was then heated, the catalyst filtered off, and the filtrate concentrated and diluted with hot water. Upon cooling, glistening white needles separated (0.60 g., 70%), m.p. 261–264°. Recrystallization from ethanol–water yielded white needles (0.25 g., 29%), m.p. 268–270°; ν_{OH} 3440 ms, ν_{NH} 3150 m, 3060 m, $\nu_{C=O}$ 1751 ms, 1689 s cm.$^{-1}$ (Nujol).

Anal. Calcd. for $C_{16}H_{23}NO_5$ (309.35): C, 62.12; H, 7.49; N, 4.53. Found: C, 62.36; H, 7.69; N, 4.54.

9,10-Dihydroxy-14-azadispiro[5.1.5.2]pentadecane-7,15-dione (Isomer 2, IVi).—Compound IVg (1.38 g., 0.00487 mole) dissolved in 95% ethanol (120 cc.) was hydrogenated over Raney nickel at 2 atm. and room temperature for 24 hr. The catalyst was filtered off and the filtrate evaporated to dryness. Crystallization of the residue from methanol–ethyl acetate gave crystals (0.95 g., 73%), m.p. 289–292°. Recrystallization from methanol–ethyl acetate yielded fine white needles, m.p. 290–292°; ν_{OH} 3340 m, ν_{NH} 3130 m, 3040 w, $\nu_{C=O}$ 1751 m, 1650 s cm.$^{-1}$ (Nujol).

Anal. Calcd. for $C_{14}H_{21}NO_4$ (267.32): C, 62.90; H, 7.92; N, 5.24. Found: C, 62.64; H, 8.00; N, 5.25.

9,10-Dihydroxy-14-azadispiro[5.1.5.2]pentadecane-7,15-dione (Isomer 3, IVj).—Compound IVf (2.0 g., 0.0062 mole) was converted to IVh by stirring with aqueous 10% hydrochloric acid (50 cc.) for 10 min. The white solid (IVh) was then filtered off, dissolved in ethanol (50 cc.), and hydrogenated over Raney nickel at 2 atm. and room temperature for 24 hr. The catalyst was filtered off and the filtrate evaporated to dryness. Crystallization from ethanol–ethyl acetate–light petroleum ether (b.p. 60–68°) gave a white solid (1.13 g. 68%), m.p. 178–180°. Two recrystallizations from ethyl acetate–light petroleum ether yielded a granular white solid, m.p. 178–180°; ν_{OH} 3310 m, $\nu_{C=O}$ 1748 mw, 1681 s cm.$^{-1}$ (Nujol).

Anal. Calcd. for $C_{14}H_{21}NO_4$ (267.32): C, 62.90; H, 7.92; N, 5.24. Found: C, 63.19; H, 8.18; N, 4.83.

Cyclohexanehydroxamic Acid (LXXIX).—The product, prepared in 38% yield from cyclohexanecarbonyl chloride[66] according to a procedure for benzohydroxamic acid,[67] was crystallized twice from chloroform, giving matted white needles, m.p. 136–137°; lit.[68] 65%, lit.[68] m.p. 132°, lit.[69] 132–133°; $\nu_{NH,OH}$ 3160 s, 3010 m, $\nu_{C=O}$ 1658 s, $\nu_?$ 1538 m cm.$^{-1}$ (Nujol).

Anal. Calcd. for $C_7H_{13}NO_2$ (143.18): C, 58.72; H, 9.15; N, 9.78. Found: C, 58.53; H, 9.06; N, 9.92.

Methylation of LXXIX: Preparation of N-Methoxycyclohexanecarboxamide (LXXX).—A solution of cyclohexanehydroxamic acid (1.4 g., 0.0098 mole), potassium hydroxide (0.6 g., 0.011 mole), and methyl iodide (2.0 g., 0.0141 mole) in methanol (10 cc.) was refluxed for 2 hr. The solution was then evaporated to dryness in a rotary evaporator. The residue was extracted with light petroleum ether (b.p. 60–68°), and the extract filtered, concentrated, and cooled, causing precipitation of feathery needles (0.23 g., 15%), m.p. 73–75°. Two recrystallizations from light petroleum ether yielded feathery white needles, m.p. 77–79°; ν_{NH} 3170 s, $\nu_{C=O}$ 1650 s, $\nu_?$ 1513 m cm.$^{-1}$ (Nujol)

Anal. Calcd. for $C_8H_{15}NO_2$ (157.21): C, 61.12; H, 9.62; N, 8.91. Found: C, 60.87; H, 9.53; N, 9.07.

Acknowledgment.—We wish to thank Professor Dorothy V. Nightingale for informing us of current work in her laboratory related to this structure determination, and for her friendly interest in the progress of the work.

(66) A. C. Cope and E. Ciganek, *Org. Syn.*, **39**, 19 (1959).

(67) L. W. Jones and C. D. Hurd, *J. Am. Chem. Soc.*, **43**, 2422 (1921).

(68) F. Winternitz and C. Wlotzka, *Bull. soc. chim. France*, 510 (1960).

(69) R. M. Gipson, F. H. Pettit, C. G. Skinner, and W. Shive, *J. Org. Chem.*, **28**, 1425 (1963).

The Preparation and Stereospecific Rearrangement of Spiro[bicyclo[2.2.1]hept-2-en-*anti*-7,2'-oxacyclopropane]. The Effect of a Nonclassical Intermediate[1]

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The addition of dimethylsulfoxonium methylide in dimethyl sulfoxide to bicyclo[2.2.1]hept-2-en-7-one occurs in a stereospecific manner to yield spiro[bicyclo[2.2.1]hept-2-en-*anti*-7,2'-oxacyclopropane]. This epoxide is rearranged stereospecifically with retention of configuration at the migration terminus by the action of heat and/or Lewis acids to yield bicyclo[2.2.1]hept-2-ene-*syn*-7-carboxaldehyde. The structures of the epoxide and aldehyde are established by chemical and physical means. A mechanism for the rearrangement is suggested which incorporates a nonclassical intermediate.

Norton[2] reports that bicyclo[2.2.1]hept-2-en-7-one (2) reacts with the nitrogen-containing nucleophiles, hydroxylamine, semicarbazide, and 2,4-dinitrophenylhydrazine with exceptional ease. Therefore, when searching for a suitable starting material for the preparation of some 7-functionally substituted bicyclo[2.2.1]hept-2-enes, we decided to examine the reactions of this ketone with some nucleophiles in which the attacking atom would be carbon rather than nitrogen. One of the more interesting nucleophiles, whose reactivity toward ketones has recently been demonstrated, is dimethylsulfoxonium methylide.[3] We report here the results of our investigation into the reaction of dimethylsulfoxonium methylide in dimethyl sulfoxide with bicyclo[2.2.1]hept-2-en-7-one (2).

Results

Bicyclo[2.2.1]hept-2-en-7-one (2) was first prepared and characterized by Norton.[2] The final step in his synthetic scheme involved the oxidation of bicyclo-[2.2.1]hept-2-en-7-ol (of unspecified configuration but probably *anti*) with chromic acid in acetone.[4] The ketone, obtained in 38% yield, was identified by its infrared and ultraviolet spectra, its facile reaction with hydroxylamine, 2,4-dinitrophenylhydrazine, and semicarbazide, and by its reduction with lithium aluminum hydride back to bicyclo[2.2.1]hept-2-en-7-ol. As the starting point for our synthesis we used bicyclo[2.2.1]hept-2-en-*anti*-7-ol (1), prepared in 21% over-all yield from bicyclo[2.2.1]heptadiene by the procedure

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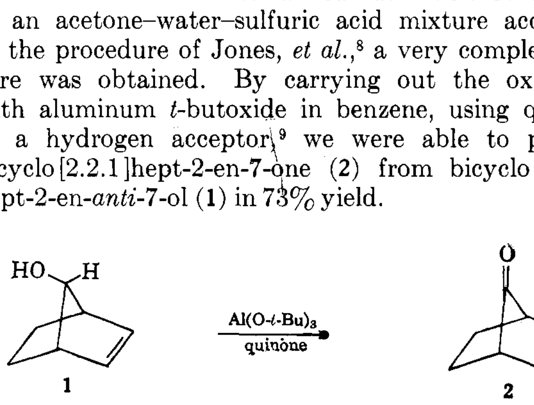
[1] (a) Portions of this work have been presented at the 14th Southeastern Regional Meeting of the American Chemical Society, Gatlinburg, Tenn., November, 1962, and at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963 (Abstracts of meeting, p. 25M); (b) Since there are presently no accepted conventions for designating the stereochemistry of 7-substituted bicycloheptenes we will arbitrarily refer to those in which the functional group of the 7-substituent and the bicycloheptene double bond are on the same side of the plane defined by the 1, 4, and 7 carbons as *syn*, those in which they are on opposite sides as *anti*.

