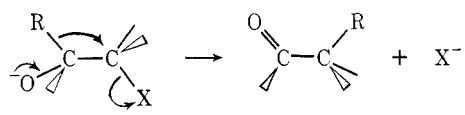
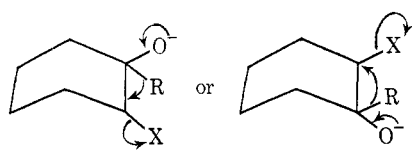
The four stereoisomeric 2-methyl-2,3-norbornanediols were prepared and the products of the decomposition of their monomesylates **12**, **17**, **20**, and **24** by sodium hydride and by potassium *tert*-butoxide were determined. **12** and **17** yielded chiefly 2-*endo*-methyl-2,3-*exo*-epoxynorbornane; **24** yielded 3-methyl-2-norbornanone; and **20** yielded either 3-methyl-2-norbornanone or 2-*exo*-methyl-2,3-*endo*-epoxynorbornane, depending on the base and solvent used. The formation of these products is interpreted in terms of solvolytic formation of the bipolar ions **15** and **23**, although concerted reaction paths, involving in one case a front-side nucleophilic displacement, are also considered.

The course of the base-catalyzed reaction of alcohols having a vicinal leaving group depends on a stereoelectronic factor. If the alcohol oxygen can be trans to the leaving group, an epoxide is formed. If, however, the stereochemistry is fixed so that the bond to the leaving group is coplanar with the bond to an alkyl or hydrogen substituent on the adjacent carbon, rearrangement to a ketone or aldehyde can occur.[2]



In all of the stereochemically defined examples reported for this rearrangement,[3] the leaving and migrating groups have been associated with a chair cyclohexane ring, and the requirement of bond coplanarity has necessarily resulted in migration of a group trans to the leaving group. In a boat cyclohexane ring, the cis vicinal substituents are coplanar, and Barton's coplanarity rule would result in migration of a group cis to the leaving group. Since such



cis migrations have not been reported, we sought for evidence of their existence by preparing the four stereoisomeric 2-methyl-2,3-norbornanediols, **4**, **5**, **8**, and **10**, and examining the base-catalyzed decomposition of their monomesylates **12**, **17**, **20**, and **24**.

The synthesis of the four diols is summarized in Chart I. Epoxidation of the acetates of 3-methylene-2-*exo*-norbornanol (**1**)[4] and of 3-methylene-2-*endo*-norbornanol[5] (**6**) gave in each case a mixture of two epoxides. Lithium aluminum hydride reduction of each of these mixtures gave a mixture of a cis and a trans diol which was separable by crystallization. The cis diol derived from **1** was identical with 2-methyl-2,3-*cis*,*exo*-norbornanediol (**4**), which has been prepared previously by hydroxylation of 2-methylnorbornene.[6] The cis diol derived from **6** was prepared independently in two steps from the adduct of cyclopentadiene and 4-methyl-1,3-dioxol-4-en-2-one, and was assigned structure **10**, it being assumed that the adduct had the endo configuration.[7]

The cis-vicinal relationship of the hydroxyl groups in diols **4** and **10** was confirmed by their reaction with periodic acid. The diols **5** and **8** did not react with periodic acid, but could be oxidized with CrO_3 to α-ketols, establishing the trans-vicinal relationship of their hydroxyl groups. The assignment of the configuration of the methyl and tertiary hydroxyl groups in the four diols rested on the assumption that the epoxides formed in greater yield from **1** and **6** were those resulting from exo attack. This assumption was verified by the alternate methods of preparation of the two cis diols.

Each of the diols could be converted to a monomesylate. The proton nmr spectra of the four mesylates provided additional evidence for the correctness of the structural and stereochemical assignments. Each had an upsplit signal for the *C*-methyl group and a downfield signal for the single proton α to the mesylate group. This latter signal appeared as a doublet, with $J = 2$ Hz for the two mesylates from **4** and **5** and $J = 5$ Hz for the mesylates from **8** and **10**. This confirmed the stereochemistry of the C-3 proton as endo in **4** and **5** and exo in **8** and **10**.[8]

Results

The results of the mesylate decompositions are summarized in Chart II. Reaction of the *cis*,*exo*-diol mesylate **12** with potassium *tert*-butoxide in refluxing *tert*-butyl alcohol gave a 90:6:4 mixture of three products, separated gas chromatographically and identified respectively as 2-*endo*-methyl-2,3-*exo*-epoxynorbornane[9] (**14**), 3-*endo*-methyl-2-norbornanone[10] (**16**), and 3-*exo*-methyl-2-norbornanone[11] (**19**). The mixture of ketones is a result of epimerization at C-3 during the

(1) Based on work by E. K. O. in partial fulfillment of the requirements for the Ph.D. degree at Stevens Institute of Technology.

(2) D. H. R. Barton, *J. Chem. Soc.*, 1027 (1953).

(3) G. Büchi, W. Hofheinz, and J. V. Paukstelis, *J. Amer. Chem. Soc.*, **91**, 6473 (1969); A. K. Bose and N. G. Steinberg, *J. Org. Chem.*, **36**, 2400 (1971); R. H. Starkey and W. H. Reusch, *ibid.*, **34**, 3522 (1969); D. J. Collins, J. J. Hobbs, and R. J. Rawson, *Aust. J. Chem.*, **22**, 607, 807 (1969); and references cited in these papers.

(4) H. Krieger, K. Manninen, and J. Paasivirta, *Suom. Kemistilehti B*, **39**, 8 (1966); *Chem. Abstr.*, **64**, 17441*d* (1966).

(5) W. F. Erman, *J. Org. Chem.*, **32**, 765 (1967).

(6) J. A. Berson, J. H. Hammons, A. W. McRowe, A. Remanick, and D. Houston, *J. Amer. Chem. Soc.*, **89**, 2590 (1967).

(7) M. S. Newman and R. W. Addor, *ibid.*, **77**, 3789 (1955).

