57 mg (0.35 mmol) of **5** at 25°. After 12 hr the mixture was acidified with 5% sulfuric acid and extracted with three 20-ml portions of carbon tetrachloride. The organic extract was dried ($MgSO_4$) and concentrated, and the residue was sublimed to give 20 mg (32%) of **7**, mp 112–113°. The two samples of **7** were shown to be identical by comparison of ir and nmr spectra as well as by the mixture melting point, 112–113°.

6-Methylbicyclo[4.2.0]oct-7-en-2-one (4).—A solution of 10.25 g (0.0925 mol) of 3-methylcyclohex-2-enone (Aldrich Chemical Co.) and 30 ml of a mixture of *cis*- and *trans*-dichloroethylenes in 1 l. of pentane was irradiated (Corex) for 5 hr. Progress of the reaction was measured by glpc (3% Carbowax 20 M, 8 ft × 0.125 in., 130°, 12 ml/min He). Removal of the solvent and excess dichloroethylene by distillation left a brown oil which was dissolved in 500 ml of benzene. This solution, together with 20 ml of ethylene glycol and a crystal of *p*-toluenesulfonic acid, was refluxed with the separation of water. After 10 hr, 100 ml of 10% sodium bicarbonate was added to the cooled reaction mixture. The organic layer was separated, extracted with water, and concentrated, and the residue was dissolved in 300 ml of anhydrous ether. The ethereal solution was then introduced into a 3-l. flask containing 2 l. of freshly distilled anhydrous ammonia. Small pieces of sodium metal were added until the solution remained dark blue. After the blue solution had stirred for an additional 2 hr, ammonium chloride was added to destroy excess sodium and the ammonia was allowed to evaporate. Water was added to the residue and the resulting solution was extracted with three 300-ml portions of ether. The ethereal extract was dried ($MgSO_4$), concentrated, and distilled to give 13.65 g (82.1%) of 6-methylbicyclo[4.2.0]oct-7-en-2-one ethylene ketal, bp 60–65° (4.0 Torr). A 13.65-g portion of the above ketal was dissolved in 200 ml of ether and stirred at room temperature along with 50 ml of 5% aqueous sulfuric acid. After 12 hr, the ethereal phase was separated, extracted with dilute sodium bicarbonate solution, dried ($MgSO_4$), concentrated, and distilled to give 8.53 g (82.6%) of **4**: bp 70–74° (5.0 Torr); ir (CCl_4) 3120, 3030 (HC=CH), and 1700 cm^{-1} (C=O); nmr (CCl_4) δ 6.00 (q, 2, J_{AB} = 4.0 Hz, Δ_{AB} = 8.0 Hz), 2.85 (s, 1), 2.4–1.5 (m, 6), and 1.30 ppm (m, 3).

The 2,4-dinitrophenylhydrazone was recrystallized from methanol–water, mp 124–125°.

Anal. Calcd for $C_{15}H_{16}N_4O_4$ (mol wt 316.30): C, 56.96; H, 5.10; N, 17.71. Found: C, 56.89; H, 4.97; N, 17.60.

1-Methylbicyclo[3.2.1]oct-6-en-8-one (21).—A solution of 1.50 g (0.0111 mol) of **4** and 50 mg of *p*-toluenesulfonic acid in 200 ml of benzene was refluxed for 5 min. The cooled reaction mixture was washed with 5% sodium bicarbonate solution, concentrated, and distilled to give 0.0472 g (3.14%): bp 90° (bath) (0.005 Torr); ir (CCl_4) 3050 (HC=CH), 1760, 1700 (C=O), and 1650 cm^{-1} (C=C); nmr (CCl_4) δ 5.95 (t, 2, J = 3.0 Hz), 2.68 (m, 1), 2.0–1.4 (m, 6), and 1.00 ppm (s, 3). The low yield of isolated **21** reflects the fact that this substance is very labile and it undergoes resinification upon distillation. No products other than **21** could be detected in the crude reaction mixture.

The 2,4-dinitrophenylhydrazone was recrystallized from methanol–water, mp 154–155°.

Anal. Calcd for $C_{15}H_{16}N_4O_4$ (mol wt 316.30): C, 56.96; H, 5.10; N, 17.71. Found: C, 57.17; H, 5.00; 6, 17.89.

Registry No.—**1**, 22241-68-5; 2,4-dinitrophenylhydrazone of **1**, 22241-69-6; **2**, 22241-70-9; *p*-toluenesulfonylhydrazone of **2**, 22241-71-0; **3**, 21604-44-4; *p*-toluenesulfonylhydrazone of **3**, 22297-90-1; **4**, 22241-72-1; 2,4-dinitrophenylhydrazone of **4**, 22297-91-2; **5**, 15674-27-8; **7**, 22241-74-3; **8**, 22241-75-4; **13**, 22241-76-5; 2,4-dinitrophenylhydrazone of **13**, 22241-77-6; **21**, 22241-78-7; 2,4-dinitrophenylhydrazone of **21**, 22241-79-8.

Acknowledgment.—It is a pleasure to thank Professor James L. Marshall, North Texas State University, for his helpful suggestions.