[2] C. J. Norton, Ph.D. thesis, Harvard University, 1955, pp. 103, 126 ff.

[3] E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 867, 868, 3782 (1962).

[4] P. Bladon, J. M. Fabian, H. B. Henbest, H. P. Koch, and W. G. Wood, *J. Chem. Soc.*, 2407 (1951).

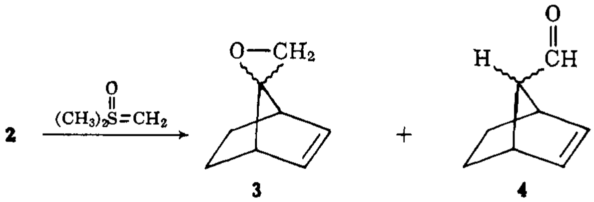
of Story.[5] Our attempts to oxidize this alcohol with chromium trioxide in pyridine,[6] and with aluminum *t*-butoxide in an acetone–benzene mixture,[7] led primarily to the recovery of unchanged starting material. When the oxidation was carried out with chromic acid in an acetone–water–sulfuric acid mixture according to the procedure of Jones, *et al.*,[8] a very complex mixture was obtained. By carrying out the oxidation with aluminum *t*-butoxide in benzene, using quinone as a hydrogen acceptor,[9] we were able to prepare bicyclo[2.2.1]hept-2-en-7-one (2) from bicyclo[2.2.1]hept-2-en-*anti*-7-ol (1) in 73% yield.



The infrared spectrum of our material and the melting point and ultraviolet spectrum of its 2,4-dinitrophenylhydrazone, were all identical to those reported by Norton.[2] The ultraviolet spectrum of the pure ketone was not. Norton reports that his material showed a strong absorption in the short wave-length region of the spectrum, $\lambda_{\max}^{\mathrm{EtOH}}$ 233 mμ (ε 1300), as well as the more normal absorption at a longer wave length, $\lambda_{\max}^{\mathrm{isooctane}}$ 275 mμ (ε 33). Norton attributed this unusual short wave-length absorption to "a very unique transannular interaction between the nonconjugated double bond and the carbonyl group."[10] This ultraviolet absorption has been widely quoted[11]; the short wave-length band has been suggested to arise from the charge transfer $\pi \rightarrow \pi^*$ transition,[11,12] and has been the object of considerable theoretical speculation. Consequently, we were disturbed when the ultraviolet spectrum of our ketone in 95% ethanol exhibited no detectable maximum at 233 mμ or thereabouts, but rose gradually to ε 2700 at 200 mμ. At 233 mμ the molar extinction coefficient was approximately 250. The absorption of our material at longer wave length was quite similar to that of Norton's, *i.e.*, $\lambda_{\max}^{\mathrm{EtOH}}$ 272 mμ (ε 38.9). The fact that the gas chromatographic analysis of our material showed it to be pure led us to conclude that we had indeed prepared bicyclo[2.2.1]hept-2-en-7-one.[13] We have no explanation for the short wave-length absorption observed by Norton.[14]

When a solution containing a stoichiometric amount of dimethylsulfoxonium methylide in dimethyl sulfoxide[3] was allowed to react with bicyclo[2.2.1]hept-2-en-7-one (2), a gas chromatographic analysis of the products on a silicone oil 200 column at 110° showed the presence of two compounds, **3** and **4**. On this column the retention time of **3** was 0.82 times that of **4**; its peak area relative to **4** was 0.053, although this ratio could be changed from 1.2 to 0 by varying the conditions of analysis, *i.e.*, column, column and preheater temperature, flow rate.

Both of these compounds were neutral and each had the empirical formula, $C_8H_{10}O$. The infrared spectrum of **3** confirmed the presence of a double bond (6.17 μ) and a vinyl hydrogen (3.26, 14.25 μ), and the absence of a hydroxyl or carbonyl function. Hence the oxygen must be present as an epoxide or as an ether. The presence of absorptions at 3.19, 7.19, 10.95, and 11.84 μ, which could be attributed to a terminal epoxide,[15] and the strong C–O stretching vibrations at 10.18 and 10.57 μ confirm this. Compound **4** showed strong absorptions at 3.26 and 14.35 (vinyl hydrogen), 3.70 (aldehydic hydrogen), 5.81 (carbonyl), and 6.12 μ (double bond). This evidence, taken collectively, indicates that compound **3** is a spiro[bicyclo[2.2.1]hept-2-ene-7,2′-oxacyclopropane],[16] and that compound **4** is a bicyclo[2.2.1]hept-2-ene-7-carboxaldehyde.



These structures were established chemically in the following manner. The reduction of **3** with lithium aluminum hydride affords a single unsaturated alcohol, $C_8H_{12}O$ (**5**), which is identical to the single alcohol produced by the reaction of **2** with methylmagnesium iodide followed by hydrolysis. Compound **4** is oxidized by silver oxide to a bicyclic unsaturated carbox-

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(5) P. Story, *J. Org. Chem.*, **26**, 289 (1961).

(6) G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *J. Am. Chem. Soc.*, **75**, 422 (1953).

(7) R. V. Oppenauer, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 207.

(8) K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

(9) R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

(10) Ref. 2, p. 126.

(11) *E.g.*, S. Winstein, L. DeVries, and R. Orloski, *J. Am. Chem. Soc.*, **83**, 2020 (1961), and references cited therein.

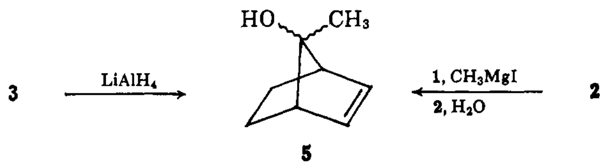
(12) (a) M. Simonetta and S. Winstein, *ibid.*, **76**, 18 (1954); (b) H. Labhart and G. Wagnière, *Helv. Chim. Acta*, **42**, 2219 (1959); R. C. Cookson and J. Hudec, *J. Chem. Soc.*, 429 (1962).

(13) The n.m.r. spectrum of this material seems compatible with this structure, *e.g.*, two vinyl protons split into a triplet (3.50 τ, $J = 2.3$ c.p.s.) by at least two other hydrogens, two bridgehead protons split into a quintet (7.25 τ) by at least three other hydrogens, and four methylene hydrogens which appear as a complex absorption (7.8–9.1 τ). While the vinyl hydrogen resonance of this ketone appears at a lower field than do those of the other 7-substituted bicyclo[2.2.1]hept-2-enes which we have examined, it is reported that the vinyl hydrogen resonances of both *anti*-7-chloro- and *syn*-7-bromobicyclo[2.2.1]hept-2-ene occur at an even lower field, *i.e.*, 3.15 τ [L. Kaplan, H. Kwart, and P. von R. Schleyer, *J. Am. Chem. Soc.*, **82**, 2341 (1960)]. It is known that both the chemical shifts and the coupling constants of hydrogens in bicyclic compounds are quite sensitive to changes in their steric and/or electronic environment [O. L. Chapman, *ibid.*, **85**, 2014 (1963)]. The fact that the vinyl hydrogens in bicyclo[2.2.1]hept-2-en-7-one appear as a triplet which shows evidence of further splitting is quite characteristic of symmetric 7-substituted bicyclo[2.2.1]heptenes (see Experimental).

(14) (a) J. J. Hurst and G. H. Whitham, *J. Chem. Soc.*, 710 (1963), report that 1,5,5-trimethylbicyclo[2.2.1]hept-2-en-7-one shows an $n \rightarrow \pi^*$ absorption, $\lambda_{\max}^{\mathrm{EtOH}}$ 270 mμ (ε 58), but only an ill-defined absorption at short wave lengths rising to ε 3000 at *ca.* 200 mμ. These authors report a private communication from R. Orloski whose reexamination of the spectrum of bicyclo[2.2.1]hept-2-en-7-one shows it to be similar to that of 1,5,5-trimethylbicyclo[2.2.1]hept-2-en-7-one; (b) K. V. Scherer, Jr., Abstracts of the 144th National Meeting of the American Chemical Society, Los Angeles, April, 1963, p. 61M, reports that the ultraviolet spectrum of Δ^5-dihydrodicyclopentadien-8-one, run in isooctane, exhibits shoulders at 203.0 (2900) and 215 mμ (ε 800), and shows a maximum at 269 mμ (ε 30.6); (c) P. G. Gassman and P. G. Pape, *Tetrahedron Letters*, No. **1**, 9 (1963), have recently reported an ultraviolet spectrum for bicyclo[2.2.1]hept-2-en-7-one similar to that which we found.

