Acid-Catalyzed Isomerizations of β,γ-Unsaturated Ketones[1]

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The tricyclo[4.3.2.0^{1,6}]undec-10-en-2-ones (1 and 2) undergo acid-catalyzed isomerization to the tricyclo-[3.3.3.0^{1,5}]undec-3-en-2-ones (5 and 8), respectively. On the other hand, the more reactive bicyclo[4.2.0]oct-7-en-2-ones (3 and 4) isomerize to bicyclo[3.2.1]oct-6-en-8-ones (13 and 21), respectively, rather than to bicyclo-[3.3.0]oct-3-en-2-ones. The isomerizations of the bicyclic ketones occur under conditions considerably milder than those required for rearrangement of the tricyclic ketones. Possible mechanisms for these isomerizations are offered.

As part of a general study of the effects of acids on polycyclic β,γ-unsaturated ketones,[3,4] we have examined the acid-catalyzed rearrangements of the ketones 1, 2, 3, and 4. We report our findings here.
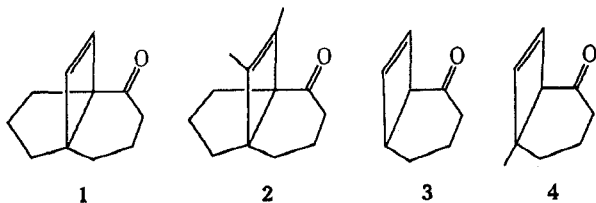

The synthesis of 1 involved photocycloaddition of 1,2-dichloroethylene to bicyclo[4.3.0]non-1(6)-en-2-one followed by dehalogenation with sodium in liquid ammonia. When care was taken to ensure the anhydrous nature of the ammonia, we found no further reduction of 1 to the corresponding alcohol. Ketone 2 was obtained from photocycloaddition of 2-butyne to the previously mentioned bicyclononenone. Ketones 3 and 4 were obtained by hydrolysis of the corresponding ketals[5,6] in 5% sulfuric acid.

When ketone 1 was treated with *p*-toluenesulfonic acid in boiling benzene, a new α,β-unsaturated ketone [λ_{max}^{EtOH} 228 nm (ε 7200), $\nu_{max}^{CCl_4}$ 1710 cm^{-1}, and δ 5.91 and 7.33 ppm (doublets, J_{AX} = 6 Hz)] was obtained in 68% yield, uncontaminated with other species of similar volatility. The rearranged ketone is assigned structure 5 on the basis of the above spectra and its oxidation to
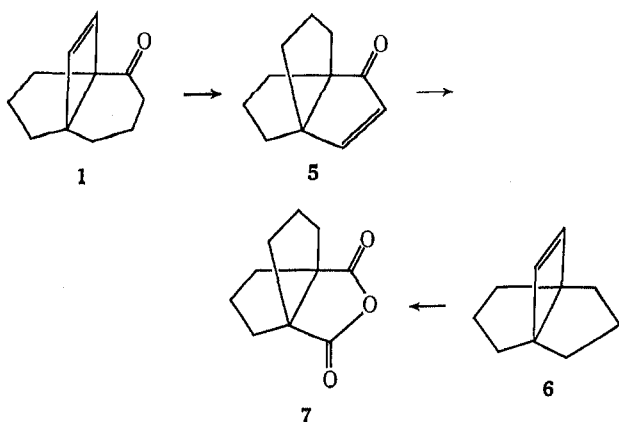

anhydride 7 which has also been obtained from olefin 6.[7]