Rearrangement–Addition Reactions of β,γ-Unsaturated Ketones in Aqueous Acid[1]

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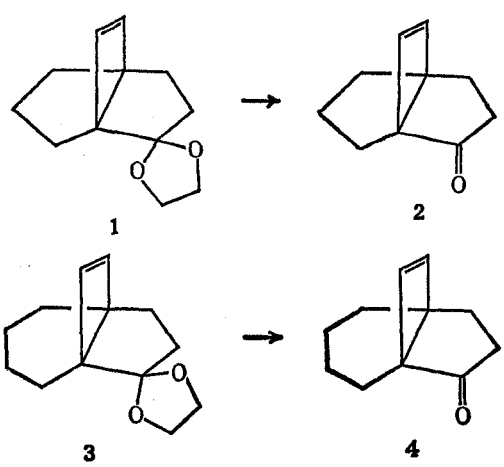
The rearrangement–addition reactions of a series of bicyclo[3.2.0]hept-6-en-2-ones are described. Thus 6,7-dimethyl- and 1,7-dimethylbicyclo[3.2.0]hept-6-en-2-one (**5** and **8**) yield *endo*-3-hydroxy-1-methyl-*anti*-7-methylbicyclo[2.2.1]heptan-2-one (**6**) and *endo*-3-hydroxy-1,3-dimethylbicyclo[2.2.1]heptan-2-one (**9**), respectively. However, bicyclo[2.2.1]hept-6-en-2-one (**19**) yields *anti*-7-chloro-1-hydroxybicyclo[2.2.1]hept-2-ene (**20**). These rearrangement–additions are rationalized in terms of Scheme I. Ketone **20** yields **19** when treated with potassium *t*-butoxide.

In this paper we report some novel rearrangement–addition reactions of certain β,γ-unsaturated ketones in aqueous acid. As will be seen, these rearrangement–additions proceed cleanly to provide high yields of otherwise difficultly available products, thereby providing a new and useful synthetic method.

The synthesis of the tricyclic β,γ-unsaturated ketone **2**, in which the final step is removal of the ketal function of **1** in aqueous acid, has been described.[2] Hydrolysis of the ketal **3** under identical conditions, 6 *M* aqueous hydrochloric acid–ether, provided not the desired ketone **4**, but a crystalline tertiary alcohol. The latter was presumed to arise from initially formed **4** by a subsequent rearrangement. We have, therefore, examined the action of 6 *M* hydrochloric acid on a series of β,γ-unsaturated ketones, and the results of this investigation are reported here.

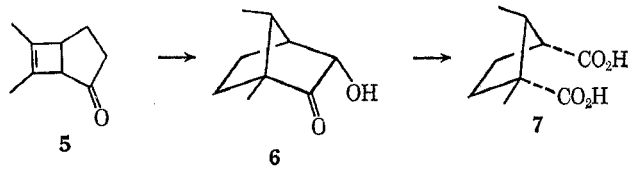


1 **2** **3** **4**

(1) We thank the National Science Foundation for generous support of this work.

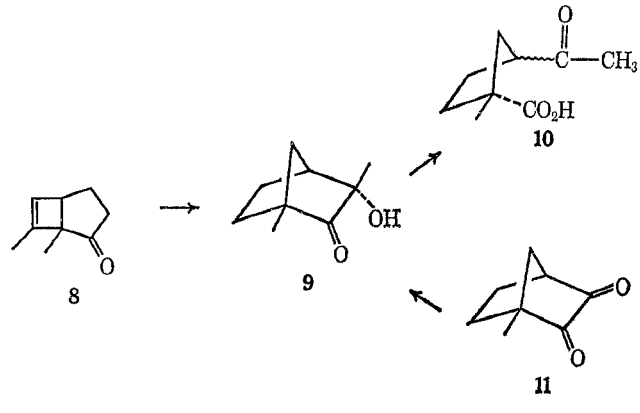
(2) (a) R. L. Cargill, J. R. Damewood, and M. M. Cooper, *J. Amer. Chem. Soc.*, **88**, 1330 (1966); (b) R. L. Cargill, *et al.*, in preparation; (c) see also H. O. House and T. H. Cronin, *J. Org. Chem.*, **30**, 1061 (1965).

The reaction of ketone **5**[3] in 6 *M* hydrochloric[4a] acid yielded a single liquid hydroxy ketone. The new material ($C_9H_{14}O_2$) exhibits spectral characteristics[4b] typical of a cyclopentanone, a secondary alcohol, one methyl on quarternary carbon, and one methyl on tertiary carbon. The new hydroxy ketone was shown to be **6** by oxidation with potassium permanganate to santenic acid (**7**).[5] Coupling of the carbinol proton with the adjacent bridgehead hydrogen (J = 4.5 Hz) shows the hydroxyl to be *endo*.[6,7]



5 6 7

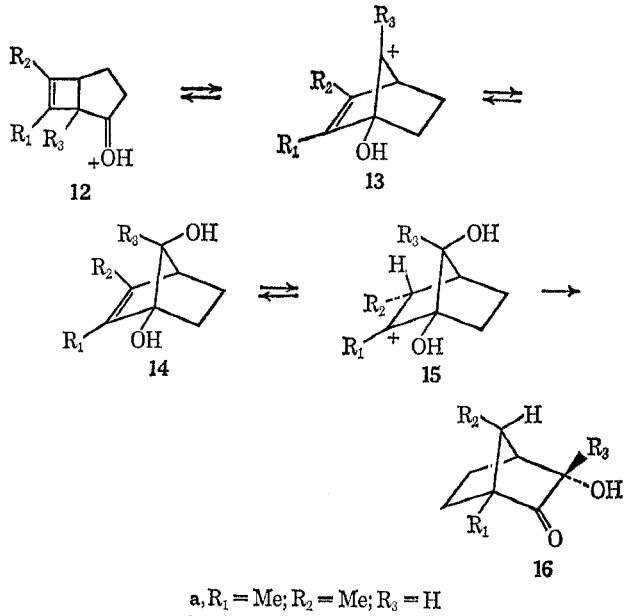
Similar treatment of **8** provided a single crystalline hydroxy ketone **9**, the structure of which was established as follows. The spectral data[4b] clearly show the presence of a tertiary alcohol and two methyls on completely substituted carbons. Oxidation with aqueous potassium permanganate gave an epimeric mixture of the keto acids **10**. Reaction of the diketone **11** with methylmagnesium iodide yields **9** as the major product. The formation of both epimers of a keto acid demonstrates that the hydroxyl is attached at C-3 and not at C-2 in **9**, and the formation of **9** from **11** indicates that the hydroxyl group is again *endo*.