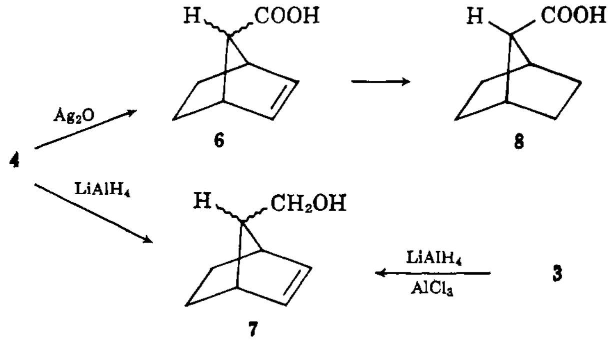
(15) (a) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1963, pp. 36, 155; (b) S. B. Soloway and S. J. Cristol, *J. Org. Chem.*, **25**, 327 (1960); (c) G. M. Barrow and S. Searles, *J. Am. Chem. Soc.*, **75**, 1175 (1953).

(16) When bicyclo[2.2.1]hept-2-en-7-one is allowed to react in the presence of excess dimethylsulfoxonium methylide, a compound which we believe to be spiro[bicyclo[2.2.1]hept-2-en-*anti*-7,2′-oxacyclobutane] is formed in good yield. We shall discuss this reaction in a separate communication since it does not bear directly on this work.



5

ylic acid, $C_8H_{10}O_2$ (**6**), and is reduced by lithium aluminum hydride to a single unsaturated alcohol, $C_8H_{12}O$ (**7**), which is different from **5**, but which is identical to the single unsaturated alcohol formed when the epoxide **3** was reduced with lithium aluminum hydride in the presence of aluminum trichloride.[17] The unsaturated acid **6** can be catalytically hydrogenated to the known bicyclo[2.2.1]heptane-7-carboxylic acid (**8**).[18]

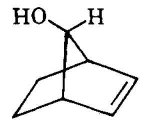


The fact that the normal product from the reaction of dimethylsulfoxonium methylide with a non-α,β-unsaturated ketone is an epoxide,[3] and that the composition of the reaction mixture obtained from this reagent and bicyclo[2.2.1]hept-2-en-7-one was dependent upon the conditions of analysis, led us to suspect that the aldehyde was being formed from the epoxide by rearrangement during gas chromatography.

In order to test this idea, we reduced a portion of the reaction mixture with lithium aluminum hydride. A gas chromatographic analysis of this reaction product showed the presence of only the tertiary alcohol **5**. No primary alcohol **7** was formed in this reduction; therefore, the reaction mixture prior to reduction could have contained no aldehyde **4**. When the same reaction mixture was treated with boron trifluoride etherate or with aluminum trichloride, it was possible to isolate small quantities of aldehyde, though the principal product(s) was apparently polymeric in nature. The epoxide can be smoothly rearranged to the aldehyde by chromatography on Merck acid-washed alumina.

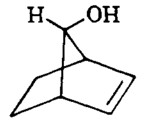
Having thus established that the epoxide **3** could be rearranged by heat and/or Lewis acids to a single aldehyde **4**, we decided to investigate the stereochemistry of this reaction. In order to observe this stereochemistry, it was necessary only to establish the configuration of the epoxide **3** and of the aldehyde **4**. This was done in the following manner.

A high-dilution infrared spectrum of the tertiary alcohol **5**,[19] shows that the principal oxygen–hydrogen stretching frequency occurs at 3622 cm.$^{-1}$. The oxygen–hydrogen stretching frequency of 7-methylbicyclo[2.2.1]heptan-7-ol (**9**), prepared by catalytic reduction of **5**, occurs at 3618 cm.$^{-1}$. The fact that the oxygen–hydrogen stretching vibration of both the saturated and the unsaturated alcohol occurs at approximately the same frequency is indicative that the hydroxyl group of **5** must be on the opposite side of the bridge from the double bond.[20] This conclusion is substantiated by the spectra of the related bicyclic alcohols **10**–**12**.[19] Thus the unsaturated tertiary alcohol **5** is 7-methylbicyclo[2.2.1]hept-2-en-*anti*-7-ol (**5a**). Since the lithium aluminum hydride reduction used to prepare **5a** from the epoxide **3** could not have affected the stereochemistry at the C-7 position, it follows that both the epoxide and the alcohol have the same configuration. The epoxide **3** is thus spiro[bicyclo[2.2.1]-hept-2-en-*anti*-7,2′-oxacyclopropane] (**3a**).



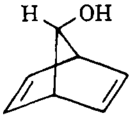
3628 cm.$^{-1}$

10



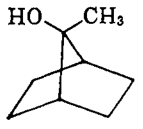
3572 cm.$^{-1}$

11



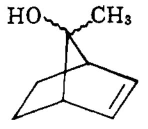
3551 cm.$^{-1}$

12



3618 cm.$^{-1}$

9



3622 cm.$^{-1}$

5

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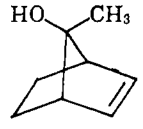
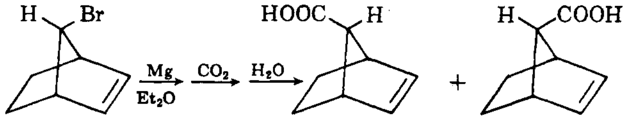


5a

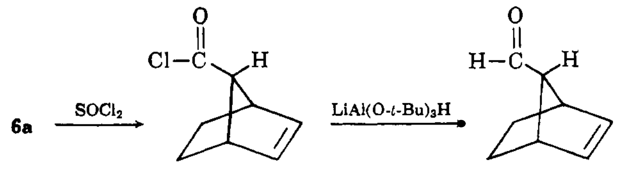
The bicyclo[2.2.1]hept-2-ene-7-carboxylic acid (**6**), m.p. 94–100°, prepared by oxidation of the aldehyde **4** is identical to one of the carboxylic acids, m.p. 91–96°, prepared from *syn*-7-bromobicyclo[2.2.1]hept-2-ene (**13**) and assigned the *syn* configuration **6b** by Sauers.[21]



13 **6a** **6b**

m.p. 70–73° 91–96°

The 2,4-dinitrophenylhydrazone of aldehyde **4** melts broadly at 126–134°, but well below the 150–151° reported by Wilt and Levin for the 2,4-dinitrophenylhydrazone of bicyclo[2.2.1]hept-2-ene-*anti*-7-carboxaldehyde (**4a**) prepared from **6a** *via* the acid chloride **14**.[22]



14 **4a**

These results indicate that the configuration of our aldehyde is *syn*, *i.e.*, **4b**. However, the stereochemical assignments of Sauers, and hence of Wilt and Levin, are not based upon chemical evidence but upon the melting points of the bicyclo[2.2.1]hept-2-ene-7-carboxylic acids (**6a,b**) and upon the relative retention

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[17] E. L. Eliel and D. W. Delmonte, *J. Am. Chem. Soc.*, **80**, 1744 (1958).

[18] (a) H. Kwart and L. Kaplan, *ibid.*, **76**, 4072 (1954); (b) L. Kaplan, Ph.D. thesis, University of Delaware, 1953.

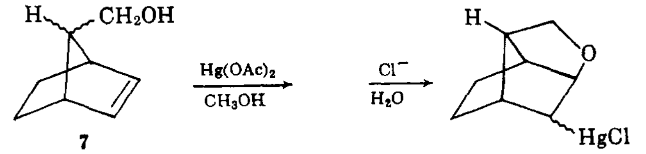
[19] This spectrum was determined on a Perkin-Elmer Model 421 grating infrared spectrophotometer by Dr. L. P. Kuhn of the Ballistics Research Laboratory, Aberdeen Proving Ground, Md.

[20] Ref. 15a, p. 31, ref. 1-7.

[21] R. R. Sauers, *Chem. Ind.* (London), 176 (1960).