(8) The vicinal coupling constant between the exo C-3 proton and the C-4 proton in norbornanes is 3–5 Hz; this coupling constant for an endo C-3 proton is 0 Hz, but the endo C-3 proton can have a long-range coupling of 1–2 Hz with the anti C-7 proton. J. Musher, *Mol. Phys.*, **6**, 93 (1963).

(9) H. C. Brown, J. H. Kawakami, and S. Ikegani, *J. Amer. Chem. Soc.*, **92**, 6914 (1970).

(10) K. Alder and A. Grell, *Chem. Ber.*, **89**, 2198 (1956).

(11) J. Wolinsky, D. R. Dimmel, and T. W. Gibson, *J. Org. Chem.*, **32**, 2087 (1967).

CHART I

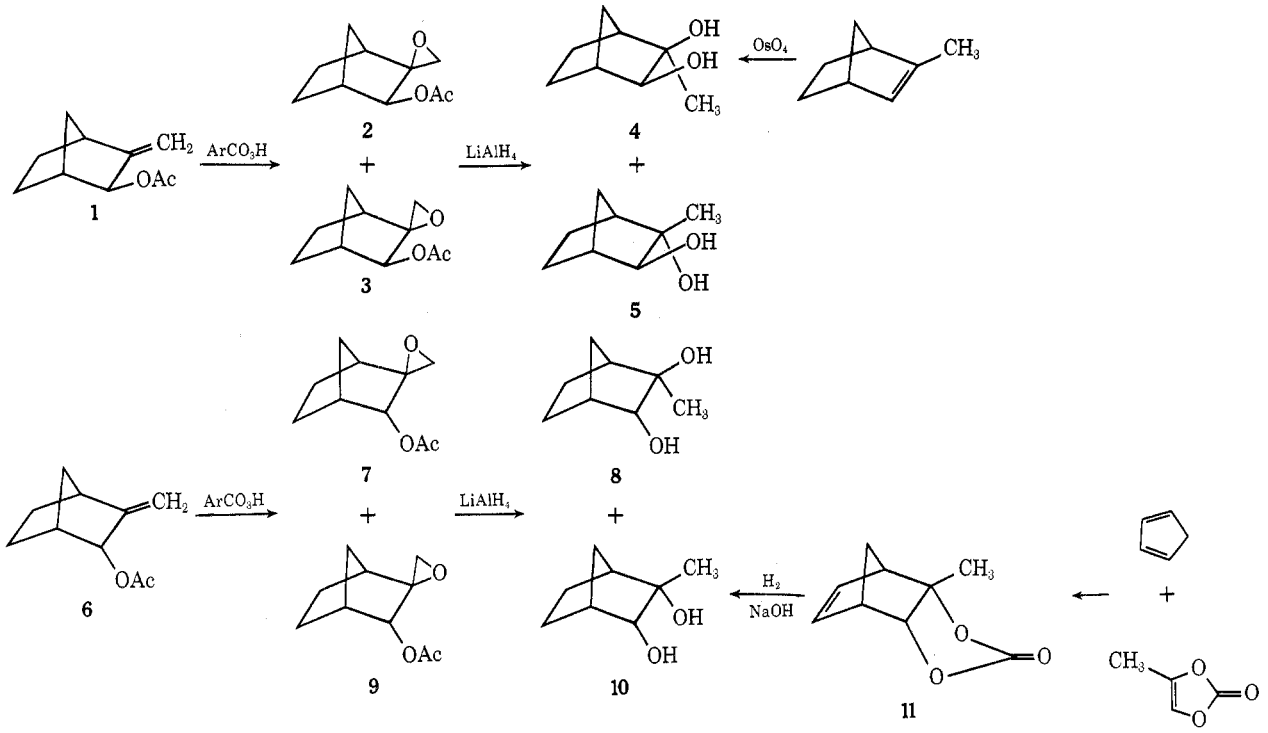
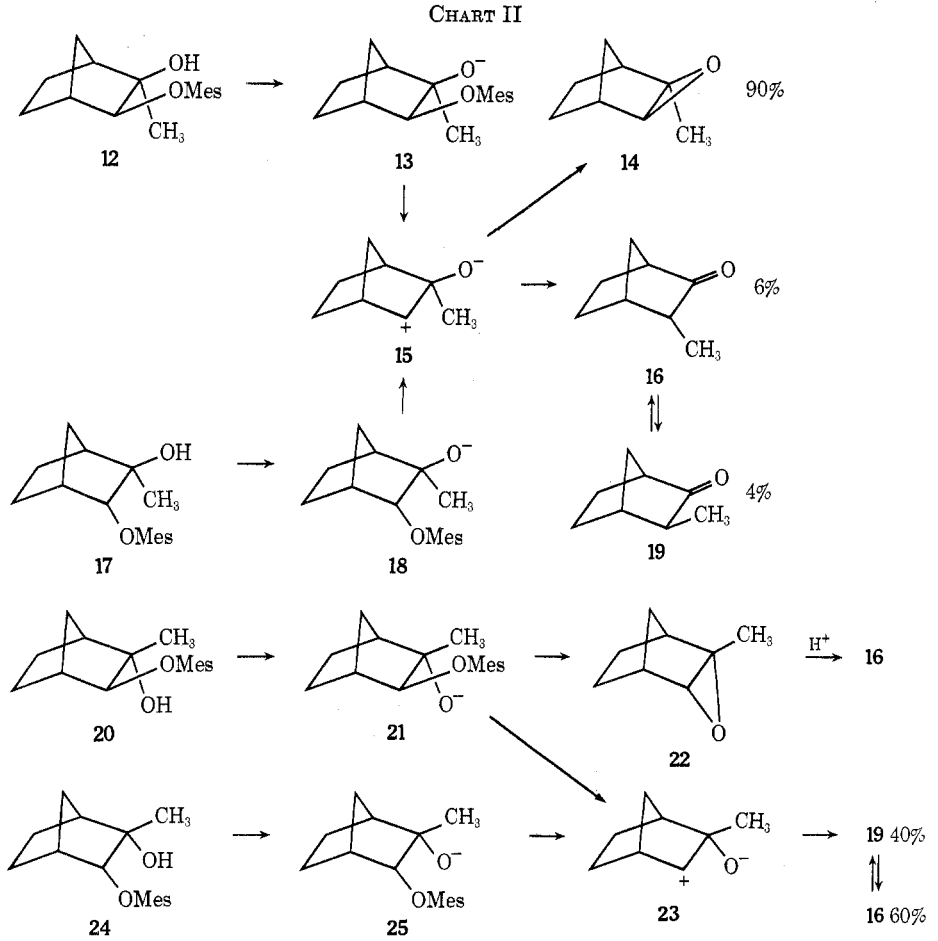