8 9 10 11

The conversions, **5** → **6** and **8** → **9**, are rationalized in terms of Scheme I. Net migration of the etheno bridge in the protonated ketone **12** leads to ion **13**, which is a 7-norbornenyl cation and is presumably well stabilized.[8] Rapid hydration of ion **13** (from the *anti* side) is followed by slow protonation of the olefinic bond of **14** from the *exo* side and a Wagner–Meerwein shift to produce the observed hydroxy ketones **16** (**16a** ≡ **6**, **16b** ≡ **9**). This sequence accounts for the gross

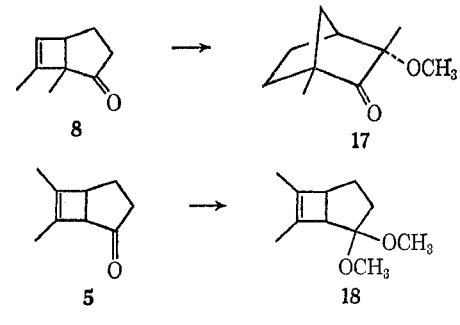
SCHEME I



a, R_1 = Me; R_2 = Me; R_3 = H
b, R_1 = Me; R_2 = H; R_3 = Me
c, R_1 = R_2 = R_3 = H

structure of the observed ketones and also for the observed stereospecificity of the reactions.

In an effort to demonstrate the role of solvent in the rearrangement–hydration reaction, a mixture of **5** and **8** was stirred in 6 *M* methanolic hydrochloric acid. Two new products, a methoxy ketone **17** and a ketal **18**, the structures of which were assigned on the basis of spectral data,[4b] were obtained. The formation of **17** from **8** is in agreement with the suggested mechanism depicted in Scheme I; the formation of **18** merely indicates that ketalization of **5** is fast and that the ketal occupies a relatively deep energy minimum.



8 17 5 18

It is of interest to note that rearrangement–addition of ketones **5** and **8** is faster than is equilibration of the two; however, when **5** and **8** are heated separately in benzene containing *p*-toluenesulfonic acid, the same equilibrium mixture containing 95% **5** and 5% **8** was obtained.[9,10]

(3) (a) P. E. Eaton, *Tetrahedron Lett.*, 4395 (1964); (b) R. Criegee and H. Furrer, *Chem. Ber.*, **97**, 2949 (1964).

(4) (a) All acid-catalyzed reactions described in this paper were carried out in a two phase, ether–aqueous hydrochloric acid system; see Experimental Section for details. (b) See Experimental Section for spectral data.

(5) We are grateful to Professor S. Beckmann for authentic sample of santenic acid (**7**): S. Beckmann and R. Schafer, *Justus Liebigs Ann. Chem.*, **585**, 154 (1954).

(6) By way of comparison, *endo*-2-hydroxy-3,3-dimethylbicyclo[2.2.1]-heptane exhibits a doublet at 3.53 ppm (J = 4.5 Hz) for the carbinol hydrogen.

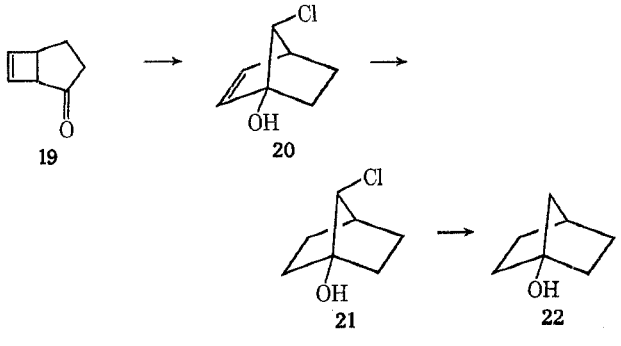
(7) F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961).

(8) See P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, Inc., New York, N. Y., 1965, for leading references.

(9) G. Büchi and E. M. Burgess, *J. Amer. Chem. Soc.*, **82**, 4333 (1960).

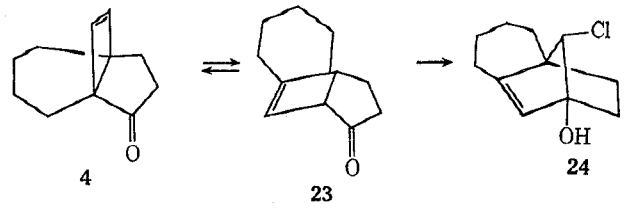
(10) For other examples of acid-catalyzed isomerizations and additions to β,γ-unsaturated ketones, see (a) R. Caple, H. W. Tan, and F. M. Hsu, *J. Org. Chem.*, **33**, 1542 (1968); (b) W. F. Erman, *J. Amer. Chem. Soc.*, **89**, 3828 (1967); (c) W. F. Erman, *ibid.*, **91**, 799 (1969); (d) J. J. Beereboom, *J. Org. Chem.*, **30**, 4230 (1965); *J. Amer. Chem. Soc.*, **85**, 3525 (1963); (e) R. B. Bates, M. J. Onore, S. K. Paknikar, C. Steelink, and E. P. Blanchard, *Chem. Commun.*, 1037, (1967); (f) R. L. Cargill and J. W. Crawford, *Tetrahedron Lett.*, 169 (1967); (g) R. L. Cargill, M. E. Beckham, A. E. Siebert, and J. Dorn, *J. Org. Chem.*, **30**, 3647 (1965); (h) R. L. Cargill, M. E. Beckham, and J. R. Damewood, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, No. P179.