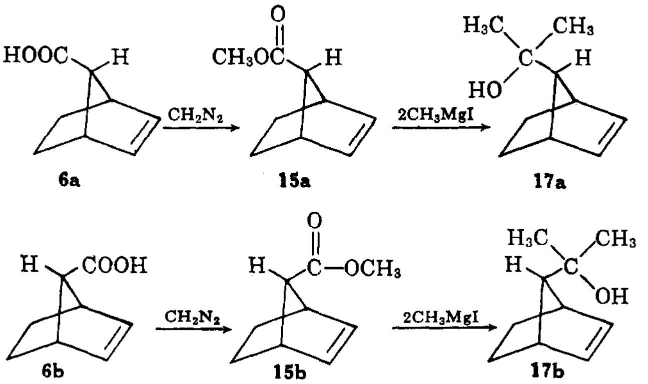
[22] J. W. Wilt and A. A. Levin, *J. Org. Chem.*, **27**, 2319 (1962).

times of their two methyl esters **15a,b** when gas chromatographed upon diethylene glycol and diethylene glycol–silver nitrate columns. Although we had no reason to doubt their conclusions, we desired a more direct indication of the stereochemistry of our bicyclo[2.2.1]hept-2-ene-7-carboxaldehyde. Since both iodolactonization, using an aqueous solution of iodine, potassium iodide, and sodium bicarbonate, and lactonization in the presence of a strong acid, have been reported to cause rearrangements with bicyclo[2.2.1]heptenecarboxylic acids,[23,24] we decided to turn our attention to the primary alcohol **7** produced from the aldehyde **4** by chemical reduction. When this alcohol is treated with mercuric acetate in methanol,[25] conditions which do not cause isomerization of the alcohol, the mercuric ion rapidly disappears, and treatment of the reaction mixture with aqueous sodium chloride causes the precipitation of a white solid, m.p. 176–180°, which we believe to be the chloromercuri tricyclic ether (**16**) of undetermined configuration.



7 **16**

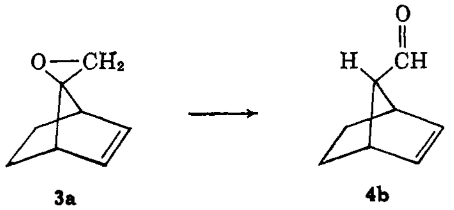
The bicyclo[2.2.1]hept-2-ene-7-methanol prepared by the lithium aluminum hydride reduction of the lower melting of Sauers' acids **6a**, and thus presumably of *anti* configuration, reacts, but does not form a tricyclic ether under these conditions. In addition, each of Sauers' two acids, *i.e.*, **6a,b**, was converted *via* its methyl ester **15a,b** to the corresponding tertiary alcohol **17a,b**, respectively. The high-dilution infrared spectrum of the tertiary alcohol **17b** shows a strong intramolecular hydrogen bond (3577 cm.$^{-1}$) and a weak nonbonded hydroxyl absorption (3617 cm.$^{-1}$), while the alcohol **17a**, derived from the lower melting of Sauers' acids, **6a**, shows only a broad nonbonded hydroxyl absorption at 3618–3629 cm.$^{-1}$.[19]



6a **15a** **17a**

6b **15b** **17b**

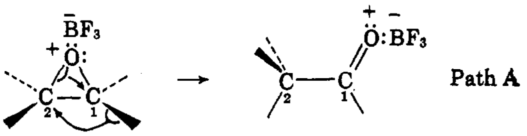
We believe that these data confirm both chemically and physically the stereochemistry of the two bicyclo[2.2.1]hept-2-ene-7-carboxylic acids (**6a,b**) the esters **15a,b**, the tertiary alcohols **17a,b**, the primary alcohols **7a,b**, and the aldehydes **4a,b**. It is now clear that the aldehyde which we have observed as a rearrangement product of spiro[bicyclo[2.2.1]hept-2-en-*anti*-7,2′-oxacyclopropane] (**3a**) is bicyclo[2.2.1]hept-2-ene-7-*syn*-carboxaldehyde (**4b**), and that this rearrangement has occurred with *retention* of configuration at the bridge carbon, C-7.



3a **4b**

Discussion

Heat or catalysis by a Lewis acid can cause an epoxide to rearrange to an aldehyde or ketone.[26] The course of the reaction is determined by the direction of ring opening and by the relative migratory aptitudes of the substituents. Electron releasing groups can enhance the rate of the reaction and promote cleavage of an adjacent carbon–oxygen bond by stabilizing the incipient positive charge in the transition state of the rate determining step. These electronic effects can be accommodated by a concerted, unimolecular process (path A) for which bond-breaking is more important in the transition state than is bond-making.[26b] By analogy with other 1,2-nucleophilic rearrangements,



epoxide-to-carbonyl conversions should normally follow this concerted path, and should undergo inversion at the migration terminus (C-2) in the process.[26,27] The boron trifluoride-catalyzed isomerizations of 5α,6α-epoxycholestane to coprostan-6-one, 5β,6β-epoxycoprostane to cholestan-6-one, 4α,5α-epoxycholestane to coprostan-4-one, and 4β,5β-coprostane to cholestan-4-one provide well defined examples of this type of reaction.[28] Other examples are known.[29] Clearly the rearrangement of spiro[bicyclo[2.2.1]hept-2-en-*anti*-7,2′-oxacyclopropane] (**3a**) with retention of configuration at the migration terminus to bicyclo[2.2.1]hept-2-ene-*syn*-7-carboxaldehyde (**4b**) cannot follow such a concerted path.

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(23) J. A. Berson and A. Remanick, *J. Am. Chem. Soc.*, **83**, 4947 (1961).

(24) S. Beckmann and H. Geiger, *Chem. Ber.*, **94**, 48 (1961).

(25) H. B. Henbest and J. B. Nicholls, *J. Chem. Soc.*, 221 (1959).

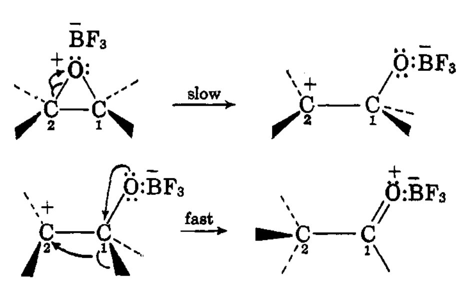
(26) These rearrangements have been reviewed by (a) S. Winstein and R. B. Henderson, "Heterocyclic Compounds," R. C. Elderfield, Ed., Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 47–54; and by (b) R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 737 (1959).

(27) (a) C. K. Ingold, "Structure, and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 478, 511; (b) P. D. Bartlett, "Organic Chemistry, An Advanced Treatise," H. Gilman, Ed., Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 59ff.

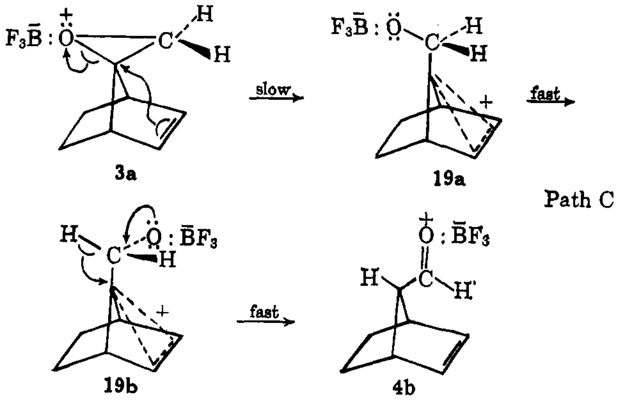
(28) (a) H. B. Henbest and T. F. Wrigley, *J. Chem. Soc.*, 4596 (1957); (b) C. W. Shoppee, M. E. H. Howden, R. W. Killick, and G. H. R. Summers, *ibid.*, 630 (1959).

(29) (a) P. Bladon, H. B. Henbest, E. R. H. Jones, B. J. Lovell, G. W. Wood, G. F. Woods, J. Elks, R. M. Evans, D. E. Hathway, J. F. Oughton, and G. H. Thomas, *ibid.*, 2921 (1953); (b) J. Elks, R. M. Evans, C. H. Robinson, G. H. Thomas, and L. J. Wyman, *ibid.*, 2933 (1953); (c) E. J. Corey and J. J. Ursprung, *J. Am. Chem. Soc.*, **78**, 183 (1956); (d) H. B. Henbest and T. F. Wrigley, *J. Chem. Soc.*, 4765 (1957); (e) R. C. Cookson and J. Hudec, *Proc. Chem. Soc.*, 24 (1957); (f) H. Linde and K. Meyer, *Experientia*, **15**, 238 (1958); *Helv. Chim. Acta*, **42**, 807 (1959); (g) A. Lardon, H. P. Sigg, and T. Reichstein, *ibid.*, **42**, 1457 (1959); (h) D. N. Kirk and V. Petrow, *J. Chem. Soc.*, 4657 (1960); (i) M. Shiota, T. Ogihara, and Y. Watanake, *Bull. Chem. Soc., Japan*, **34**, 40 (1961).

