Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.42; H, 7.78.

Separate oxidations of diols **29a** and **29b** by the same manner provided (2*RR*,2α*SS*)-2-(α-hydroxy-α-methyl)benzylcyclohexanone, bp 88–90° (0.4 mm), $n^{25}D$ 1.524; nmr δ 1.64 (s, 3, CH_3), ir ($CHCl_3$) 1698 cm^{-1}.

Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.85; H, 8.36.

Deuteration of *trans*-2-Benzoylcyclopentanol (20b).—A solution of **20b** (0.6 g) in dimethoxyethane (10 ml), D_2O (3 ml), and 40 mg of anhydrous Na_2CO_3 were refluxed for 16 hr. Extraction with ether and chromatography of the residue on a dry column afforded 0.32 g of 2-d_1-*trans*-2-benzoylcyclopentanol which was eluted with 40% ether and pentane. Nmr showed no chemical shift in the δ 3.5–4.0 region, mol wt 191 (mass spectrum).

Grignard reaction of deuteriated **20b** (0.3 g) with PhMgBr by the usual procedure yielded, along with other products, **20a** (30 mg) and **20b** (65 mg) which were separated by dry column chromatography as shown for the reaction of **1b** and PhMgBr. The exchange of deuterium on hydrogen was proven by nmr analysis and by mass spectral determination of molecular weight of **20a** and **20b** (190).

Registry No.—**2**, 32338-46-8; **3**, 32338-48-0; **4**, 32338-47-9; **6**, 30614-37-0; **7**, 33831-21-9; **11**, 33831-22-0; **12**, 33831-23-1; **13** *p*-nitrobenzoate, 33847-00-6; **14**, 33831-24-2; **15a**, 33831-25-3; **15b**, 33831-26-4; **16**, 33831-27-5; **17**, 33831-28-6; **18**, 33831-29-7; **19a**, 33872-39-8; **19b**, 33831-30-0; **20a**, 32346-66-0; **20b** *p*-nitrobenzoate, 33831-32-2; **21a**, 32435-36-2; **21b**, 33830-23-8; **22a**, 33830-24-9; **22b**, 33830-25-0; *trans*-**23**, 33830-26-1; **24a**, 33830-27-2; **24b**, 33830-28-3; **25a**, 33830-29-4; **25b** *p*-nitrobenzoate, 33847-01-7; **26a**, 33830-30-7; **26b**, 33830-31-8; **27a**, 33830-32-9; **27b** *p*-nitrobenzoate, 33847-02-8; **29a**, 33872-40-1; **29b**, 33830-33-0; **30b**, 33830-34-1; 1-benzocyclopentene, 21573-70-6; 2-benzylhydrylidenecyclopentanone, 14636-29-4; 1-phenyl-*c*-2-acetyl-*r*-1-cyclopentanol, 33830-37-4; (2*RR*,2α*SS*)-2-(α-hydroxy-α-methyl)benzylcyclopentanone, 33830-38-5; (2*RS*,2α*SR*)-2-(α-hydroxy-α-methyl)benzylcyclopentanone, 33830-39-6; (2*RR*,2α*SS*)-2-(α-hydroxy-9-methyl)benzylcyclohexanone, 33830-40-9.

Acknowledgments.—The authors wish to thank Miss R. Shapiro for technical help. We also thank Dr. S. Pinhas for the determination of hydroxyl stretching frequencies in the infrared spectra and Mr. R. Heller and associates for the elemental analyses.

Acid-Catalyzed Rearrangement of 6-Methyltricyclo[4.4.0.0^{2,7}]decan-3-one

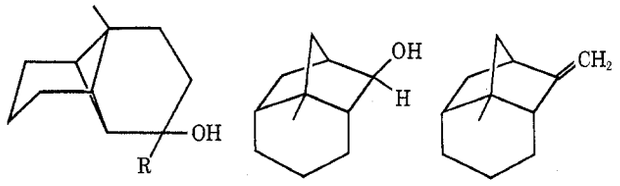
CLAYTON H. HEATHCOCK* AND BRUCE E. RATCLIFFE

Department of Chemistry, University of California, Berkeley, California 94720

Received August 27, 1971

Tricyclic ketone **5** reacts in concentrated sulfuric acid to give rearrangement products **6**, **7**, **8**, and **9** in a ratio of 19:32:10:38. Tricyclic ketone **6** is produced by a mechanism involving ring expansion while compounds **7**–**9** arise by a route involving initial ring opening of ketone **5**. The structures of the rearrangement products were rigorously defined.