When ketone **19** was stirred in a mixture of ether and 6 *M* hydrochloric acid, it was very slowly converted into a new unsaturated chloro alcohol, **20**. The presence of a single chlorine atom was established from elemental analysis and by mass spectrometry. The two vinyl protons give a three-line multiplet centered at 6.08 ppm,[11] and the C-7 proton gives a broadened singlet[12] at 3.54 ppm. That the alcohol is tertiary was established by determination of the nmr spectrum in dimethyl sulfoxide, whereupon the hydroxyl proton signal appears as a sharp singlet (5.68 ppm). Catalytic hydrogenation of **20** gave the saturated **21**, which upon dechlorination (sodium–liquid ammonia) gave the known alcohol **22**.[13] The stereochemistry of the chlorine is inferred from the solvolytic half-life of **20**, 180 min in 50% aqueous ethanol (55.53°), which is only a factor of 60 greater than that of *anti*-7-chloronorbornene.[14]

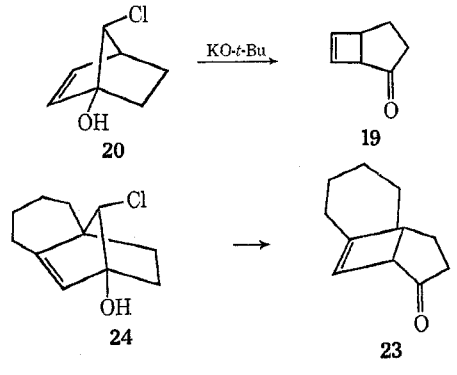


That ketone **19** yields the chloro alcohol **20** rather than the expected hydroxy ketone may be explained in terms of Scheme I as follows. Conversion of **19** (**12c**) into the diol **14c** is rapid and reversible *via* ion **13c**. Protonation of the disubstituted double bond in **14c** is very slow compared with that in **14a**, or **b**, which gives in each case tertiary carbonium ion **15a**, or **b**. The slow rate of protonation of **14c** allows ion **13c** to be captured by chloride ion. The resulting **20** is effectively inert under the reaction conditions.

We now return to the experiment which led us into the present study. Removal of the ketal function from **3** with 6 *M* hydrochloric acid gave in low yield a crystalline tertiary alcohol. Subsequent experiments showed, however, that hydrolysis of **3** with 3 *M* hydrochloric acid provides **4** in good yield. When **4** was subjected to the rearrangement–hydration conditions described above, a new crystalline chloro alcohol was obtained. The new chloro alcohol is assigned structure **24** on the basis of spectral data,[4b] which show the presence of a single vinyl hydrogen, a secondary chlorine, and a tertiary alcohol. The stereochemistry of the chlorine follows from the solvolytic half-life of 2.38 min (50% aqueous ethanol, 55.53°) which is only slightly different from that of *anti*-7-chloronorbornene under similar conditions.[14] Furthermore, ketone **23**, which may be obtained from **4** by photoisomerization,[15] also yields **24** when subjected to the rearrangement–addition conditions.[16]



In addition to the synthetically useful rearrangement–additions described above, we have found that the chloro alcohols **20** and **24** undergo base-induced rearrangement–elimination to provide in each case the ketonic precursor, **19** or **23**, respectively, in high yield. The use of this transformation allows the synthesis, for example, of **23** in a pure state. Irradiation of **4** leads to a photostationary mixture of **4** and **23** (30:70).[15]



Experimental Section[17]

Acid-Catalyzed Interconversion of 6,7-Dimethylbicyclo[3.2.0]-hept-6-en-2-one (5) and 1,7-Dimethylbicyclo[3.2.0]hept-6-en-2-one (8). A.—A rapidly stirred solution containing 0.091 g (0.00067 mol) of **5** and 0.010 g of *p*-toluenesulfonic acid in 5 ml of dry benzene was refluxed for 10 hr. Gas–liquid partition chromatography (3% DEGS, 8 ft × 0.125 in., 100°, 25 ml/min He) indicated that the reaction mixture consisted of 95% **5** and 5% **8**. Continued refluxing led to decomposition of the ketones.

B.—A solution containing 0.078 g (0.00057 mol) of **8** and 0.009 g of *p*-toluenesulfonic acid in 5 ml of dry benzene was refluxed for 10 hr. Analysis by glpc indicated that the reaction mixture consisted of 5% **8** and 95% **5**.

Acid-Catalyzed Rearrangement of 1,7-Dimethylbicyclo[3.2.0]-hept-6-en-2-one (8) in Hydrochloric Acid.—A solution containing 0.060 g (0.00044 mol) of **8** in 10 ml of ether was stirred at room temperature with 3 ml of 6 *N* hydrochloric acid for 10 hr. The reaction mixture was poured into 10 ml of water and extracted with ether. The extracts were combined, dried ($MgSO_4$), and concentrated to dryness by distillation (steam bath), giving 0.066

(11) The nmr spectrum of 1-hydroxybicyclo[2.2.1]hept-2-ene exhibits a similar multiplet at 5.87 ppm.

(12) Failure to detect resolvable coupling in a similar case has been reported by S. Ho, T. Omoto, Y. Fujise, and K. Sakan, *Chem. Commun.*, 782 (1968).

(13) C. J. Norton, Ph.D. Thesis, Harvard University, Cambridge, Mass., 1955.

(14) W. G. Woods, R. A. Carboni, and J. D. Roberts, *J. Amer. Chem. Soc.*, **78**, 5653 (1956).

(15) D. M. Pond, Ph.D. Thesis, University of South Carolina, Columbia, S. C., 1968. A manuscript describing the photochemistry of a series of bicyclic and tricyclic β,γ-unsaturated ketones, including **4** and **23**, is in preparation. The characterization of **23** will be described there.

(16) The interconversion of **4** and **23** in the aqueous acid system used here and the absence of such interconversion in the case of **5** and **8**, merely indicates that the activation free energy for the **4** → **23** change is lower than that of the rearrangement–addition, whereas $\Delta G^{\pm}$ for **5** → **8** is greater than that for rearrangement–addition.