Conceptually, an epoxide–carbonyl rearrangement could follow a nonconcerted path B whose slow first step would be analogous to that of an acid-catalyzed epoxide cleavage,[26b] and whose fast second step would resemble that of a nonconcerted pinacol rearrangement[30] or of a semipinacolic deamination.[31]



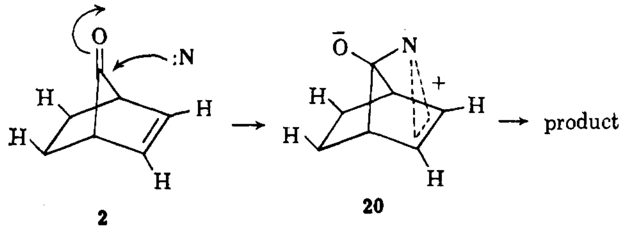
The presence in the molecule of groups which could strongly stabilize the developing positive charge at the migration terminus, C-2, should favor reaction by path B relative to the concerted route (path A).[26b] We believe that the π-electrons of the double bond in spiro[bicyclo[2.2.1]hept-2-en-*anti*-7,2'-oxacyclopropane] (**3a**) exert such an effect, and cause the rearrangement of this epoxide to follow the nonconcerted path C. Thus the first and probable rate-determining step would consist of the heterolysis of the C-7 oxygen bond, assisted by the coordinated Lewis acid and by a backside "push" from the π-electrons, to form the intermediate ion **19a**. The C-7–C-8 bond of this intermediate could then rotate with a minimum of steric interference to a conformation **19b** that would allow the migrating nucleophile (hydride) to attack the delocalized carbonium ion from the preferred *anti* side.[32] The resulting aldehyde **4b** would then have the same configuration at C-7 as the starting epoxide **3a**.



We believe that this represents the first clear case of an epoxide–carbonyl rearrangement which occurs with complete retention of configuration at the migration terminus.[33]

It seems probable that the highly stereospecific nature of this rearrangement together with the almost total absence of a conformational effect in the intermediates (**19**) will combine to make this system ideal for the study of relative migratory aptitudes. We plan to extend this work to some related nucleophilic rearrangements and to some other bicyclic ketones.

It is interesting to note that bicyclo[2.2.1]hept-2-en-7-one (**2**) reacts with methylmagnesium iodide and with dimethylsulfoxonium methylide (possibly also with diazomethane[1a]) in a stereospecific manner. In each case the product formed, *anti*-alcohol **5a** or *anti*-epoxide **3a**, respectively, is the result of a nucleophilic addition to the carbonyl from the side of the double bond. We do not know whether this observed stereospecificity is due to steric or to electronic effects, but we suspect that both may be important. Attack from the side of the double bond is probably less sterically hindered than is attack from the side of the *exo* hydrogens. Since the nucleophiles which we have studied possess no net charge prior to reaction, coulombic repulsion by the π-electrons of the double bond is probably not an important factor. The dipolar intermediate **20** which results from the attack of a neutral nucleophile, :N, on the ketone **2** from the side of the double bond, is probably more stable than that which would result from attack on the opposite side of the molecule. Not only is the negative charge on the oxygen farther removed from the region of high π-electron density, but the positive charge which is developed on the nucleophile can be partially delocalized by these π-electrons. We expect to be in a better position to evaluate the relative importance of these effects when we have examined the reaction with a greater variety of nucleophiles.



Experimental[34]

Bicyclo[2.2.1]hept-2-en-7-one (2).[35]—Ten grams of aluminum *t*-butoxide (Aceto Chemical Co.) was added to a solution of 10 g. of bicyclo[2.2.1]hept-2-en-*anti*-7-ol (**1**)[5] and 16 g. of *p*-benzoquinone in 300 ml. of dry benzene. The mixture was heated at reflux and an additional 10-g. portion of aluminum *t*-butoxide was added in small increments over a 24-hr. period Heating was continued for an additional 50 hr. The reaction mixture was cooled and 200 ml. of 3 *N* hydrochloric acid was added. After filtration of the reaction mixture through a Celite

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(30) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, p. 602.

(31) (a) Ref. 30, pp. 602ff; (b) B. M. Benjamin, H. S. Schaeffer, and C. J. Collins, *J. Am. Chem. Soc.*, **79**, 6160 (1957).

(32) (a) S. Winstein, M. Shatavsky, C. Norton, R. B. Woodward, *ibid.*, **77**, 4183 (1955); (b) S. Winstein and M. Shatavsky, *ibid.*, **78**, 592 (1956); (c) S. Winstein and A. T. Stafford, *ibid.*, **79**, 505 (1957); (d) S. Winstein and C. Ordonneau, *ibid.*, **82**, 2084 (1960).

(33) There are some examples of acid-catalyzed oxide cleavages which occur with retention of configuration at the migration terminus (see ref. 26b, pp. 756ff). In each case this retention can be attributed to restricted rotation about the C-1–C-2 bond (path B) either because of bridged-ion formation by a neighboring aryl or acyl group, or because of a conformational or steric effect. Such effects are not present in path C.

(34) Melting and boiling points are uncorrected. Microanalyses were performed by either Bernhardt Mikroanalytisches Laboratorium, Mülheim, or Gailbraith Laboratories, Incorporated, Knoxville, Tenn. Except where noted, infrared spectra were taken on a Perkin-Elmer Model 21 spectrophotometer equipped with sodium chloride optics. Ultraviolet spectra were recorded on a Cary, Model 14M, spectrophotometer, using 1-cm. quartz cells. The nuclear magnetic resonance spectra were recorded on a Varian A-60 n.m.r. spectrometer using tetramethylsilane as an internal standard. Gas chromatographic analyses were performed with a Perkin-Elmer vapor fractometer, Model 154D, or an F & M Model 500 linear temperature programmed gas chromatograph.

(35) We thank Dr. O. R. Vail for working out the experimental details of this preparation; abstracted from the Ph.D. dissertation of Oakley R. Vail, University of South Carolina, 1963.

mat, the aqueous layer was discarded, and the benzene layer was washed successively with six 150-ml. portions of 3 N hydrochloric acid, enough 5% sodium hydroxide solution to extract the hydroquinone, and two 50-ml. portions of saturated sodium chloride solution. The benzene solution was dried over anhydrous potassium carbonate, the solvent was removed by distillation at atmospheric pressure, and the residue was distilled under reduced pressure; b.p. 54–56° (17 mm.); yield, 7.2 g. (73%).

Anal. Calcd. for C_7H_8O: C, 77.75; H, 7.46. Found: C, 77.45; H, 7.55.

Infrared[15a]: λ_{max}^{film} 3.27, 14.30 (>C=CH—); 5.62 (>C=O in 7-ketobicyclo[2.2.1]heptane); 6.15 μ (>C=C<); in agreement with Norton.[36]

N.m.r.: $\nu_{max}^{CCl_4}$ 3.50, triplet, J = 2.5 c.p.s. (2 >C=CH—); 7.25, quintet (2 ⋗C—H, bridgehead); 7.5–9.1 τ, multiplet (2 >CHH, 2 >CHH).

Ultraviolet: λ_{max}^{EtOH} 272 mμ (ϵ 38.9); $\lambda_{inflection}^{EtOH}$ 222 mμ (ϵ 465).[2,14a]

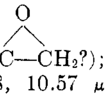
The 2,4-dinitrophenylhydrazone, prepared by the method of Shriner, Fuson, and Curtin,[37] and recrystallized from ethanol, melted at 135–135.5° (lit.[2] m.p. 134–135°).

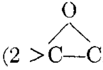
Anal. Calcd. for $C_{13}H_{12}N_2O_4$: C, 54.16; H, 4.20; N, 19.44. Found: C, 54.35; H, 4.09; N, 19.31.

Ultraviolet: λ_{max}^{EtOH} 224 (ϵ 19,700); 358 mμ (24,000).[2]

Spiro[bicyclo[2.2.1]hept-2-en-*anti*-7,2′-oxacyclopropane] (**3a**).—Eleven grams of trimethylsulfoxonium iodide[3] was added, in small portions to a nitrogen-blanketed, stirred suspension of 1.20 g. of sodium hydride (supplied as a 53% dispersion in mineral oil by Metal Hydrides, Inc.) in 40 ml. of dimethyl sulfoxide. When the evolution of hydrogen had ceased, a solution of 5.40 g. of bicyclo[2.2.1]hept-2-en-7-one in 20 ml. of dimethyl sulfoxide was added dropwise with cooling. The reaction mixture was stirred at room temperature for 1 hr., diluted with 100 ml. of water, and extracted with three 50-ml. portions of pentane. The pentane extract was washed with water and dried over anhydrous sodium sulfate. The solvent was removed by distillation at atmospheric pressure, and the product was distilled under vacuum; b.p. 60–61° (28 mm.); yield, 4.32 g. (72%).

Anal. Calcd. for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 78.31; H, 8.23.

Infrared[15a]: $\lambda_{max}^{CCl_4}$ 3.19, 7.91, 10.95, 11.84 ( $>\overset{O}{C—CH_2}$?); 3.25, 14.25 (—C=CH—); 6.17 (>C=C<); 10.18, 10.57 μ (C—O?).