In the previous paper,[1] we reported that tricyclic alcohols **1** and **2** rearrange in the heterogeneous medium hexane–50% aqueous sulfuric acid to yield compounds **3** and **4**, respectively. In this paper, we describe the

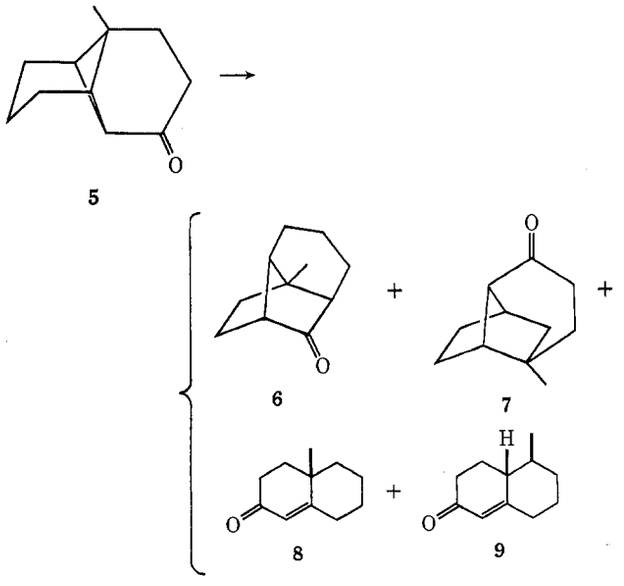


1, R = H
2, R = CH_3
3
4

acid-catalyzed rearrangement of the parent tricyclic ketone, 6-methyltricyclo[4.4.0.0^{2,7}]decan-3-one (**5**).

When ketone **5** is dissolved in concentrated sulfuric acid and the resulting solution kept at room temperature for periods ranging from 2 hr to 2 weeks, four isomeric ketones are produced. These isomeric products, subsequently shown to have structures **6**–**9** (*vide infra*), were each isolated in a pure state by a combination of column chromatography and preparative glpc. The product analyses from several such runs are tabulated in Table I. Control experiments showed that none of the products react further when treated with concentrated sulfuric acid at 25° for 2 days.

The structures of the four products were assigned on



the following grounds. Ketone **8** is a known compound and was identified by comparison with an authentic specimen.[2]

Product **9** also exhibits spectral properties characteristic of an α,β-unsaturated ketone [ν_{max} 1680 and 1629 cm^{-1}, λ_{max} 238 nm (ε 12,200)]. The pmr spectrum

(1) B. E. Ratcliffe and C. H. Heathcock, *J. Org. Chem.*, **37**, 531 (1972).

(2) J. A. Marshall and W. I. Fanta, *ibid.*, **29**, 2501 (1964), and references cited therein.

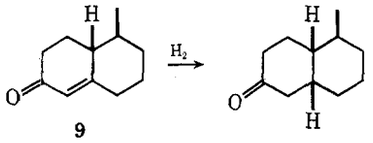
TABLE I

ACID-CATALYZED REARRANGEMENT OF KETONE 5

Run	Reaction time	Reaction temp, °C	Product analysis, %[a] 5	6	7	8	9	Others
1	2 hr	25	39	15	23	3	19	0
2	2 days	25	0	17	32	16	35	0
3	1 week	25	0	19	33	10	38	0
4	2 weeks	25	0	19	32	10	38	1

[a] Product analysis by glpc (6 ft × 0.25 in. 10% FFAP at 180°).