(17) All boiling points and melting points are uncorrected. Microanalyses were performed by Bernhardt Microanalytisches Laboratorium, Elbach über Engleskirken, Germany, or by Gailbraith Laboratories, Inc., Knoxville, Tenn. Infrared spectra were determined in carbon tetrachloride unless otherwise stated, using a Perkin–Elmer Model 337 or 257 grating spectrophotometer. All nmr spectra were determined in carbon tetrachloride containing 5% tetramethylsilane as an internal standard using a Varian A-60 nmr spectrometer. Analytical gas–liquid partition chromatograms were determined using a Varian Aerograph Model 1200 chromatograph and preparative glpc separations were conducted using a Varian Aerograph 90-P-3 chromatograph.

g of *endo*-3-hydroxy-1,3-dimethylbicyclo[2.2.1]heptan-2-one (**9**) as a solid residue. Preparative glpc (20% SE-52, 10 ft × 0.25 in., 150°, 100 ml/min He) gave a pure sample of **9**: mp 85–86°; ir (CCl_4) 3570, 3460 (OH), 1745 (C=O), and 1156 cm^{-1} (CO); nmr (CCl_4) δ 3.22 (s, 1, COH), 1.20 (s, 3, $COHCH_3$), 1.12 (s, 3, CCH_3), and 1.44–2.32 ppm (m, 7); nmr (DMSO)[18] 5.23 ppm (s, 1 COH); mass spectrum[19] (70 eV) *m/e* (rel intensity) 154 (1), 126 (17), 111 (4), 95 (1), 94 (2), 71 (100), 70 (1), and 57 (3).

Anal. Calcd for $C_9H_{14}O_2$ (mol wt 154.21): C, 70.10; H, 9.15. Found: C, 70.22; H, 9.10.

Acid-Catalyzed Rearrangement of 6,7-Dimethylbicyclo[3.2.0]-hept-6-en-2-one (5) in Hydrochloric Acid.—A solution of 0.511 g (0.00375 mol) of **5** in 15 ml of ether was stirred at room temperature with 10 ml of 6 *N* hydrochloric acid for 48 hr. The reaction mixture was poured into 100 ml of water and extracted with ether. The ether extracts were combined, washed with 5% sodium bicarbonate and water, dried ($MgSO_4$), and concentrated by distillation to give 0.521 g of a brown oil. Preparative glpc (20% SE-52, 10 ft × 0.25 in., 150°, 100 ml/min He) gave a pure sample of *endo*-3-hydroxy-1-methyl-*anti*-7-methylbicyclo[2.2.1]-heptan-2-one (**6**): ir (CCl_4) 3560, 3440 (OH), 1750 (C=O), and 1080 cm^{-1} (CO); nmr (CCl_4) δ 4.20 (br s, 1, CHOH), 3.86 (d, 1, J = 4.5 Hz, CHOH), 1.02 (s, 3, CCH_3), 0.97 (d, 3, J = 5.0 Hz, $CHCH_3$), and 1.30–2.50 ppm (m, 6); nmr (DMSO) δ 5.53 ppm (d, 1, J = 5.0 Hz, CHOH); mass spectrum (70 eV) *m/e* (rel intensity) 154 (39), 126 (21), 111 (21), 95 (47), 71 (57), 70 (100), and 57 (67).

Anal. Calcd for $C_9H_{14}O_2$ (mol wt 154.21): C, 70.10; H, 9.15. Found: C, 70.13; H, 9.11.

Acid-Catalyzed Rearrangement of 6,7-Dimethylbicyclo[3.2.0]-hept-6-en-2-one (5) and 1,7-Dimethylbicyclo[3.2.0]hept-6-en-2-one (8) in Hydrochloric Acid.—A solution containing 1.877 g (0.01378 mol) of a mixture of **5** and **8** (ratio 2:1) in 100 ml of ether was stirred at room temperature with 60 ml of 6 *N* hydrochloric acid for 40 hr. The reaction mixture was poured into 200 ml of water and extracted with ether. The extracts were combined, washed with 5% sodium bicarbonate and water, dried (Na_2SO_4), concentrated, and distilled to give 1.649 g (77.60%) of a mixture consisting of *ca.* 65% *endo*-3-hydroxy-1-methyl-*anti*-7-methylbicyclo[2.2.1]heptan-2-one (**6**) and *ca.* 35% *endo*-3-hydroxy-1,3-dimethylbicyclo[2.2.1]heptan-2-one (**9**), bp 65–70° (0.30 Torr). Pure samples of **6** and **9** were obtained by preparative glpc (20% SE-52, 10 ft × 0.25 in., 155°, 100 ml/min He).

1-Methylbicyclo[2.2.1]heptane-2,3-dione (11).—To a solution containing 2.51 g (0.0179 mol) of 1-methylbicyclo[2.2.1]heptan-2-one[20] in 20 ml of *o*-xylene was added at once 2.25 g (0.0203 mol) of selenium dioxide[21] and the resulting solution was refluxed for 17 hr. The reaction mixture was filtered and concentrated by distillation (steam bath) at reduced pressure (*ca.* 22 Torr) to give a dark yellow oil. Trituration with cold hexane gave a bright yellow oil which amounted to 0.916 g (33.2%). Preparative glpc (20% SE-30, 8 ft × 0.125 in., 130°, 120 ml/min He) and subsequent sublimation (bath temperature 54–55°) at reduced pressure (0.1 Torr) gave a pure sample of 1-methylbicyclo[2.2.1]-heptane-2,3-dione (**11**): mp 46.0–47.5°; uv max (95% C_2H_5OH) 266 nm (ε 80.7) and 312 (34.6); ir (CCl_4) 1770 and 1745 cm^{-1} (C=O); nmr (CCl_4) δ 2.88 (d, 1, J = 3.5 Hz, C-4 bridgehead proton), 1.27 (s, 3, CCH_3), and 1.78 ppm (m, 6).