CHART II



reaction, since either **16** or **19**, when subjected to the reaction conditions, was transformed to a 60:40 mixture of the two. Hence no information is available on the stereochemistry of the ketone initially formed from **12**.

Since the formation of the exo epoxide **14** from **12** represents substitution with retention at C-3, some additional experiments were carried out aimed at clarifying the process of epoxide formation. The process does not involve nucleophilic participation by *tert*-

butoxide ion, because the same 90:6:4 mixture of **14**, **16**, and **19** was formed when mesylate **12** was treated with sodium hydride in boiling benzene. The epoxide did not result from solvolysis of the mesylate, since **12** was recovered unchanged from refluxing benzene or *tert*-butyl alcohol.[12] Finally, the tricyclanol **28** (R = CH_3) cannot be an intermediate in the process, since a synthetic sample[13] was unchanged by either potassium *tert*-butoxide or sodium hydride under the reaction conditions.

A 90:6:4 mixture of **14**, **16**, and **19** was also formed when the mesylate **17** was treated with either potassium *tert*-butoxide or sodium hydride. There was no qualitative evidence for a large difference in the rate of decomposition of **12** and **17**.

The similarity in the composition of the product mixture from the two mesylates suggests a common intermediate. We propose that this intermediate is the bipolar ion **15**, formed by solvolysis of the alkoxide ions **13** and **18**.

The reaction of the *endo,cis*-diol mesylate **24** with either potassium *tert*-butoxide or sodium hydride gave only the ketones **16** and **19** in the equilibrium 60:40 proportion. The same mixture was obtained from the reaction of mesylate **20** with sodium hydride. Again, this result can be rationalized in terms of a common intermediate, the bipolar ion **23**, which could undergo *exo*-methyl migration to **19**, followed by epimerization by excess base.

In contrast, the *endo*-methyl ketone **16** was the sole product isolated from the reaction of **20** with potassium *tert*-butoxide in *tert*-butyl alcohol. We concluded that **16** was an artifact formed during the isolation procedure, since it would have been epimerized had it been present in the reaction solution. In agreement with this reasoning, we found that a modified isolation procedure, in which precaution was taken against the presence of any acidic substances, permitted the isolation of a crude product whose nmr spectrum was consistent with the presence of the endo epoxide **22**, having an unsplit signal from a *C*-methyl group at δ 1.35 and a doublet (J = 3 Hz) from an exo C-3 proton at δ 3.15. The corresponding resonances in the exo epoxide **14** are at δ 1.35 and 2.67, the latter being an unresolved multiplet (J < 1 Hz). Addition of *p*-toluenesulfonic acid to this substance caused immediate transformation to **16**. Attempts to purify and further characterize the endo epoxide were frustrated by the extraordinary ease with which it was transformed to the *endo*-methyl ketone[14] (see Experimental Section).

If methyl migration to form **19** from **20** in the reaction with sodium hydride in benzene occurs by way of the bipolar ion **23**, then formation of the endo epoxide **22** from **20** with *tert*-butoxide ion in *tert*-butyl alcohol must be attributed to direct displacement of mesylate ion in the alkoxide **21**.

(12) The other three mesylates, **17**, **20**, and **24**, were also recovered unchanged from refluxing benzene or *tert*-butyl alcohol in the absence of base.

(13) H. Krieger, *Ann. Acad. Sci. Fenn., Ser. A*, **109**, 39 (1961); *Chem. Abstr.*, **58**, 5979*a* (1961).

(14) Indirect evidence for the instability of an *endo*-epoxynorbornane has been presented by R. M. Moriarty, *Tetrahedron Lett.*, 3715 (1969).

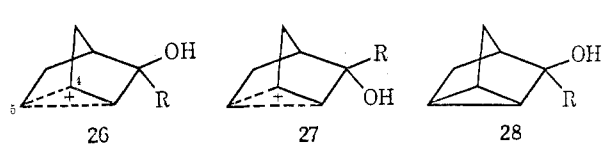
Discussion

The solvolytic formation of carbonium ion intermediates in base-catalyzed reactions in solvents as nonpolar as *tert*-butyl alcohol or benzene has little precedent, but can be attributed to electrostatic assistance to ionization by the negatively charged alkoxide oxygen. Similar electrostatic assistance has been observed in the solvolyses of 4-bromobicyclo[2.2.2]-octane-1-carboxylate,[15] 2-bromonorbornane-1-carboxylate,[16] and in substituted α-bromoacetate ions.[17] It may even be argued that the ionization is facilitated by nonpolar solvents, if the bipolar ions formed have lesser solvation requirements than do the alkoxide ions. Bordwell and Knipe report a remarkable lack of solvent dependence in the solvolysis rates of α-bromoacetate ions.[17]

The reaction paths proposed for the bipolar ions, *viz.*, collapse of **15** to epoxide and rearrangement of **23** to *exo*-methyl ketone, are in accord with expectations. Reactions involving three-membered transition states exo to the norbornyl system are facile, while those involving an endo three-membered transition state are less favored.[6,18] This difference has been explained as being due to eclipsing of the C-1 and C-4 bonds with C-2 and C-3 exo substituents caused by the endo three-ring fusion.[18]

The reactions proposed for **15** and **23** are markedly different from those reported for the hydroxynorbornyl cations **26**[19] and **27**, R = Ph.[20] The latter, formed from a variety of precursors, are interconverted by a rapid 5,4-hydride shift; the major products are the nortricyclanol **28**, R = Ph, and rearranged glycols resulting from solvent attack following the hydride shift. No rearranged ketones or epoxides were observed under reaction conditions where their formation would have been irreversible.[19,20] In our experiments, no nortricyclanol (**28**, R = CH_3) could be detected, and rapid 5,4-hydride shift could be excluded, since such a shift would interconvert **15** and **23** and would result in the same product mixture being formed from all four mesylates.