N.m.r.: $\nu_{max}^{CCl_4}$ 3.86, triplet, J = 2.1 c.p.s. (2 >C=CH—); 7.23, singlet, (2  $>\overset{O}{C—CH_2}$); 7.75, quintet (2 ⋗C—H, bridgehead); 7.9–8.3, multiplet (2 >CHH); 8.8–9.1 τ, multiplet (2 >CHH).

7-Methylbicyclo[2.2.1]hept-2-en-*anti*-7-ol (**5a**). **A. From Spiro[bicyclo[2.2.1]hept-2-en-*anti*-7,2′-oxacyclopropane]** (**3a**).—To a stirred slurry of 40 mg. of lithium aluminum hydride in 1 ml. of anhydrous ether was added a solution containing 80 mg. of epoxide in 2 ml. of anhydrous ether. The mixture was heated at reflux for 6 hr., cooled, and then decomposed with water and 15% sodium hydroxide solution. The precipitated salts were removed by filtration, and the solvent was distilled from the filtrate through a 10-cm. Vigreux column. The residue was purified by sublimation at 60° (90 mm.) to give 47 mg. (58%) of white needles, m.p. 74–76°. Gas chromatographic analysis on the silicone oil column, both separately and as a mixture with bicyclo[2.2.1]hept-2-ene-*syn*-7-methanol (**7b**) and bicyclo[2.2.1]-hept-2-ene-*anti*-7-methanol (**7a**), from which it was well resolved, showed the resulting alcohol to be 99% pure. A small sample was resublimed for analysis.

Anal. Calcd. for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.17; H, 9.84.

Infrared[15a]: $\lambda_{max}^{CCl_4}$ 2.77, 2.90 (O-H); 3.26, 14.04 (>C=CH—); 6.14 (>C=C<); 7.29 (C—CH_3); 8.9 μ (C—O). $\nu_{max}^{CCl_4}$ 3622 cm.$^{-1}$ (nonbonded O—H).[19]

N.m.r.: $\nu_{max}^{CCl_4}$ 4.06, triplet, J = 2.5 c.p.s. (2 >C=CH—); 7.71, quintet (2 ⋗C—H, bridgehead); 7.9–8.2, multiplet (2 >CHH); 8.5, singlet (shifted to 7.84 by the addition of a drop of trifluoroacetic acid; 1 O—H); 8.71, singlet (3 —CH_3); 8.8–9.3 τ, multiplet (2 >CHH).

B. From Bicyclo[2.2.1]hept-2-en-7-one (**2**).—Methylmagnesium iodide was prepared from 56 mg. of magnesium and 300 mg. of methyl iodide in 5 ml. of anhydrous ether.

A solution of 205 mg. of the ketone in 3 ml. of ether was added slowly to the Grignard reagent. After the addition was complete, the reaction mixture was heated at reflux for 1 hr. The mixture was cooled, the complex was decomposed by the addition of water and wet sodium sulfate, and the precipitated salts were removed by filtration. The ethereal filtrate was dried over anhydrous sodium sulfate. A gas chromatographic analysis on the silicone oil column revealed the presence of unchanged starting material (40%) and one other component (60%) which had the same retention time as the alcohol **5a** prepared by the reduction of the epoxide with lithium aluminum hydride. The infrared spectrum of this component, collected from the gas chromatographic column, was identical with that of the tertiary alcohol **5a**, prepared from the epoxide **3a**.

The solvent was removed from the reaction by distillation through a 10-cm. Vigreux column, and the unchanged bicyclo-[2.2.1]hept-2-en-7-one (**2**) was recovered by distillation at 73 mm. The residual alcohol was purified by sublimation at 60° (80 mm.); yield, 83 mg. (41%); m.p. 74–76°.

7-Methylbicyclo[2.2.1]heptan-7-ol (**9**).—A 20-mg. sample of the tertiary alcohol **5a** was hydrogenated at atmospheric pressure in 95% ethanol using 5% palladium on charcoal as a catalyst. The hydrogenated sample was purified by sublimation at 60° (90 mm.); m.p. 97–98°.

Anal. Calcd. for $C_8H_{14}O$: C, 76.29; H, 10.91. Found: C, 76.14; H, 11.18.

Infrared[15a]: $\lambda_{max}^{CCl_4}$ 2.77, 2.90 (O–H); 7.29 (C–CH_3); ~8.8 μ (C–O?). The maxima at 3.26, 6.14, and 14.04 μ, present in the spectrum of the unsaturated alcohol **5a** were missing from this spectrum.

The n.m.r. spectrum was too complex to analyze but showed a peak whose position varied with added trifluoroacetic acid (1 O–H), a total of 14 H's, and no vinyl hydrogens.

Bicyclo[2.2.1]hept-2-ene-*syn*-7-carboxaldehyde (**4b**). **A. By Rearrangement of the Epoxide 3a during Gas Chromatography.**—When the epoxide **3a** was subjected to gas chromatographic analysis on the silicone rubber column (110°, 120 ml. He/min.) two compounds were detected with retention times of 3.0 and 4.2 min. The ratio of the area of the first to the second peak was 1.0 under these conditions. When the silicone oil column was used for analysis of the epoxide (110°, 150 ml. of He/min.), two peaks were again observed with retention times of 8.6 and 10.5 min., but the ratio of their areas was now 0.053.

These peak-area ratios were difficult to duplicate. They varied with the conditions of the analysis, *i.e.*, column and preheater temperature, flow rate, and sometimes changed drastically after a given column had been used for the analysis and/or collection of other materials.

The first component was collected from the silicone rubber column. Its infrared spectrum showed all the absorptions present in the spectrum of spiro[bicyclo[2.2.1]hept-2-en-*anti*-7,2′-oxacyclopropane] (**3a**) plus an additional small peak at 5.81 μ which was presumed to arise from a trace of aldehyde contaminant formed by rearrangement of the epoxide in the postheater of the gas chromatograph.

The second component was obtained by collection from the silicone oil column. By using a 30-μl. sample, it was possible to collect 15–18 mg. (60–70%) of this material from each injection.

Infrared[15a]: $\lambda_{max}^{CCl_4}$ 3.26, 14.10 (>C=CH—); 3.55, 3.70 (—CHO); 5.81 (>C=O); 6.15 μ, weak, (>C=C<).

N.m.r.: $\nu_{max}^{CCl_4}$ 0.36, doublet, J = 2.5 c.p.s. (1 —CHO); 3.96, triplet, J = 1.8 c.p.s. (2 >C=CH—); 6.83, poorly defined sextet (2 ⋗C—H, bridgehead); 7.88, broad singlet (1 >CH—CHO); 8.0–9.2 τ, multiplet (2 >CHH, 2 >CHH).

This material was found to be very unstable. Upon even brief exposure to air it was rapidly oxidized to the corresponding carboxylic acid **6b**. The rate of this oxidation could be conveniently followed by n.m.r. Because of its instability, we were unable to obtain a good analysis of this material.

The 2,4-dinitrophenylhydrazone, prepared in the usual manner[37] and recrystallized from ethanol, melted at 126–130°.

Anal. Calcd. for $C_{14}H_{14}O_4N_4$: C, 55.63; H, 4.67; N, 18.54. Found: C, 55.42; H, 4.68; N, 18.54.

B. By Rearrangement of the Epoxide 3a on Alumina.—A 300-mg. sample of the epoxide **3a** was dissolved in 5 ml. of pentane and chromatographed on a 1 × 15 cm. column packed with 12

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(36) Ref. 2, Plate IV.

(37) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th Ed., John Wiley and Sons, New York, N. Y., 1956, p. 219.

g. of Merck acid-washed alumina. The column was eluted with 30 ml. of pentane followed by 10% ether in pentane. Ten-milliliter fractions were collected. All of the nonpolymeric material eluted in fractions 5 through 10. An infrared analysis of fraction 5 indicated the presence of some unrearranged epoxide. Fractions 6–10 were combined and concentrated by distillation of most of the solvent through a 10-cm. Vigreux column at atmospheric pressure. The remainder of the material, when short-path distilled at ~90° (7 mm.) in a semimicro still, yielded 53 mg. (18%) of a material whose infrared spectrum was identical with the aldehyde **4b** collected from the gas chromatograph.

C. By Rearrangement with Lewis Acids.—Small samples of the epoxide **3a**, collected from the silicone rubber column and containing about 10% of the aldehyde **4b** as a contaminant, were treated with ethereal solutions of boron trifluorode etherate and of aluminum trichloride at room temperature. After the solutions had been allowed to stand for about 15 min. they were washed with aqueous base and analyzed by gas chromatography on the silicone rubber column at 80°. Neither of the reaction mixtures showed any epoxide; each showed small amounts of the aldehyde **4b** together with a large amount of very high boiling material, probably polymer, which was not identified. No isomeric aldehyde was detected.