Anal. Calcd for $C_8H_{10}O_2$ (mol wt 138.17): C, 69.54; H, 7.30. Found: C, 69.28; H, 7.58.

Addition of Methylmagnesium Iodide to 1-Methylbicyclo-[2.2.1]heptane-2,3-dione (11).—An ethereal solution of methylmagnesium iodide was added dropwise to a solution (rapidly stirred) of 0.199 g (0.00129 mol) of **11** in 25 ml of ether until the yellow color vanished. The reaction mixture was poured into 200 ml of water and extracted with three 100-ml portions of ether. The extracts were combined, washed with 5% sodium thiosulfate, dried ($MgSO_4$), and concentrated by slow distillation to give 0.182 g of a yellow oil. Gas–liquid partition chromatography (20% SE-30, 8 ft × 0.25 in., 131°, 100 ml/min He) showed the oil to be a mixture of three components, present in amounts of 55, 41, and *ca.* 4%. The component representing 55% of the product was partially separated into two compounds using a flow rate of 75 ml/min. These two components proved to be **11** and a hydroxy ketone which was presumably the product of Grignard addition at the C-2 carbonyl: ir (CCl_4) 3660, 3430, 1750, 1144, and 1043 cm^{-1}. The component representing 41% of the product mixture was obtained in a like manner and was shown to be **9**. The component representing 4% of the isolated mixture could not be characterized because of lack of material.

Oxidation of *endo*-3-Hydroxy-1-methyl-*anti*-7-methylbicyclo-[2.2.1]heptan-2-one (6) with Potassium Permanganate.—A solution containing 0.140 g (0.000908 mol) of **6** in 20 ml of 4% aqueous potassium permanganate solution was stirred at room temperature for 30 hr. Sodium sulfite (*ca.* 100 mg) was added to destroy excess permanganate and the solution was acidified (*ca.* pH 2) with concentrated hydrochloric acid. The clear aqueous solution was concentrated by distillation (steam bath) at reduced pressure (22–30 Torr) and a gray solid precipitated. The remaining water was decanted and the crude diacid was dried (25–30°) at reduced pressure (0.1 Torr) for 6 hr, giving 0.101 g (60.4%). Two recrystallizations from benzene and subsequent drying (steam bath) at reduced pressure (0.1 Torr) gave a pure sample of santenic acid (**7**): mp 170–171°; mmp 170–171°. Treatment of santenic acid with diazomethane gave dimethyl santenate: ir (CCl_4) 1740 (C=O), 1186, 1166, and 1104 cm^{-1} (CO); nmr (CCl_4) δ 3.61 (s, 6, OCH_3), 1.06 (s, 3, CCH_3), 0.95 (d, 3, J = 6.5 Hz, $CHCH_3$), and 1.88 ppm (m, 6).

Anal. Calcd for $C_{11}H_{18}O_4$ (mol wt 210.23): C, 61.66; H, 8.47. Found: C, 61.94; H, 8.66.

Oxidation of *endo*-3-Hydroxy-1,3-dimethylbicyclo[2.2.1]heptan-2-one (9). A. With Lead Tetraacetate.—A mixture containing 0.119 g (0.773 mmol) of **9** and 0.300 g of lead tetraacetate in 6 ml of 90% acetic acid was stirred for 1 hr at 25° and concentrated *in vacuo* to afford a viscous oil. Water was added to decompose the remaining lead tetraacetate and the resulting suspension was extracted with ether. The crude keto acid **10** obtained upon removal of solvent was esterified with diazomethane. A pure sample was obtained by preparative glpc (20% DEGS, 5 ft × 0.25 in., 120 m./min He): ir (CCl_4) 1735 (ester) and 1720 cm^{-1} (ketone); nmr (CCl_4) δ 1.23 (s, 3, CCH_3), 2.07 (s, 3, $O{=}CCH_3$), and 3.59 ppm (s, 3, CO_2CH_3).

Anal. Calcd for $C_{10}H_{16}O_3$ (mol wt 184.23): C, 65.19; H, 8.75. Found: C, 65.11; H, 8.82.

B. With Potassium Permanganate.—Oxidation of 0.340 g (0.221 mmol) of **9** as described above for the oxidation of **6** gave 0.308 g of a colorless oil, a mixture of epimers of **10**.[22] The nmr spectrum exhibits a broad singlet at 7.95 ppm (COOH) and a multiplet extending between 2.75 and 0.80 ppm (relative areas, 1:13). Two similar pairs of singlets are prominent at 2.12 and 2.03 (acetyl) and 1.20 and 1.11 (CCH_3) ppm. The ir spectrum (CCl_4) shows broad OH absorption and bands at 1710 and 1735 cm^{-1}.

Acid-Catalyzed Rearrangement of 6,7-Dimethylbicyclo[3.2.0]-hept-6-en-2-one (5) and 1,7-Dimethylbicyclo[3.2.0]hept-6-en-2-one (8) in Methanolic Hydrochloric Acid.—A solution containing 1.08 g (0.00793 mol) of a mixture of **5** and **8** (ratio 1:2) in 40 ml of 6 *N* methanolic hydrochloric acid was stirred at room temperature for 17.5 hr. The methanolic solution turned very dark as the reaction progressed. This dark solution was poured into 200 ml of water and extracted with ether. The ether extracts were combined, washed with 5% sodium bicarbonate and water, dried ($MgSO_4$), and concentrated by distillation to give 0.750 g of a brown oil. Gas–liquid partition chromatography (20% SE-52, 10 ft × 0.25 in., 130°, 100 ml/min He) showed this oil to consist of five components. Two of these, present in about equal amounts, constituted 83% of the isolated product mixture. Preparative glpc (20% SE-52, 10 ft × 0.25 in., 130°, 100 ml/min He) gave samples of these two components. The compound representing 41% of the product is presumed to be **18**: ir (CCl_4) 2820 (OCH_3), 1740 (weak), 1127, and 1024 cm^{-1} (CO); nmr (CCl_4) δ 3.24 (s, 6, OCH_3) and 1.61 ppm (br s, 6, $=CCH_3$). The compound isolated as 42% of the product has been assigned the structure **17**: ir (CCl_4) 2820 (OCH_3, 1741 (C=O), 1105, and

(18) O. L. Chapman and R. W. King, *J. Amer. Chem. Soc.*, **86**, 1256 (1964).