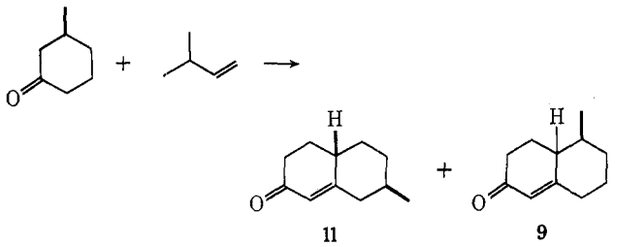
of this material contains a broad one-proton singlet at δ 5.65, attributed to a vinyl hydrogen, and a broad three-proton singlet at δ 1.07, attributed to a methyl doublet broadened by virtual coupling. Hydrogenation of **9** in ethyl acetate over palladized carbon affords a single product **10** (ν_{max} 1716 cm^{-1}), the pmr spectrum



9 **10**

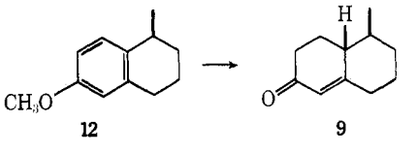
of which shows a clean methyl doublet at δ 0.98 with J = 6.0 Hz. The cis stereochemistry assigned to the ring juncture in **10** is tenuous. Augustine reports that $\Delta^{1,9}$-octal-2-one itself gives approximately equal amounts of *cis*- and *trans*-2-decalones when reduced over palladium in neutral ethanol.[3] However, 10-methyl-$\Delta^{1,9}$-octal-2-one is hydrogenated in neutral medium primarily to the cis product.[4,5] Base-catalyzed deuterium exchange studies showed that compounds **9** and **10** have six and four enolizable hydrogens, respectively.

Consideration of the above data, along with mechanistic considerations (*vide infra*), led us to propose the structure shown for compound **9**. This hypothesis was verified by independent synthesis of **9**. Robinson annelation of 3-methylcyclohexanone with methyl vinyl ketone afforded the isomeric enones **11** and **9**, along with



11 **9**

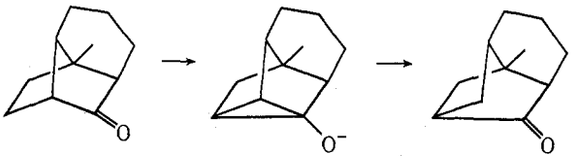
a third unidentified product in a ratio of 67:20:13, respectively. The major isomer produced in this annelation can confidently be assigned the 7-methyl structure **11**, since 3-methylcyclohexanone is known to undergo base-catalyzed condensations predominantly at C-6, rather than C-2.[6] The minor α,β-unsaturated ketone produced in the annelation reaction is therefore assigned the 5-methyl structure **9**. Both **11** and **9** are assumed to be the thermodynamically more stable isomers, with methyl equatorial, since the angular hydrogen is epimerizable under the conditions of their formation. Structure **9** was also verified by comparison of a



12 **9**

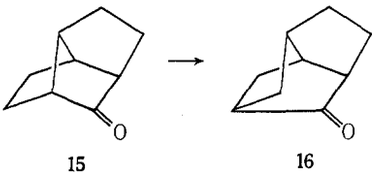
sample prepared from 1-methyl-5-methoxytetralin (**12**) by Birch reduction and subsequent hydrolysis of the resulting enol ether.[7]

Ketone **6** was suspected to be a cyclopentanone on the basis of its ir spectrum (ν_{max} 1750 cm^{-1}). The compound is obviously tricyclic, since it shows no vinyl proton absorption in its pmr spectrum, fails to react under catalytic hydrogenation conditions, and gives no color with tetracyanoethylene. The pmr spectrum showed an unsplit methyl resonance at δ 1.17 and a one-proton doublet at δ 2.37 (J = 4 Hz). The ketone failed to undergo deuterium exchange, indicating the absence of an enolizable α hydrogen. The structure of ketone **6** was revealed when it was treated with potassium *tert*-butoxide in *tert*-butyl alcohol at 185° for 1 week. Under these conditions, ketone **6** was transformed into ketone **13** in 84% yield. This transformation requires that compounds **6** and **13** be related by a common homoenolate, **14**. Since the structure of tricyclic ketone **13**



6 **14** **13**

has been rigorously proven,[1] the structure of ketone **6** is secure. A similar homoenolization has been reported by Nickon and coworkers[8] in the brexanone–brendanone system (**15** → **16**). In Nickon's system, as in ours, the endo-bridged isomer predominates at equilibrium.