We explain this difference in reactivity by proposing that in **15** and **23** the negative charge on oxygen causes localization of the positive charge on C-3. Thus **15** and **23**, unlike **26** and **27**, are written as unbridged, classical ions. In agreement with this, we find that the solvolysis of **12** in aqueous acetone, a reaction which presumably involves the hydroxy carbonium ion **26**, R = CH_3, does not yield any epoxide or rearranged ketones.



26 27 28

(15) R. C. Fort, Jr., and P. v. R. Schleyer in "Advances in Alicyclic Chemistry," Vol. 1, H. Hart and G. J. Karabatsos, Ed., Academic Press, New York, N. Y., 1966, p 334.

(16) W. R. Vaughan, R. Caple, J. Csapilla, and P. Scheiner, *J. Amer. Chem. Soc.*, **87**, 2204 (1965).

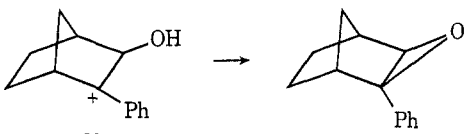
(17) F. G. Bordwell and A. C. Knipe, *J. Org. Chem.*, **35**, 2959 (1970).

(18) P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 699 (1967), and references cited therein.

(19) C. J. Collins and B. M. Benjamin, *J. Amer. Chem. Soc.*, **89**, 1652 (1967), and earlier papers cited therein.

(20) C. J. Collins, V. F. Raaen, B. M. Benjamin, and I. T. Glover, *ibid.*, **89**, 3940 (1967).

It is of interest to note that the cation **29**, tertiary at C-3 and thus classical, yields the epoxide **30** without 5,4-hydride shift or nortricyclanol formation.[21]



29 30

An alternate pathway for the formation of the exo epoxide **14** from mesylate **12** is by direct displacement, loss of mesylate ion from **13** being concerted with formation of the new C–O bond. Although this is consistent with all of our data, it does constitute a front-side nucleophilic displacement, a reaction type generally regarded as being impossible.[23] In the case of **13**, however, front-side displacement may be considerably facilitated by the circumstance that the negatively charged nucleophile is rigidly held almost within bonding distance from the substitution center. As the C-3 mesylate bond is stretched, electrostatic interaction between the negative charge on oxygen and the developing positive charge on C-3 will become increasingly important. If, at some point before the mesylate group is completely ionized, a decrease in the O^-–C-3 distance results in a net decrease in potential energy, then **15** would be bypassed as a reaction intermediate, and the ionization and displacement mechanisms would be merged.

Similar considerations apply to the formation of ketone **19** from the alkoxide ion **21**. A concerted reaction involving migration of the methyl group cis to the leaving group is a conceivable alternative to the intermediacy of **23**. Further experiments to distinguish between these alternatives are in progress.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Infracord spectrophotometer, either as thin films or as Nujol mulls. Nuclear magnetic resonance spectra were run on a Varian HA-60 spectrometer, using tetramethylsilane as internal reference. Chemical shifts are given as parts per million on the δ scale. Melting and boiling points are uncorrected. Microanalyses were performed by MHW Laboratories, Garden City, Mich.

2-*endo*-Methyl-2,3-*cis*,*exo*-norbornanediol (4).—Oxidation of 2-methyl-2-norbornene with osmium tetroxide[6] gave **4** as a waxy solid: mp 126–128° from hexane; ir (film) 3.02, 9.01 μ (OH); nmr (CCl_4) δ 4.1 (broad s, 1 H, hydroxyl proton), 3.8 (broad s, 1 H, hydroxyl proton), 3.12 (broad s, 1 H, endo C-3 proton), 2.0 (m, 2 H, C-1, C-4 protons), 1.20 (s, 3 H, C-2 methyl protons), and 0.9–1.5 (m, 6 H).

***exo*- and *endo*-Spiro[2-*exo*-norbornanol-3,2′-oxirane] Acetates (2 and 3).**—A solution of 37.6 g of 85% *m*-chloroperoxybenzoic acid in 500 ml of methylene chloride was added during 30 min to a cooled solution of 27.8 g of 3-methylene-2-*exo*-norbornanol acetate (**1**)[4] in 200 ml of methylene chloride. The mixture was stirred for 10 hr at room temperature and was then cooled, and the *m*-chlorobenzoic acid was removed by filtration. The filtrate was washed successively with 5% sodium sulfite and saturated sodium bicarbonate, dried ($MgSO_4$), and evaporated. Distillation of the residue gave 24.7 g (81%) of product: bp 63–68° (0.3 mm); ir (film) 5.78, 8.1 (acetate), 11.15, 11.3 μ. The nmr spectrum showed the presence of two isomers; in the more abundant, the C-2 endo proton appeared as a doublet at δ 4.58 (J = 2.5 Hz) and the oxirane protons appeared as an AB pattern at δ 2.55 and 2.90 (J_{AB} = 7 Hz); in the less abundant isomer, the corresponding resonances were at δ 4.28 (J = 2 Hz) and 2.58, 2.82 (J_{AB} = 5.5 Hz). The acetate methyl signal in both isomers appeared at δ 1.95.

Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 66.16; H, 7.83.