(19) We thank Dr. A. L. Burlingame and Mr. B. R. Simoneit, University of California, Berkeley, for all mass spectra reported here.

(20) P. D. Bartlett and G. D. Sargent, *ibid.*, **87**, 1297 (1965).

(21) (a) K. B. Wiberg, B. R. Lowry, and T. H. Colby, *ibid.*, **83**, 3998 (1961); (b) J. Meinwald, C. B. Jensen, A. Lewis, and C. Swithenbank, *J. Org. Chem.*, **29**, 3469 (1964)

(22) The *cis* isomer of keto acid **10** has been characterized by Yates: P. Yates and A. G. Fallis, *Tetrahedron Lett.*, 4621 (1967). Comparison of the spectra of our pure ester with those of Yates' pure acid leaves little doubt of the assigned structures (**10**). We are pleased to thank Professor Yates for making the comparison.

1074 cm^{-1} (CO); nmr (CCl_4) δ 3.27 (s, 3, OCH_3), 1.17 (s, 3, CCH_3), 1.05 (s, 3, CCH_3), and 1.42–2.33 ppm (m, 5).

Anal. Calcd for $C_{10}H_{16}O_2$ (mol wt 168.24): C, 71.39; H, 9.59. Found: C, 71.54; H, 9.57.

Acid-Catalyzed Rearrangement of Bicyclo[3.2.0]hept-6-en-2-one (19)[23] in Hydrochloric Acid.—A solution containing 1.335 g (0.01235 mol) of **19** in 100 ml of ether was stirred with 25 ml of 6 *N* hydrochloric acid at room temperature for 148 hr and progress of the reaction was followed by glpc (3% SE-30, 8 ft × 0.125 in., 140°, 25 ml/min He). The reaction mixture was then poured into 100 ml of water and extracted with ether. The extracts were combined, dried ($MgSO_4$), and concentrated at atmospheric pressure leaving a brown oil. The brown color was removed by passing a pentane–ether (1:1) solution of the oil repeatedly through activated charcoal. Removal of the solvent gave a colorless oil which readily crystallized below room temperature and amounted to 1.181 g (66.13%) of *anti*-7-chloro-1-hydroxybicyclo[2.2.1]hept-2-ene (**20**). Preparative glpc (20% SE-52, 10 ft × 0.25 in., 140°, 90 ml/min He) gave a pure sample of **20**: ir (CCl_4) 3580, 3410 (OH), 3055 (CH=CH), and 1195 cm^{-1} (CO); nmr (CCl_4) δ 6.08 (m, 2, HC=CH), 3.54 (s, 1, CHCl), 3.05 (s, 1, COH), 2.64 (s, 1, C-4 bridgehead proton), and 1.67 ppm (m, 4, CH_2CH_2); nmr (DMSO) δ 5.68 (s, 1 COH); mass spectrum (70 eV) *m/e* (rel intensity) 144 (O), 109 (6), 108 (50), 107 (12), 91 (1), 79 (100), 77 (29), 66 (18), and 55 (24).

Anal. Calcd for C_7H_9ClO (mol wt 144.60): C, 58.14; H, 6.27; Cl, 24.52. Found: C, 58.32; H, 6.39; Cl, 24.32.

7-Chloro-1-hydroxybicyclo[2.2.1]heptane (21).—A solution containing 0.296 g (0.00205 mol) of *anti*-7-chloro-1-hydroxybicyclo[2.2.1]hept-2-ene (**20**) and *ca.* 25 mg of platinum dioxide in 10 ml of methanol was hydrogenated (at 49 lb/in.^{2}) for 3.5 hr. The methanolic solution was filtered and carefully concentrated by distillation to give 0.242 g (80.7%) of a colorless oil which crystallized on standing in the cold. Preparative glpc (20% SE-52, 10 ft × 0.25 in., 165°, 25 ml/min He) followed by sublimation (bath temperature 58–60°) at reduced pressure (0.075 Torr) gave a pure sample of 7-chloro-1-hydroxybicyclo[2.2.1]heptane (**21**): mp 113–114°; ir (CCl_4) 3575, 3435 (OH), and 1136 cm^{-1} (CO); nmr (CCl_4) δ 3.72 (s, 1, CHCl), 1.98 (s, 1, COH), and 1.76 ppm (m, 9).

Anal. Calcd for $C_7H_{11}ClO$ (mol wt 146.60): C, 57.34; H, 7.56; Cl, 24.18. Found: C, 57.40; H, 7.61; Cl, 24.13.

1-Hydroxybicyclo[2.2.1]heptane (22).—To a solution containing 0.242 g (0.00165 mol) of 7-chloro-hydroxybicyclo[2.2.1]-heptane (**21**) in 50 ml of freshly condensed ammonia, small pieces of sodium metal were added until the solution remained dark blue. This blue solution was refluxed for 0.5 hr and then the reaction was quenched by the addition of 1 g of ammonium chloride. Evaporation of the ammonia left a salt residue which was dissolved in 10 ml of water and extracted with two 10-ml portions of ether. The extracts were combined, dried ($MgSO_4$), and concentrated to dryness by careful distillation to give 0.157 g (84.9%) of a white, crystalline material. Preparative glpc (20% SE-52, 10 ft × 0.25 in., 150°, 100 ml/min He) indicated the presence of a single compound, which was shown to be 1-hydroxybicyclo-[2.2.1]heptane (**22**):[13] mp 155–156° (sealed tube); ir (CCl_4) 3605, 3310 (OH), and 1133 cm^{-1} (CO); nmr (CCl_4) δ 3.06 (s, 1, COH), 1.98 (m, 1, C-4 bridgehead), and 1.52 ppm (m, 10).