Similar treatment of 2 led to the formation of an isomeric, conjugated ketone in 85% yield, having the spectral properties expected for 8, the structure assigned to this new ketone. The latter change, 2 → 8, is exactly analogous with the previously mentioned 1 → 5 change.
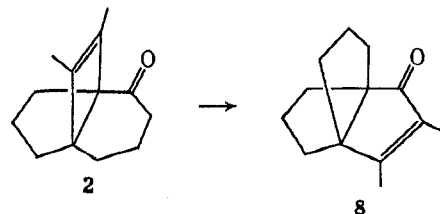
We suggest that the two isomerizations discussed above occur as is outlined in Scheme I. Net migration of the etheno bridge from C-1 to C-2 in the protonated ketone 9, a process in which considerable strain relief is realized, leads to 10, a substituted 8-bicyclo[3.2.1]-octenyl cation which is presumably well stabilized.[8] A Wagner–Meerwein shift leads to the observed products 11 (11a ≡ 5, 11b ≡ 8).

SCHEME I

a, R = H
b, R = CH₃
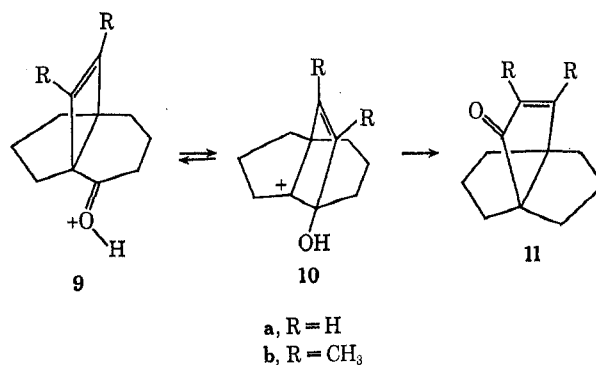
Attempts to purify ketone 3 by gas chromatography under conditions which 1 and 2 survived without any rearrangement or decomposition were unsuccessful in that the collected material exhibited spectra and tlc data indicative of the presence of two compounds; however, pure 3 (tlc, nmr) could be obtained after ketal hydrolysis by distillation. Injection of pure 3 into the gas chromatograph led to the formation of a second compound, whereupon we suspected that an acid-catalyzed rearrangement had occurred on the column.

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

(2) National Science Foundation Trainee, 1966–1969.

(3) For a preliminary account of this work, see R. L. Cargill and J. W. Crawford, *Tetrahedron Lett.*, 169 (1967).

(4) 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.

(5) H. O. House and T. H. Cronin, *J. Org. Chem.*, **30**, 1961 (1965).

(6) C. G. Scouten, F. E. Barton, J. R. Burgess, P. R. Story, and J. F. Garst, *Chem. Commun.*, 78 (1969).

(7) J. R. Damewood, Ph.D. Thesis, University of South Carolina, Columbia, S. C., 1967.

(8) G. W. Klumpp, G. Ellen, and F. Bickelhaupt, *Rec. Trav. Chim. Pays-Bas*, **88**, 474 (1969).

Several attempts to carry out the presumed rearrangement with various acids in solution led only to rapid decomposition of **3**; no volatile material was detected.[9] However, when **3** was passed in a stream of helium through a column of acid-washed alumina maintained at 200°, a new crystalline ketone was obtained in 28% yield. No starting material was recovered, indicating that considerable decomposition of either **3** or the new product had occurred.

Based on the analogy of the rearrangements discussed above in terms of Scheme I, we felt that **3** should undergo isomerization to **12**; however, comparison of the spectral data for the new ketone [λ_{max}^{EtOH} 272 nm (ϵ 13) and $\nu_{max}^{CCl_4}$ 1750, 1720, 1660, and 1620 cm^{-1}] with those of **12**[10,11] [λ_{max}^{EtOH} 224 nm (ϵ 11,600) and 319 (39) and $\nu_{max}^{CCl_4}$ 1705 and 1590 cm^{-1}] clearly showed our reasoning to be in error. That the product of this rearrangement is **13** became evident from its hydrogenation to the known ketone **15**[12,13] coupled with its nonidentity with the known enone **14** (see Scheme II).