2-*exo*-Methyl-2-*endo*,3-*exo*-norbornanediol (5).—The mixture of **2** and **3** obtained above (24.7 g) was added dropwise with stirring to 20.0 g of lithium aluminum hydride in 650 ml of anhydrous ether at a rate which caused vigorous refluxing. After the addition was completed, the mixture was refluxed overnight. The reaction mixture was then decomposed with 10% sodium hydroxide and the ether layer was dried ($MgSO_4$) and evaporated. The residue (15.7 g) was dissolved in 300 ml of warm 9:1 hexane–ether. Cooling the solution caused the separation of 3.75 g of **5**: mp after recrystallization from ethyl acetate 124–125°; ir (mull) 3.09, 8.9, 9.6 μ (OH); nmr (acetone-d_6) δ 3.7 (d, J = 5 Hz, 1 H, C-3 hydroxyl proton), 3.38 (m, 1 H, C-3 endo proton), 2.97 (s, 1 H, C-2 hydroxyl proton), 1.7–2.2 (m, 2 H, C-1 and C-4 protons), 1.22 (s, 3 H, C-2 methyl protons), 1.0–1.5 (m, 6 H).

Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.60; H 10.10.

2-*endo*-Methyl-2,3-*cis*,*exo*-norbornanediol 3-Methanesulfonate (12).—The filtrate from the crystallization of **5** gave on evaporation 11.5 g of a semicrystalline mass whose infrared spectrum was identical with that of authentic **4**. This material was dissolved in cold pyridine and 12.6 g of methanesulfonyl chloride was added. The solution was stored at 5° for 24 hr and then poured into 500 ml of ice water and extracted with four 200-ml portions of ether. The ethereal layers were washed with cold dilute hydrochloric acid, dried ($MgSO_4$), and evaporated. The residue (10.5 g) was dissolved in warm 1:1 hexane–ether. Cooling gave 0.5 g of a solid methanesulfonate, mp 118–120° after recrystallization from ethyl acetate, which was tentatively identified from its nmr spectrum as the bismethanesulfonate of 3-*exo*-hydroxynorbornane-2-*exo*-methanol: nmr ($CDCl_3$) δ 4.80 (d, J = 7 Hz, 1 H, C-3 endo proton), 4.28 (d, J = 8 Hz, 2 H, C-2 methylene protons), 3.09 (s, 6 H, mesylate methyl protons), 2.3–2.6 (m, 2 H, C-1 and C-4 protons), and 1.0–1.9 (m, 7 H).

Anal. Calcd for $C_{10}H_{18}O_6S_2$: C, 40.27; H, 6.08; S, 21.46. Found: C, 40.20; H, 6.28; S, 21.27.

The filtrate from the crystallization of this substance was evaporated, and the residue (9.1 g) was recrystallized from carbon tetrachloride to give **12**: mp 60–62°; ir (mull) 3.01 (OH), 7.4, 8.65 (mesylate), 11.5 μ; nmr (CCl_4) δ 4.03 (d, J = 2 Hz, 1 H, endo C-3 proton), 3.00 (s, 3 H, mesylate methyl protons), 2.27, 2.58 (m, 2 H, C-1 and C-4 protons), 2.05 (broad s, 1 H, C-2 hydroxyl proton), 1.27 (s, 3 H, C-2 methyl protons), 1.0–1.8 (m, 6 H).

Anal. Calcd for $C_9H_{16}O_4S$: C, 49.08; H, 7.32; S, 14.53. Found: C, 48.89; H, 7.24; S, 14.42.

2-*exo*-Methyl-2-*endo*,3-*exo*-norbornanediol 3-Methanesulfonate (20).—A solution containing 2.3 g of **5** and 2.5 g of methanesulfonyl chloride in 30 ml of pyridine was stored at 5° for 24 hr. The solution was added to 200 ml of ice water and extracted with five 100-ml portions of ether. The extracts were washed with dilute hydrochloric acid and water, dried ($MgSO_4$), and evaporated, yielding **20** as a yellow oil: ir (film) 2.96 (OH), 7.6, 8.6 μ (mesylate); nmr (CCl_4) δ 4.17 (d, J = 2 Hz, endo C-3 proton), 2.97 (s, 3 H, mesylate methyl protons), 2.29, 2.02 (m, 2 H, C-1 and C-4 protons), 1.68 (broad s, 1 H, C-2 hydroxyl proton), 1.27 (s, 3 H, C-2 methyl protons), 1.1–1.8 (m, 6 H).

Anal. Calcd for $C_9H_{16}O_4S$: C, 49.08; H, 7.32; S, 14.53. Found: C, 49.20; H, 7.61; S, 14.72.

This mesylate decomposes on heating to 80° in the absence of solvent.

3-Methylene-2-*endo*-norbornanol Acetate (6).—3-Methylene-2-*endo*-norbornanol[5] (23.3 g) in 125 ml of pyridine and 50 ml of acetic anhydride was refluxed overnight. The solution was added to 1.2 l. of water and extracted with three 500-ml portions of ether. The ethereal extracts were successively washed with dilute hydrochloric acid and saturated sodium bicarbonate, dried ($MgSO_4$), and evaporated. Distillation of the residue gave 23.9 g (77%) of **6**: bp 102–103° (25 mm); ir (film) 5.77, 8.10 (acetate), 11.1 μ (=CH_2); nmr (CCl_4) δ 5.08 (m, 1 H, exo C-2 proton), 4.76, 4.71 (two d, J = 2 Hz, C-3 methylene vinyl protons), 2.48, 2.69 (m, 2 H, C-1 and C-4 protons), 1.93 (s, 3 H, acetate methyl protons), and 1.1–1.8 (m, 6 H).

(21) D. C. Kleinfelter and J. H. Long, *Tetrahedron Lett.*, 347 (1969). In more acidic media, where formation of **30** is reversible, **29** gives 3-*endo*-phenyl-2-norbornanone by successive 6,2 and *exo*-3,2-hydride shifts.[22]

(22) D. C. Kleinfelter and T. E. Dye, *J. Amer. Chem. Soc.*, **88**, 3174 (1966).