Bicyclo[2.2.1]hept-2-ene-*syn*-7-carboxylic Acid (6b).—A 100-mg. sample of the aldehyde (**4b**), collected from the silicone oil column at 110°, was dissolved in 1.5 ml. of methanol. Water (1 ml.) and of silver nitrate (360 mg.) were added. The mixture was stirred to dissolve the silver nitrate, and 200 mg. of sodium hydroxide was added. Stirring was continued at room temperature for 2 hr. The precipitated silver and silver oxide were removed by filtration and washed with water. The combined filtrate and washings was saturated with sodium chloride, and the still basic solution was extracted with ether to remove any unchanged aldehyde. The solution was acidified and extracted with ether in a small continuous extractor for 24 hr. The ethereal extract was dried over anhydrous sodium sulfate, the solvent was removed by distillation through a 10-cm. Vigreux column, and the residue was purified by sublimation at 80° (5 mm.) to yield 90 mg. (80%) of a white crystalline acid, m.p. 94–100°.

Anal. Calcd. for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: C, 69.32; H, 7.20.

Infrared[15a]: λ_{max}^{KBr} 3.37 broad (O—H); 5.70 (—COOH, monomeric); 5.86 (—COOH, dimeric); 6.05 (>C=C<); 14.30 μ (>C=C*H*—).

The methyl ester (15b) was prepared by treating a small sample of the acid **6b** with an ethereal solution of diazomethane. When analyzed by gas chromatography on the Carbowax column at 170°, conditions which will separate and resolve the methyl esters of the *syn*- and *anti*-bicyclo[2.2.1]hept-2-ene-7-carboxylic acids, only one ester was found. The infrared spectrum was determined on a sample of this ester **15b** collected from the Carbowax column.

Infrared[15a]: $\lambda_{max}^{CCl_4}$ 3.26, shoulder, 14.17, broad, (>C=C*H*—); 5.76 (—C*O*—O—); 6.17 μ, very weak (>C=C<).

Bicyclo[2.2.1]heptane-7-carboxylic Acid (8).—A small sample of the unsaturated acid **6b** was hydrogenated at atmospheric pressure in 95% ethanol using 5% palladium on charcoal as catalyst. The catalyst was removed by filtration, the solvent was distilled through a 10-cm. Vigreux column, and the residual acid was purified by sublimation at 85° (5 mm.) to yield a new acid, m.p. 72–75° (lit.[18] m.p. 77.5–78.5°).

Infrared[15a]: $\lambda_{max}^{CCl_4}$ 3.38 μ, broad (O–H); 5.71 μ (-COOH, monomeric); 5.87 μ (-COOH, dimeric). This spectrum showed no evidence of a double bond and was in good agreement with the infrared spectrum (KBr) reported by Kwart and Kaplan for bicyclo[2.2.1]heptane-7-carboxylic acid.[18]

Bicyclo[2.2.1]hept-2-ene-*syn*-7-methanol (7b). A. From Bicyclo[2.2.1]hept-2-en-*syn*-7-carboxaldehyde (4b).—To a stirred slurry of 100 mg. of lithium aluminum hydride in 3 ml. of anhydrous ether was added 240 mg. of aldehyde **4b** in 5 ml. of anhydrous ether. The reaction mixture was stirred at reflux for 2 hr., cooled, and decomposed by the addition of water and 15% aqueous sodium hydroxide. The precipitated salts were removed by filtration and washed with ether. The ethereal solution was concentrated to about 0.5 ml. by distillation of the solvent through a 10-cm. Vigreux column. A gas chromatographic analysis of this concentrate on the Ucon column at 140° showed the presence of only one compound whose retention time was different from that of the starting material **4b** or the tertiary alcohol **5a**. This product was collected from the Ucon column, yield 130 mg. (53%).

Anal. Calcd. for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.46; H, 9.90.

Infrared[15a]: $\lambda_{max}^{CCl_4}$ 2.75, 3.00 (O–H); 3.27, 14.05, broad (>C=C*H*—); 6.16 (>C=C<); 9.78 μ, broad (–CH$_2$–OH). This spectrum was identical with that of the alcohol formed by esterification and lithium aluminum hydride reduction of the higher-melting of Sauers' bicyclo[2.2.1]hept-2-ene-7-carboxylic acids (**6b**).[21]

N.m.r.: $\nu_{max}^{CCl_4}$ 4.15, poorly defined assymmetric quartet (2 >C=C*H*—); 6.3–6.7, broad, concentration dependent (1 —CH$_2$O*H*); 6.62, doublet, J = 7 c.p.s. (2 —C*H*$_2$—OH); 7.29, poorly defined doublet, J = 2 c.p.s. (2 ⋟C$_1$—*H*, bridgehead); 8.1–9.2 τ, complex multiplet (1 ⋟C$_7$—*H*, 2 >C*H*H, 2 >CH*H*).

B. From Spiro[bicyclo[2.2.1]hept-2-en-*anti*-7,2′-oxacyclopropane] (3a).[17]—To a cold slurry of 15 mg. of lithium aluminum hydride in 2 ml. of anhydrous ether was added a cold solution of 32 mg. of aluminum trichloride in 2 ml. of anhydrous ether. The mixture was cooled to −10° in an ice–salt bath, and a solution of 100 mg. of epoxide **3a** in 3 ml. of anhydrous ether was added dropwise to the stirred slurry. The reaction mixture was stirred for 30 min. in the ice–salt bath and then at room temperature for an additional 30 min. A 15% solution of sodium hydroxide was added, the precipitated salts were removed by filtration, and the filtrate was dried over anhydrous magnesium sulfate.

A gas chromatographic analysis of the ethereal solution on the silicone oil column showed the presence of bicyclo[2.2.1]hept-2-ene-*syn*-7-methanol (**7b**) (90%), 7-methylbicyclo[2.2.1]hept-2-en-*anti*-7-ol (**5a**) (4%), and 6% of two unidentified components. No bicyclo[2.2.1]hept-2-ene-*anti*-7-methanol (**7a**) could be detected.

The ethereal solution was concentrated to about 1 ml. by distillation of the solvent through a 10-cm. Vigreux column, and the primary alcohol **7b** was isolated by collection from the silicone oil column. The yield of pure material isolated in this manner was 41 mg. (40%).

The infrared spectrum of this material was identical to that of the alcohol prepared by the reduction of the aldehyde **4b**, *i.e.*, **7b**.

The formation of the tertiary alcohol **5a** could be completely suppressed by using twice as much aluminum trichloride. However, under these conditions the proportion of unidentified material was increased to about 20%, and the proportion of the primary alcohol **7b** was reduced to 80% of the product mixture.

C. From the Higher-Melting of Sauers' Acids (6b).—A solution of a small amount of the higher-melting of the two bicyclo[2.2.1]hept-2-ene-7-carboxylic acids,[21] (m.p. 94–100°) in ether was treated with a stoichiometric amount of ethereal diazomethane. The solution was dried over anhydrous magnesium sulfate and treated with an excess of lithium aluminum hydride in 2 ml. of anhydrous ether. The mixture was heated under reflux for 1 hr., and enough 15% sodium hydroxide was added to decompose the complex and the excess hydride. The ethereal solution was decanted from the precipitated salts, dried over anhydrous magnesium sulfate, and analyzed by gas chromatography on the silicone oil column. Only one compound was present, the retention time and infrared spectrum of which were identical to those of the alcohol **7b** prepared by reduction of the aldehyde **4b**.

Bicyclo[2.2.1]hept-2-ene-*anti*-7-methanol (7a).—A solution of 25 mg. of bicyclo[2.2.1]hept-2-ene-*anti*-7-carboxylic acid[21] (m.p. 70.5–71.5°) in 0.5 ml. of ether was treated with a stoichiometric amount of ethereal diazomethane. The solution was dried over anhydrous magnesium sulfate and added dropwise to a stirred slurry of 30 mg. of lithium aluminum hydride in 1 ml. of ether. The mixture was heated under reflux for 1 hr. A 15% solution of sodium hydroxide was added, the precipitated salts were removed by filtration, and the filtrate was concentrated to about 0.2 ml. through a 2-in. Vigreux column. Gas chromatographic analysis of the product on the silicone oil and on the Ucon column showed the presence of only one component. The product was collected from the silicone oil column; yield, 13 mg. (60%).

Anal. Calcd. for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.57; H, 9.83.

Infrared[15a]: λ_{max}^{film} 3.00 (O—H); 3.29, 14.30, broad (>C=C*H*—); 6.22 (>C=C<); 9.79 μ, broad (CH$_2$—OH).