SCHEME II
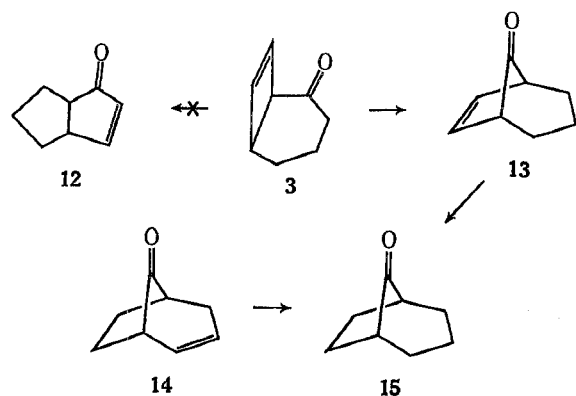
The intermediacy of ion **18** is almost certainly required for the conversion of **3** into **13**. Two paths from **3** to **18** are evident (Scheme III). One, path a, is similar to the changes outlined earlier in Scheme I: migration of the etheno bridge to yield **17** followed by an alkyl shift *via* path c leads to **18**. The second, path b, only requires a shift of the C-1–C-6 bond in **16** from C-1 to C-2, giving **18** directly.[14] The absence of **12** in the product would be very difficult to rationalize if path a were the preferred one, since **17** would be expected to rearrange to the more stable ion **19** (*via* path d) in the manner already outlined in the isomerizations of **1** and **2**.

(9) Similar attempts to observe the acid-catalyzed isomerization of quadricyclanone to bicyclo[3.2.0]hepta-3,6-dien-2-one in solution were unsuccessful: P. R. Story and S. R. Farenholtz, *J. Amer. Chem. Soc.*, **87**, 1623 (1965). We thank Professor Story for informing us of these nonresults.

(10) W. E. Parham, R. W. Soeder, J. R. Throckmorton, K. Kuncl, and R. M. Dodson, *ibid.*, **87**, 32 (1965).

(11) D. M. Pond, Ph.D. Thesis, University of South Carolina, Columbia, S. C., 1968.

(12) A. C. Cope, J. M. Grisar, and P. E. Peterson, *J. Amer. Chem. Soc.*, **82**, 4299 (1960).

(13) C. S. Foote and R. B. Woodward, *Tetrahedron*, **20**, 687 (1964).

(14) Although path b is inoperative in the related bicyclo[3.2.0]heptenyl systems, it is evidently the favored path in the less rigid bicyclo[4.2.0]-octyl and -octenyl systems. See G. Büchi and E. M. Burgess, *J. Amer. Chem. Soc.*, **82**, 4333 (1960); S. C. Lewis and G. H. Whitham, *J. Chem. Soc.*, *C*, 274 (1967); R. L. Cargill, D. M. Pond, and S. O. LeGrand, *J. Org. Chem.*, **35**, 359 (1970); A. C. Cope, R. W. Gleason, S. Moon, and C. H. Park, *ibid.*, **32**, 942 (1967); and S. P. Pappas, B. C. Pappas, and N. A. Portnoy, *ibid.*, **34**, 520 (1969).