(23) J. March, "Advanced Organic Chemistry," McGraw-Hill, New York, N. Y., 1968, pp 251–255. For a recent instance where front-side nucleophilic displacement has been proposed, see T. Nishiguchi, H. Tochio, A. Nabeya, and Y. Iwakura, *J. Amer. Chem. Soc.*, **91**, 5835 (1969).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.50. Found: C, 72.36; H, 8.34.

exo- and endo-Spiro[2-endo-norbornanol-3,2′-oxirane] Acetates (7 and 9).—6 (23.9 g) was oxidized with 32.2 g of *m*-chloroperoxybenzoic acid in 500 ml of methylene chloride, using the same reaction conditions and isolation procedure used in the preparation of **2** and **3**. Distillation of the crude product gave 20.0 g of a mixture of **7** and **9**, bp 59–65° (0.2 mm), ir 5.73, 8.05 μ (acetate). In the nmr spectrum of the mixture, the more abundant isomer had signals at δ 4.70 (d, J = 5 Hz, exo C-2 proton), 2.55, 2.72 (AB quartet, J = 5.5 Hz, oxirane protons), and 1.95 (s, acetate methyl protons). The corresponding signals from the less abundant isomer were at δ 4.88 (d, J = 5 Hz), 2.57, 2.82 (AB quartet, J = 7 Hz), and 1.92 (s).

2-endo-Methyl-2-exo,3-endo-norbornanediol (8).[24]—The mixture of **7** and **9** (20.0 g) was added to 13.5 g of lithium aluminum hydride in 650 ml of anhydrous ether at a rate which caused vigorous refluxing. After addition was complete, the mixture was refluxed overnight. The mixture was then decomposed by addition of 10% sodium hydroxide and was filtered. The granular precipitate of aluminum salts was washed several times with large quantities of boiling ethyl acetate and acetone to dissolve the sparingly soluble **8**. The combined nonaqueous filtrates were dried ($MgSO_4$) and evaporated, and the residue (15.1 g) was dissolved in 50 ml of hot ethyl acetate. Cooling gave 7.1 g of **8**: mp 166–167°; ir (mull) 3.03, 8.90 μ (OH); nmr (acetone-d_6) 3.64 (q, J = 5, 7 Hz, C-3 exo proton), 2.82 (s, 1 H, C-2 hydroxyl proton), 1.6–2.3 (m, 3 H, C-1, C-4, and C-3 hydroxyl protons), 1.07 (s, 3 H, C-2 methyl proton), and 0.9–1.5 (m, 6 H).

Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.69; H, 10.08.

Evaporation of the filtrate from the crystallization of **8** yielded a residue whose ir spectrum indicated the presence of the cis,-endo diol **10**.

2-exo-Methylnorborn-5-ene-2,3-cis,endo-diol Cyclic Carbonate (11).—A solution of 6.0 g of freshly distilled cyclopentadiene and 9.0 g of 4-methyl-1,3-dioxol-4-en-2-one[25] in 27 g of benzene was heated in a sealed tube at 210° for 48 hr. The black mixture was distilled; redistillation of the crude product gave 6.08 g of **11**, bp 97–98° (0.1 mm). It solidified on standing, mp 64–68° after recrystallization from 3:5 hexane–ethyl acetate: ir (mull) 5.62 μ (C=O); nmr (CCl_4) δ 6.45 (m, 2 H, vinyl protons), 4.60 (d, J = 4 Hz, C-3 exo proton), 3.01, 3.26 (m, 2 H, C-1 and C-4 protons), 1.09 (s, 3 H, C-2 methyl protons), 1.3–1.9 (m, 2 H, C_7 protons).

Anal. Calcd for $C_9H_{10}O_3$: C, 65.05; H, 7.27. Found: C, 65.15; H, 6.99.

2-exo-Methyl-2,3-cis,endo-norbornanediol (10).—**11** (3.67 g) in 125 ml of acetone was shaken with 1.0 g of Pd metal and 40 psi of hydrogen in a Paar apparatus. Filtration and evaporation gave 3.60 g of 2-*exo*-methyl-2,3-*cis*,*endo*-norbornanediol cyclic carbonate as a waxy solid, ir (mull) 5.57 μ (C=O).

Anal. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.18. Found: C, 64.21; H, 7.08.

This compound was hydrolyzed overnight at room temperature with 100 ml of 5% sodium hydroxide solution. The reaction solution was extracted with four 100-ml portions of ether. Drying ($MgSO_4$) and evaporation of the extract yielded 2.8 g of **10**: mp after recrystallization from hexane 47–49.5°; ir (film) 3.03, 9.06 μ (OH); nmr (CCl_4) δ 4.17 (broad s, 1 H, C-3 hydroxyl proton), 3.71 (broad s, 1 H, C-2 hydroxyl proton) 3.40 (m, 1 H, C-3 exo proton), 2.20, 2.45 (m, 2 H, C-1 and C-4 protons), 1.19 (s, 3 H, C-2 methyl protons), 1.0–1.9 (m, 6 H).

Anal. Calcd for $C_8H_{14}O_2$: C, 67.59; H, 9.92. Found: C, 67.77; H, 9.81.

2-endo-Methyl-2-exo,3-endo-norbornanediol 3-Methanesulfonate (17).—**8** (2.0 g) was treated with 2.0 g of methanesulfonyl chloride in 20 ml of pyridine, using reaction conditions and isolation procedure identical with those employed in the preparation of **20**. The methanesulfonate **17**, 2.18 g, was obtained as an oil: ir (film) 3.05 (OH), 7.6, 8.65 μ (mesylate); nmr (CCl_4) δ 4.53 (d, J = 5 Hz, 1 H, C-3 exo proton), 2.97 (s, 3 H, mesylate methyl protons), 2.55 and 1.88 (m, 2 H, C-1 and C-4 protons), 2.07 (s, 1 H, C-2 hydroxyl proton), 1.22 (s, 3 H, C-2 methyl protons), and 1.0–1.6 (m, 6 H).