Acid-Catalyzed Rearrangement of Tricyclo[4.3.2.0^{1,6}]undec-10-en-7-one (4)[2] in Hydrochloric Acid.—A solution containing 1.797 g (0.01110 mol) of **4** in 150 ml of ether was stirred with 65 ml of 6 *N* hydrochloric acid at room temperature for 24 hr. The reaction mixture was poured into 150 ml of water and extracted with three 100-ml portions of ether. The extracts were combined, dried ($MgSO_4$), and concentrated to give a light brown oil which solidified on standing in the cold. The solid was dissolved in 5 ml of a pentane–ether (9:1) solution and passed through activated charcoal several times to remove the color. Removal of solvent gave white crystals which were washed with cold pentane and dried (25–30°) at reduced pressure (0.1 Torr) for 24 hr to give 1.143 g (51.95%) of *anti*-11-chloro-8-hydroxytricyclo[6.2.1.0^{1,6}]undec-6(7)-ene (**24**): mp 107–108°; ir (CCl_4) 3560, 3415 (OH), 3035 (CH=C), and 1130 cm^{-1} (CO); nmr (CCl_4) δ 5.34 (s, 1, CH=C), 3.46 (s, 1, CHCl), 2.11 (s, 1, COH), and 1.99 ppm (m, 12); nmr (DMSO) 5.30 ppm (s, 1, COH); mass spectrum (70 eV) *m/e* (rel intensity) 200 (17), 198 (55), 182 (20), 180 (60), 163 (100), 149 (39), 145 (64), and 91 (58).

Anal. Calcd for $C_{11}H_{15}ClO$ (mol wt 198.70): C, 66.49; H, 7.61; Cl, 17.84. Found: C, 66.37; H, 7.49; Cl, 18.00.

Acid-Catalyzed Rearrangement of Tricyclo[6.3.0.0^{1,6}]undec-6(7)-en-9-one (23) in Hydrochloric Acid.—A solution containing 0.125 g (0.000771 mol) of **23** in 20 ml of ether was stirred at room temperature with 10 ml of 6 *N* hydrochloric acid for 26 hr. The reaction mixture was then poured into 50 ml of water and extracted with two 50-ml portions of ether. The extracts were combined, dried (Na_2SO_4), and concentrated to dryness by distillation to give 0.177 g of a colorless oil which appeared to be a single substance (glpc). Preparative glpc (20% SE-52, 10 ft × 0.25 in., 180°, 250 ml/min He) gave 0.032 g of *anti*-11-chloro-8-hydroxytricyclo[6.2.1.0^{1,6}]undec-6(7)-ene (**24**).

Base-Catalyzed Rearrangement of *anti*-11-Chloro-8-hydroxytricyclo[6.2.1.0^{1,6}]undec-6(7)-ene (24).—To a solution prepared from 0.137 g (0.00351 g-atom) of potassium metal in 100 ml of dry *t*-butyl alcohol was added at once 0.403 g (0.00203 mol) of **24** in 10 ml of *t*-butyl alcohol. The resulting solution was refluxed with rapid stirring for 24 hr. The reaction mixture was then poured into 200 ml of water containing 5 g of sodium chloride and extracted with three 100-ml portions of pentane. The extracts were combined, dried ($MgSO_4$), concentrated, and distilled to give 0.238 g (72.3%) of a colorless oil which glpc (3% SE-30, 8 ft × 0.125 in. 180°, 25 ml/min He) showed to be a single compound. Preparative glpc (20% DEGS, 5 ft × 0.25 in., 120°, 120 ml/min He) gave a pure sample of tricyclo[6.3.0.0^{1,6}]undec-6-en-9-one (**23**).

Base-Catalyzed Rearrangement of *anti*-7-Chloro-1-hydroxybicyclo[2.2.1]hept-2-ene (20).—To a solution prepared from 0.250 g (0.00639 g-atom) of potassium metal in 65 ml of dry *t*-butyl alcohol was added at once 0.800 g (0.00553 mol) of **20** in 10 ml of *t*-butyl alcohol. The resulting solution was refluxed with rapid stirring for 10 hr and then stirred for an additional 6 hr at room temperature. The reaction mixture was then poured into 400 ml of water containing 5 g of sodium chloride and extracted with five 100-ml portions of ether. The extracts were combined, dried (Na_2SO_4), and concentrated to give 0.538 g (90.1%) of a colorless oil which glpc (20% SE-52, 10 ft × 0.25 in., 110°, 100 ml/min He) showed to be a single compound. Preparative glpc gave a pure sample of bicyclo[3.2.0]hept-6-en-2-one (**19**).

Solvolyses of Chloro Alcohols 20 and 24.—The solvolyses of **20** and **24** in 50% aqueous ethanol (by volume) were conducted at 55.53 ± 0.05° by the standard ampoule technique.[14] The extent of solvolysis was determined by titration of the ampoule contents with standard base. The half-reaction times were thus determined to be 180 min for **20** and 2.4 min for **24**.

Registry No.—**6**, 22257-23-1; **9**, 22256-24-2; **11**, 1194-35-0; **17**, 22256-25-3; **18**, 22241-66-3; **20**, 22256-26-4; **21**, 22241-67-4; **24**, 22256-27-5.

(23) This ketone is prepared from cyclopentenone as is described for the similar tricyclic compounds in ref 2. See also L. A. Paquette and O. Cox, *J. Amer. Chem. Soc.*, **89**, 5633 (1967).