SCHEME III
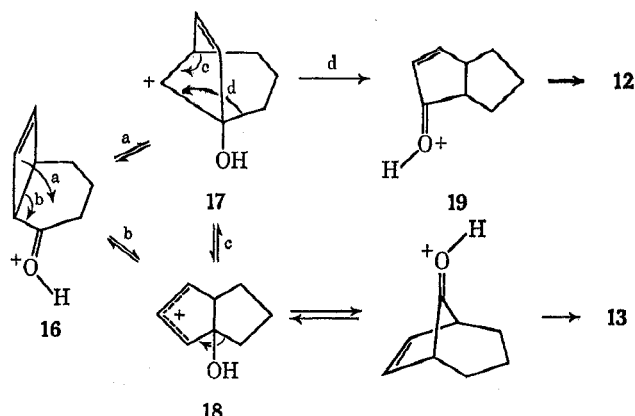
The question of which of the two proposed paths is in fact the favored one is easily resolved by a simple labeling experiment. Thus, rearrangement *via* path a leads to conversion of C-6 of **3** into a trigonal C-6 in **13**, whereas isomerization *via* path b allows the bridgehead C-6 of **3** to remain at a bridgehead in **13**. Rearrangement of ketone **4** may yield either **20** or **21** *via* path a or b, respectively.
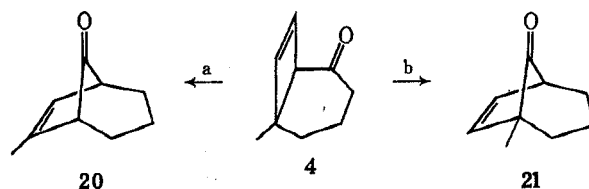
Ketone **4** was found to undergo isomerization when warmed in benzene containing *p*-toluenesulfonic acid to yield a single product. That the new isomer is **21** follows from the nmr spectrum, which shows the presence of two vinyl hydrogens and a methyl on quarternary carbon, as well as other spectroscopic data (see Experimental Section). Path a is therefore eliminated and the correctness of path b is corroborated, if not established.

The absence of **12** in the rearrangement product from **3** is now readily explained: the required intermediate, **17**, is bypassed in favor of direct isomerization of **16** to **18**, thus providing no path from **3** to **12**. In the tricyclic systems, **1** and **2**, isomerization *via* path b leads to ion **22**, a relatively poor bridgehead carbonium ion and one whose only available path of deactivation, if formed in the absence of nucleophiles, is reversion to starting material. The next higher energy path is, therefore, followed.
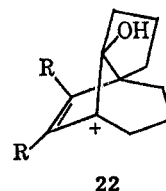
In summary, we have described acid-catalyzed isomerizations which lead in two cases to the [3.3.3]-propellane system[15,16] and in a second pair of cases to the previously unknown bicyclo[3.2.1]oct-6-en-8-ones.

(15) D. Ginsburg, *Accounts Chem. Res.*, **2**, 120 (1969).

(16) H. W. Thompson, *J. Org. Chem.*, **32**, 1222 (1967).

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The synthetic utility of these rearrangements is obvious, and in subsequent publications we shall discuss other examples of the usefulness of these transformations as well as the chemistry of the isomerization products.

Experimental Section[17]

Tricyclo[4.3.2.0^{1,6}]undec-10-en-2-one (1).—A solution of 2.60 g (0.0191 mol) of bicyclo[4.3.0]non-1(6)-en-2-one[18] and 3 ml of a mixture of *cis*- and *trans*-1,2-dichloroethylenes in 80 ml of pentane was irradiated (Corex) for 30 min. Progress of the reaction was measured by glpc (3% DEGS, 8 ft × 0.125 in., 120°, 12 ml/min He). Removal of the solvent and excess dichloroethylene by distillation left a brown oil, which was dissolved in 100 ml of dry ether and 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 10 min, 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 100-ml portions of ether. The ethereal extract was dried (Na$_2$SO$_4$), concentrated, and distilled, giving 2.38 g (77.0%) of 1: bp 71–73° (0.25 Torr); uv max (95% C$_2$H$_5$OH) 296 nm (ϵ 85); ir (CCl$_4$) 3120, 3030 (HC=CH), and 1700 cm^{-1} (C=O); nmr (CCl$_4$) δ 5.97 (q, 2, J_{AB} = 2.8 Hz, Δ_{AB} = 10.5 Hz) and 1.75 ppm (m, 12).

The 2,4-dinitrophenylhydrazone was recrystallized from methanol–water, mp 123.0–123.5°.

Anal. Calcd for C$_{17}$H$_{18}$N$_4$O$_4$ (mol wt 342.35): C, 59.64; H, 5.30; N, 16.37. Found: C, 59.61; H, 5.40; N, 16.28.