N.m.r.: $\nu_{max}^{CCl_4}$ 3.94, triplet, J = 2 c.p.s. (2 >C=C*H*—); 6.77, doublet, J = 7 c.p.s. (2 —C*H*$_2$OH); ~7, singlet, concentration dependent (1 —CH$_2$O*H*); 7.32, poorly defined quartet

(2 ⩾C_1—H, bridgehead); 8.0–9.3 τ, complex multiplet (1 ⩾C_7—H, 2 >C*H*H, 2 >CH*H*).

α,α-Dimethylbicyclo[2.2.1]hept-2-ene-*syn*-7-methanol (17b).—A solution of 80 mg. of bicyclo[2.2.1]hept-2-ene-*syn*-7-carboxylic acid (**6b**) in 2 ml. of ether was treated with a stoichiometric amount of ethereal diazomethane. The solution was dried over anhydrous magnesium sulfate and then was added dropwise to 5 ml. of an ethereal solution of methylmagnesium iodide, prepared from 110 mg. of magnesium turnings and 700 mg. of methyl iodide. The reaction mixture was heated under reflux for 3 hr., stirred at room temperature overnight, and cooled in an ice bath. Ten milliliters of water and 500 mg. of sodium sulfate were carefully added, the mixture was shaken in a separatory funnel, the two layers were separated, and the aqueous layer was washed with 10 ml. of ether. The combined ethereal solution was washed with water, dried over anhydrous magnesium sulfate, and concentrated to about 1 ml. by distillation of the solvent through a 10-cm. Vigreux column.

A gas chromatographic analysis of this concentrate on the silicone oil column at 140° showed the presence of the tertiary alcohol **17b** (95%) and some relatively volatile compounds (5%) which were probably formed by dehydration of the tertiary alcohol during the work-up and/or analysis. The alcohol **17b** was isolated by collection from the silicone oil column at 140° and was purified for analysis by distillation in a semimicro short-path still heated in an oil bath at 90–95° under 10 mm. pressure. The yield was 46 mg. (52%) of collected material.

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.94; H, 10.31.

Infrared[15a]: $\lambda_{max}^{CCl_4}$ 2.79 (O—H); 3.27, 14.02 (>C═C*H*—); 7.26, 7.36, 8.25, 8.35 (>C(CH_3)$_2$); 6.12 (>C═C<); 8.81 μ (⩾C—OH). $\nu_{max}^{CCl_4}$ 3617 cm.$^{-1}$, weak (free O—H); 3577 cm.$^{-1}$, strong (π-electron, hydrogen-bonded O—H).[19]

N.m.r.: $\nu_{max}^{CCl_4}$ 4.03, triplet, J = 2 c.p.s. (2 >C═C*H*); 7.10, poorly defined doublet (2 ⩾C_1—*H*, bridgehead); 8.29, singlet (1 O—*H*) superimposed on a multiplet at 8.0–8.5, (1 ⩾C_7—H, 2 >C*H*H); 8.9–9.3, multiplet (2 >CH*H*) superimposed on a singlet at 8.97 τ (6 —CH_3).

α,α-Dimethylbicyclo[2.2.1]hept-2-ene-*anti*-7-methanol (17a).—This alcohol was prepared in the same manner as the *syn* isomer **17b** starting with 150 mg. of a mixture of bicyclo[2.2.1]hept-2-ene-7-*syn*- and 7-*anti*-carboxylic acids (35% *syn*, 65% *anti*).[21] The resulting mixture of tertiary alcohols was separated by gas chromatography on the Ucon column at 135°. The yield was 24 mg. (14%) of the *syn* alcohol (identical in all respects with **17b** as described) and 58 mg. (35%) of the *anti* alcohol **17a**. An analytical sample of **17a** was obtained by distillation of the collected material in a semimicro short-path still heated in an oil bath at 90–95° under 10-mm. pressure.

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.76; H, 10.61.

Infrared[15a]: $\lambda_{max}^{CCl_4}$ 2.76, 2.85 (O—H); 3.27, 14.23 (>C═C*H*—); 6.14 (>C═C<); 7.35 (C—CH_3); 8.10, 8.23 (C-(CH_3)$_2$); 8.72 μ (⩾C—OH?). $\nu_{max}^{CCl_4}$ 3618–3629 cm.$^{-1}$, broad (nonbonded O—H).[19]

N.m.r.: $\nu_{max}^{CCl_4}$ 3.89, triplet, J = 2 c.p.s. (2 >C═C*H*—); 7.23, poorly defined doublet (2 ⩾C_1—*H*, bridgehead); 8.85 τ, singlet (—CH_3). The remainder of the spectrum was too complex to make definite assignments, but the total integrated peak area between 7.8 and 9.3 τ corresponded to twelve hydrogens.

2-Chloromercuri-9-oxatricyclo[4.3.0.0^{3,7}]nonane (16).—To a solution of 22 mg. of bicyclo[2.2.1]hept-2-ene-*syn*-7-methanol (**7b**) in 0.2 ml. of methanol was added 53 mg. of anhydrous mercuric acetate.[25] After the solution had stood at room temperature for 90 min., a test for the presence of mercuric ion, using 15% sodium hydroxide and a small sample of the solution, was negative. A solution of 20 mg. of sodium chloride in 0.5 ml. of 50% methanol was added to the reaction mixture. A white precipitate formed immediately. The precipitate was filtered and dried to yield 41 mg. (64%) of product which melted with decomposition from 176–180°. After two recrystallizations from benzene the melting point was unchanged.

Anal. Calcd. for $C_8H_{11}OHgCl$: C, 26.75; H, 3.09; O, 4.45; Hg, 55.69. Found: C, 27.61; H, 3.36; O, 4.63; Hg, 55.05.

The infrared spectrum, determined in a potassium bromide pellet, was too complex to analyze properly (thirty strong peaks between 6.75 and 13.0 μ). However, it did not show any evidence for a hydroxyl, a methoxyl, or a double bond.

Gas Chromatographic Analysis.—The following columns were used for the gas chromatographic work described herein: a 0.25 in. × 8 ft. coiled stainless steel tube packed with 25% Dow-Corning silicone oil 200 on 60–80-mesh Chromasorb P; a 0.25 in. × 8 ft coiled copper tube packed with 20% General Electric SE 30 silicone rubber on 80–100-mesh acid-washed firebrick; a 0.25 in. × 6 ft. double hairpin copper tube packed with 15% Carbowax 20M on 80–100-mesh neutral firebrick; a 0.25 in. × 7 ft. coiled copper tube packed with 20% Ucon, water insoluble, on 60–80-mesh Chromasorb P. Helium was used as a carrier gas at flow rates ranging from 50–100 ml./minute.

Nuclear Magnetic Resonance Spectra.—During the course of this work we have examined the n.m.r. spectra of fifteen symmetric, 7-substituted bicyclo[2.2.1]hept-2-enes, nine of which are reported here. A characteristic feature in each of these spectra is the resonance of the two vinyl hydrogens, H-2 and H-3, whose gross appearance is that of a triplet centered at 3.86 to 4.13 τ (but see ref. 13) and split by 1.8 to 2.4 c.p.s. It has also been reported that the vinyl hydrogen resonance of bicyclo-[2.2.1]hept-2-ene appears as "an unsymmetrical triplet" centered at 4.06 τ.[38] The gross appearance of the vinyl hydrogen resonance as a triplet in these spectra instead of as a more complex A_2X_2 pattern,[39] can probably be attributed to the fact that the coupling between a vinyl hydrogen and the nearest bridgehead hydrogen is of the same approximate magnitude as the coupling between the two vinyl hydrogens themselves, *i.e.*, $J_{12} \sim J_{23}$,[40] The values which we report must therefore approximate the average of the vinyl bridgehead and the vinyl–vinyl couplings, *i.e.*, $(J_{12} + J_{23})/2$, and are probably accurate to about 0.5 to 1.0 c.p.s. The presence of further fine splitting in the vinyl resonance region of most of our spectra is evidence that the longer range couplings which have been reported in the case of bicyclo-[2.2.1]heptadiene,[40,41a] 5-substituted bicyclo[2.2.1]hept-2-enes,[41b] and 5-substituted 7-isopropylidenebicyclo[2.2.1]hept-2-enes[41c] are also present in the symmetric, 7-substituted bicyclo[2.2.1]-heptenes. We have observed that this further splitting of the vinyl hydrogen resonance in each of these compounds is more pronounced in the *syn* isomers and can thus serve as an indication of molecular configuration.

We note that most of the "average" vinyl couplings, *i.e.* $(J_{12} + J_{23})/2$, which we find are smaller than those reported elsewhere, *e.g.*, J_{12} = 2.2–3.3 c.p.s.,[40,41a] J_{23} = 3.45–6.0 c.p.s.[40,41a,c] We suspect that this may be due in part to the fact that our spectra were usually determined from solutions which were quite dilute and which had not been degassed.[34]

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