Anal. Calcd for $C_9H_{16}O_4S$: C, 49.08; H, 7.32; S, 14.53. Found: C, 48.95; H, 7.52; S, 14.50.

2-exo-Methyl-2,3-cis,endo-norbornanediol 3-Methanesulfonate (24).—**10** (3.0 g) was treated with 3.0 g of methanesulonyl chloride, using the same reaction conditions and isolation procedure employed in the preparation of **20**. The crude mesylate was recrystallized from 2:1 CS_2–CCl_4, giving 2.1 g of **24**: mp 56–58°; ir (film) 2.92 (OH), 7.55, 8.55 μ (mesylate); nmr (CCl_4) δ 4.40 (d, J = 5 Hz, exo C-3 proton), 3.11 (s, 3 H, mesylate methyl protons), 2.53, 2.13 (m, 2 H, C-1 and C-4 protons), 1.78 (s, C-2 hydroxyl proton), 1.15 (s, 3 H, C-2 methyl protons), 1.0–1.6 (m, 6 H).

Anal. Calcd for $C_9H_{16}O_4S$: C, 49.08; H, 7.32; S, 14.53. Found: C, 48.87; H, 7.39; S, 14.38.

Reaction of Mesylates 12, 17, 20, and 24 with Potassium *tert*-Butoxide.—A solution of 1.0 g of **12** in 10 ml of *tert*-butyl alcohol was added to a solution of 0.5 g of potassium in 50 ml of *tert*-butyl alcohol. The solution was allowed to stand for 1 hr at room temperature, and then was refluxed for 2 hr. After cooling, the solution was added to 250 ml of water, and then extracted with four 100-ml portions of ether. Drying ($MgSO_4$) and evaporation of the extract yielded 0.27 g of crude product, which was analyzed by gas chromatography on a 6 ft × 1.25 in. stainless steel column packed with 10% lac on 60–80 mesh Chromosorb W, using an F & M Model 720 gas chromatograph. The reference compounds were prepared by literature procedures. Retention times are given for isothermal operation with a column temperature of 115°, an inlet temperature of 250°, and a helium flow rate of 50 ml/min: 2-*endo*-methyl-2,3-*exo*-epoxynorbornane (**14**),[9] 2.0 min; 3-methyltricyclo[2.2.1.$0^{2,6}$]heptan-3-ol (**28**, R = CH_3),[13] 3.5 min; 3-*exo*-methyl-2-norbornanone (**19**),[11] 4.5 min; and 3-*endo*-methyl-2-norbornanone (**16**),[10] 5.0 min. The crude reaction product, whose ir spectrum showed the absence of any unreacted mesylate, gave three peaks, identified by retention time as **14**, **19**, and **16**, with relative areas of 90:6:4. Their identity was confirmed by comparison of the ir spectra of the trapped peaks with those of synthetic samples.

Each of the mesylates **17**, **20**, and **24** was decomposed with potassium *tert*-butoxide, using the same reaction conditions and analysis procedure. From **17** was obtained **4**, **16**, and **19** in the proportions 90:6:4; from **24** a 60:40 mixture of **16** and **19** was obtained, and from **20** the sole product was **16**.

Reaction of the Mesylates 12, 17, 20, and 24 with Sodium Hydride.—A solution of 1.0 g of **12** in 10 ml of benzene was added to 0.25 g of sodium hydride in 100 ml of benzene. The mixture was stirred for 1 hr at room temperature followed by 2 hr of refluxing. After cooling, water was added and the mixture was stirred until all solids had dissolved. Drying ($MgSO_4$) and evaporation of the benzene layer gave 0.29 g of crude product, whose ir spectrum had no bands attributable to the starting mesylate.

Gas chromatographic analysis of the crude product showed the presence of **14**, **16**, and **19** in the proportion 90:6:4.

The mesylates **17**, **20**, and **24** were subjected to the same reaction conditions and analysis. **17** yielded a 90:6:4 mixture of **14**, **16**, and **19**. Both **20** and **24** gave a 60:40 mixture of **16** and **19**.

3-Methyltricyclo[2.2.1.$0^{2,6}$]heptan-3-ol (**28**, R = CH_3), when treated with either potassium *tert*-butoxide or sodium hydride, using the above reaction conditions and isolation procedures, gave crude product whose ir was indistinguishable from that of the starting material.

2-exo-Methyl-2,3-endo-epoxynorbornane (22).—The mesylate **20** was decomposed with potassium *tert*-butoxide in *tert*-butyl alcohol using the reaction conditions described above. Isolation of **22** was possible only when the following modifications were made in the isolation procedure. All operations were carried out in a drybox under dry N_2, all glassware was previously rinsed with NH_4OH before drying, ether was replaced by CCl_4 for extraction, solutions were dried with K_2CO_3 instead of $MgSO_4$, and evaporations were carried out at temperatures below 40°. The nmr of the crude product had peaks ascribable to **22** at δ 3.15 (d, J = 3 Hz, C-3 exo proton) and 1.35 (s, C-2 methyl protons). Addition of a crystal of *p*-toluenesulfonic acid to the nmr tube caused immediate transformation of the spectrum to that of **16**. The same transformation occurred when solutions of **22** were exposed to the laboratory air.

Solvolysis of 12 in Aqueous Acetone.—The mesylate **12** was heated in aqueous acetone, using the same reaction conditions and isolation procedure reported for the solvolysis of 2-*endo*-

(24) The preparation of **8** has been reported by A. Krieger, *Suom. Kemistilehti B*, **35**, 71 (1962); *Chem. Abstr.*, **57**, 14959 (1962). Our observations suggest that the substance isolated by Krieger was a mixture of isomeric diols.

(25) P. H. Moss, U. S. Patent 3,020,290 (Feb 6, 1962); *Chem. Abstr.*, **56**, 12904e (1962).

phenyl-2,3-*cis*,*exo*-norbornanediol 3-*p*-toluenesulfonate.[19] Gas chromatographic analysis of the crude product showed the presence of mesityl oxide, diacetone alcohol, and a mixture of glycols, of long retention time, which was not investigated further. No peaks due to **14**, **16**, or **19** were detectable.