10,11-Dimethyltricyclo[4.3.2.0^{1,6}]undec-10-en-2-one (2).—A solution of 2.40 g (0.0176 mol) of bicyclo[4.3.0]non-1(6)-en-2-one and 4 ml of 2-butyne in 80 ml of pentane was irradiated (Corex) for 30 min. The progress of the reaction was measured by glpc (3% DEGS, 8 ft × 0.125 in., 120°, 12 ml/min He). Removal of the pentane and excess 2-butyne left a residue from which 2.23 g (66.5%) of 2 was distilled: bp 114–116° (7 Torr); uv max (95% C$_2$H$_5$OH) 296 nm (ϵ 168); ir (CCl$_4$) 1695 (C=O) and 1410 cm^{-1} (COCH$_3$); nmr (CCl$_4$) δ 1.45 ppm (m).

An analytical sample was further purified by preparative glpc (20% DEGS, 10 ft × 0.25 in., 160°, 120 ml/min He) and subsequent distillation.

Anal. Calcd for C$_{13}$H$_{18}$O (mol wt 190.27): C, 82.06; H, 9.54. Found: C, 81.88; H, 9.67.

The *p*-toluenesulfonylhydrazone was recrystallized from methanol–water, mp 136.0–136.5°.

Anal. Calcd for C$_{20}$H$_{28}$N$_2$O$_2$S: (mol wt 347.50): C, 67.02; H, 7.31; N, 7.82. Found: C, 67.17; H, 7.25; N, 7.89.

Bicyclo[4.2.0]oct-7-en-2-one (3).—A solution of 5.95 g (0.0359 mol) of bicyclo[4.2.0]oct-7-en-2-one ethylene ketal[5,6] in 200 ml of ether was stirred at 25° with 30 ml of 5% sulfuric acid for 15 hr. The aqueous phase was extracted with 100 ml of ether and the ethereal solutions were combined, washed with aqueous sodium bicarbonate and water, dried (MgSO$_4$), concentrated, and distilled, giving 3.34 g (76.3%) of 3: bp 78–80° (20 Torr); ir (neat) 3105, 3040 (HC=CH), 1700 (C=O), and 780 and 700 cm^{-1} (*cis* HC=CH); nmr (CCl$_4$) δ 6.0 (q, 2, J_{AB} = 5.0 Hz, Δ_{AB} = 20.0 Hz, vinyl), 3.30 (m, 2, bridgehead), and 1.90 ppm (m, 6, methylene).

The *p*-toluenesulfonylhydrazone was recrystallized from methanol–water, mp 146–147°.

Anal. Calcd for C$_{15}$H$_{18}$N$_2$O$_2$S (mol wt 290.31): C, 62.05; H, 6.25; N, 9.65. Found: C, 62.02; H, 6.08; N, 9.80.

Tricyclo[3.3.3.0^{1,5}]undec-3-en-2-one (5).—A solution of 1.92 g (0.0118 mol) of 1 and 0.8 g of *p*-toluenesulfonic acid mono-

hydrate in 50 ml of benzene was refluxed for 10 min. The cooled reaction mixture was washed with 20% sodium bicarbonate, concentrated, and distilled, giving 1.32 g (68.7%) of 5: bp 95° (bath) (0.25 Torr); uv max (95% C$_2$H$_5$OH) 228 nm (ϵ 7200) and 314 (73); ir (CCl$_4$) 1710 (C=O) and 1595 cm^{-1} (C=C); nmr (CCl$_4$) δ 7.33 (d, 1, J_{AX} = 6.0 Hz), 5.91 (d, 1, J_{AX} = 6.0 Hz, O=CCH=CH), and 1.3–2.1 ppm (m, 12, methylene).

An analytical sample was further purified by preparative glpc (20% DEGS, 10 ft × 0.25 in., 180°, 50 ml/min He) and subsequent distillation.

Anal. Calcd for C$_{11}$H$_{14}$O (mol wt 162.22): C, 81.44; H, 8.70. Found: C, 81.37; H, 8.65.

3,4-Dimethyltricyclo[3.3.3.0^{1,5}]undec-3-en-2-one (8).—A solution of 0.92 g (0.0048 mol) of 2 and 50 mg of *p*-toluenesulfonic acid monohydrate in 50 ml of benzene was refluxed for 72 hr. The cooled reaction mixture was washed with 5% sodium bicarbonate, concentrated, and distilled, giving 0.78 g (85%) of 8: bp 125° (bath) (0.55 Torr); uv max (95% C$_2$H$_5$OH) 248 nm (ϵ 10,380) and 314 (83); ir (CCl$_4$) 1700 (C=O) and 1645 cm^{-1} (C=C); nmr δ 1.91 (m) and 1.50 ppm (m).

An analytical sample was further purified by preparative glpc (20% DEGS, 10 ft × 0.25 in., 160°, 120 ml/min He) and subsequent distillation.

Anal. Calcd for C$_{13}$H$_{18}$O (mol wt 190.27): C, 82.06; H, 9.54. Found: C, 81.81; H, 9.41.

Bicyclo[3.2.1.]oct-6-en-8-one (13).—A total of 0.573 g (0.00421 mol) of 3 was injected in 50-μl portions into a stream of helium flowing at 4 ml/min over a column (1 × 15 cm) of acid-washed alumina (Merck), which was maintained at 200° by means of a heating tape. The eluate was trapped in an air-cooled U tube and amounted to 0.147 g (28.8%) of 13: mp 110.5–111°; uv max (95% C$_2$H$_5$OH) 272 nm (ϵ 13); ir (CCl$_4$) 3050 (=CH), 1750, 1720 (C=O), 1660, 1620 (C=C), and 750 and 720 cm^{-1} (HC=CH); nmr (CCl$_4$) δ 6.12 (t, 2, J = 2 Hz, vinyl), 2.61 (m, 2, bridgehead), and 1.68 ppm (m, 6, methylene).

The 2,4-dinitrophenylhydrazone was recrystallized from methanol–water, mp 158–159°. The 2,4-dinitrophenylhydrazone of bicyclo[3.2.1]oct-2-en-8-one had a melting point of 176.4–177.2°.[13]

Anal. Calcd for C$_{14}$H$_{14}$N$_4$O$_4$ (mol wt 302.28): C, 55.62; H, 4.67; N, 18.54. Found: C, 55.81; H, 4.82; N, 18.70.

Bicyclo[3.2.1]octan-8-one (15).—A solution of 0.298 g (0.00244 mol) of 13 in 50 ml of methanol was hydrogenated over 50 mg of palladium (5% on charcoal) at 1-atm pressure. The catalyst was removed and the filtrate was combined with 75 ml of water and extracted with three 50-ml portions of pentane. The pentane extracts were combined, dried (MgSO$_4$), and concentrated, and the residue was purified by glpc (20% DEGS, 10 ft × 0.25 in., 170°, 50 ml/min He), giving 0.113 g (38.1%) of 15, mp 140–141° (lit.[18] mp 140–141°).

The 2,4-dinitrophenylhydrazone was recrystallized from methanol–water, mp 174–175° (lit.[13] mp 175.4–176.2°).