Registry No.—**2**, 35623-80-4; **3**, 35623-81-5; **4**, 35623-82-6; **5**, 35623-83-7; **6**, 35623-84-8; **7**, 35623-85-9; **8**, 35623-86-0; **9**, 35623-87-1; **10**, 35623-88-2; **11**, 35623-89-3; **12**, 35623-90-6; **17**, 35623-91-7; **20**, 35623-92-8; **22**, 35623-93-9; **24**, 35623-94-0; bismethanesulfonate of 3-*exo*-hydroxynorbornane-2-*exo*-methanol, 35623-95-1; 2-*exo*-methyl-2,3-*cis*,*endo*-norbornanediol cyclic carbonate, 35623-96-2.

Structural Constraints on Electrocyclic Reactions of Unsaturated Ketenes. Synthesis and Irradiation of 2,4,4,5-Tetramethylbicyclo[4.4.0]deca-1,5-dien-3-one

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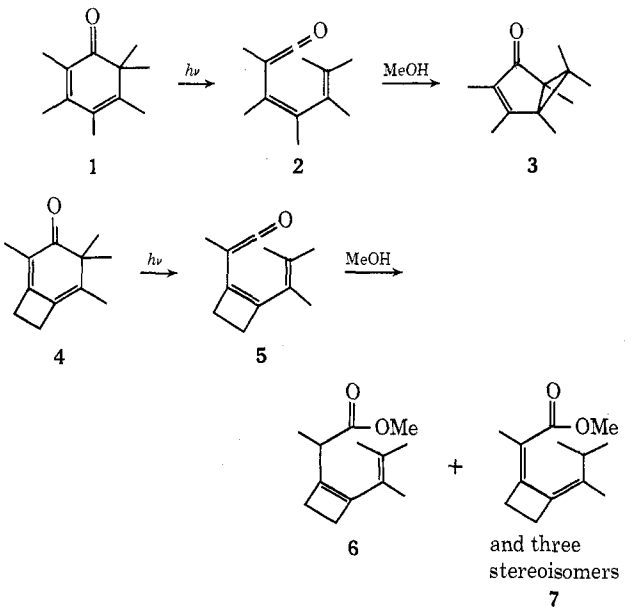
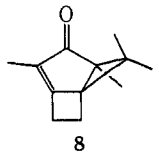
Oxidation of 5,6,7,8-tetramethyltetralin (**9**) with peroxytrifluoracetic acid–boron fluoride gave a mixture of three 2,4-cyclohexadienones (**10**, **11**, and **12**) and the 2,5-cyclohexadienone **13**, as a result of electrophilic attack at all possible ring positions. Irradiation of **13** at 2537 Å gave the expected lumiproducts **14** and **15**; similarly, irradiation of **11** and **12** at 3000 Å gave **14** and **15**, respectively. Irradiation of **10** at 3000 Å in methylene chloride or methanol gave the tetracyclic enone **26**; no methyl esters were formed. Thus the ketene **25** derived from **10** undergoes the electrocyclic reaction faster than it reacts with the nucleophile methanol; its behavior is analogous to that of **2**, not **5**.

The two ketenes formed on irradiation of the 2,4-cyclohexadienones **1** and **4**, respectively, react very differently in methanol. Ketene **2** does not react with the nucleophile to form methyl esters but cyclizes quantitatively to **3**.[1] Ketene **5**, on the other hand,



reacts with methanol to produce a mixture of esters **6** and **7**, and does not cyclize to **8**, the highly strained



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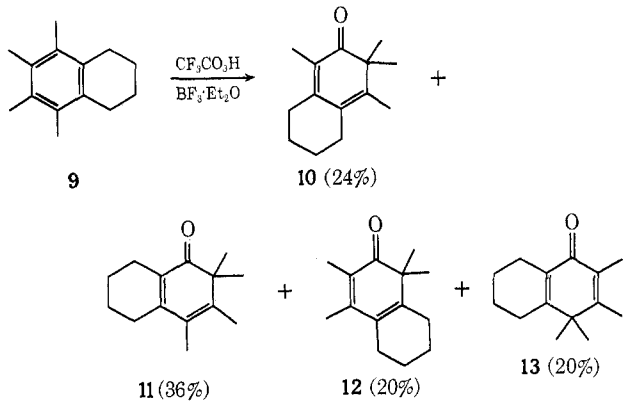
analog of **3**.[2] In the present paper we explore the consequence of enlarging the four-membered ring in **5** to a six-membered ring on the behavior of the ketene toward methanol.

Oxidation of 5,6,7,8-Tetramethyltetralin.—The oxidation of highly substituted aromatic compounds with peroxytrifluoracetic acid–boron fluoride affords a useful general route to 2,4-cyclohexadienones.[3] It was anticipated that the oxidation of 5,6,7,8-tetramethyltetralin (**9**)[4] would give the desired cyclohexadienone **10**, together with other isomeric dienones. Oxidation of **9** with peroxytrifluoracetic acid–boron fluoride etherate at −10° gave an 84% yield of a mixture of isomeric dienones **10**–**13**. Unfortunately it was not



possible to obtain **10** free of contamination with **11** and **12**. However it was possible to obtain **11**, **12**, and **13** pure (by column and gas-liquid chromatography), to identify each, and to identify the photoisomerization product(s) of each. Irradiation of a mixture of **10**–**12** then permitted us to establish the photochemical behavior of **10** and to isolate its photoproduct on irradiation in methanol.

The oxidation product with the longest vpc retention time was a crystalline solid, mp 87–89°, identified as **13**. Its uv and ir spectra were characteristic of a 2,5-

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(2) R. J. Bastiani and H. Hart, *J. Org. Chem.*, **37**, 2830 (1972).
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(4) B. V. Gregorovitch, C. S. Liang, D. M. Auguston, and S. F. MacDonald, *Can. J. Chem.*, **46**, 3291 (1968).