***cis*-Bicyclo[3.3.0]octan-1,5-dicarboxylic Acid Anhydride (7).—** **A. From Tricyclo[3.3.2.0^{1,6}]dec-9-ene (6).**—A solution of 33 mg (0.20 mmol) of ruthenium tetroxide in 20 ml of carbon tetrachloride, generated by the method of Mercer and Meyer,[19] was combined with a solution of 427 mg (3.19 mmol) of 6 in 50 ml of carbon tetrachloride. After ruthenium dioxide began to precipitate, a solution of g of sodium *m*-periodate in 50 ml of water was added and the resulting two-phase mixture was stirred at 25° for 12 hr. The organic phase was separated, stirred with 3 ml of isopropyl alcohol for 20 min, filtered to remove ruthenium dioxide, dried (MgSO$_4$), and concentrated to yield 300 mg of a yellow oil. The oil was treated with ethereal diazomethane and the resulting mixture of anhydride 7 and the corresponding diester was separated by preparative glpc (20% DEGS, 10 ft × 0.25 in., 180°, 300 ml/min He). The collected diester, 30 mg, had ir (CCl$_4$) 1740 cm^{-1}; nmr (CCl$_4$) δ 3.57 (s, 6, CO$_2$CH$_3$) and 1.80 ppm (br m, 12). The collected anhydride 7 amounted to 183 mg (31.9%), mp 111–112°. An analytical sample of 7 was obtained by sublimation at 80°: mp 112–113°; ir (CCl$_4$) 1840 and 1783 cm^{-1}; nmr (CCl$_4$) δ 1.90 ppm (br m). Continuous extraction of the acidified aqueous phase (see above) for 48 hr gave an additional 353 mg (61.5%) of 7.

Anal. Calcd for C$_{10}$H$_{12}$O$_3$ (mol wt 180.20): C, 66.65; H, 6.71. Found: C, 66.62; H, 6.78.

B. From Tricyclo[3.3.3.0^{1,5}]undec-3-en-2-one (5).—A solution containing *ca.* 5 mg of potassium permanganate and 1.0 g of sodium *m*-periodate in 20 ml of water was stirred along with

(17) All boiling points and melting points are uncorrected. Microanalyses were performed by Bernhardt Microanalytisches Laboratorium, Elbach über Engelskirken, 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 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. Irradiations were carried out using a Hanovia high-pressure mercury arc (450 W), internal probe, type L, and the filter specified.

(18) R. K. Hill and R. T. Conley, *J. Amer. Chem. Soc.*, **82**, 645 (1960).

(19) E. E. Mercer and S. M. Meyer, personal communication.

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 (MgSO₄) 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 (MgSO₄), 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 (MgSO₄), concentrated, and distilled to give 8.53 g (82.6%) of 4: bp 70–74° (5.0 Torr); ir (CCl₄) 3120, 3030 (HC=CH), and 1700 cm⁻¹ (C=O); nmr (CCl₄) 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 C₁₅H₁₈N₄O₄ (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 (CCl₄) 3050 (HC=CH), 1760, 1700 (C=O), and 1650 cm⁻¹ (C=C); nmr (CCl₄) 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 C₁₅H₁₈N₄O₄ (mol wt 316.30): C, 56.96; H, 5.10; N, 17.71. Found: C, 57.17; H, 5.00; 6, 17.89.

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-methyl-bicyclo[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, ex-
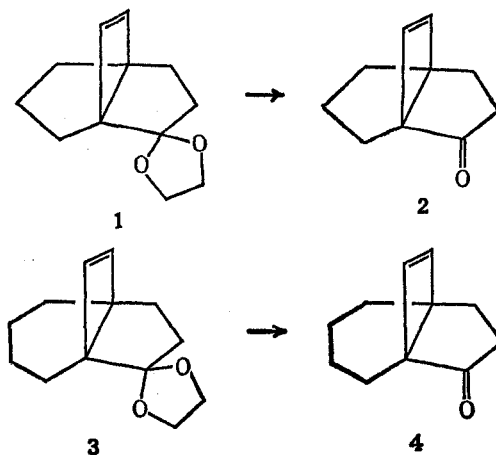
1 → 2

3 → 4

amined the action of 6 *M* hydrochloric acid on a series of β,γ-unsaturated ketones, and the results of this investigation are reported here.