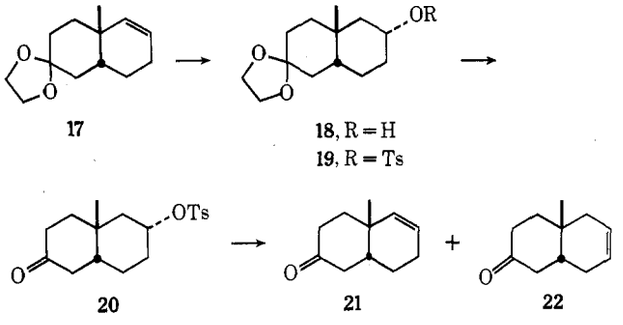
15 **16**

The fourth rearrangement product, ketone **7**, was obtained as a low-melting solid (mp 35–36°). Its ir spectrum shows that it is a cyclohexanone with an α-methylene group (ν_{max} 1706 and 1410 cm^{-1}). The ketone exchanges two hydrogens for deuterium when passed through a deuterated glpc column.[9] The pmr

(3) R. L. Augustine, *J. Org. Chem.*, **23**, 1853 (1958); **28**, 152 (1963).
(4) R. Futaki, *ibid.*, **23**, 451 (1958).
(5) F. Sondheimer and D. Rosenthal, *J. Amer. Chem. Soc.*, **80**, 3995 (1958).
(6) See, *inter alia*, (a) G. Descotes and S. Laurent, *C. R. Acad. Sci., Ser. C*, **265**, 1167 (1967); (b) G. Descotes and Y. Querou, *ibid.*, **263**, 1231 (1966).
(7) W. G. Dauben and J. I. Seeman, unpublished results. We thank Drs. Dauben and Seeman for providing us with a sample of their ketone **9** for comparison.
(8) A. Nickon, H. Kwasnik, T. Swartz, R. O. Williams, and J. B. DiGiorgio, *J. Amer. Chem. Soc.*, **87**, 1615 (1965).
(9) (a) M. Senn, W. J. Richter, and A. L. Burlingame, *ibid.*, **87**, 680 (1965); (b) G. J. Kallos and L. B. Westover, *Tetrahedron Lett.*, 1223 (1967).

spectrum contains a singlet methyl resonance at δ 1.12 and a broad three-proton envelope in the region δ 2.10–2.42, attributable to hydrogens α to the carbonyl group. Mechanistic speculation led to the postulate that this material might have the tricyclic structure indicated in structure **7**, which is also consistent with the above data. This hypothesis was confirmed by an independent synthesis of the material.

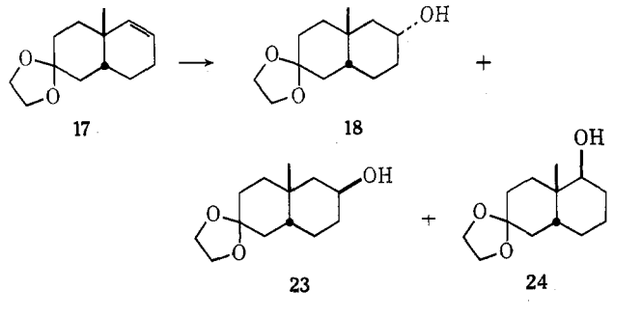
Oxymercuration–demercuration[10] of the readily available unsaturated ketal **17**[11] affords a single alcohol **18** in 90% yield. Compound **18** reacts with *p*-toluenesulfonyl chloride in pyridine to give the crystalline tosylate **19**, which is hydrolyzed to keto tosylate **20**. Evidence for both the position and configuration of the tosylate group in **20** was obtained by treating it with methylsulfinyl carbanion in dimethyl sulfoxide.[12] The product obtained from this reaction is a 60:40 mixture of octalones **21** and **22**.[13] The formation of both



17 18, R = H 19, R = Ts 20 21 22

octalones shows that the tosylate group in **20** must be at C-6 rather than C-5. Since the tosylate epimeric at C-6 is expected to undergo base-catalyzed *cyclization* (*vida infra*), the stereochemistry shown for **20** (and hence alcohol **18**) is strongly suggested.

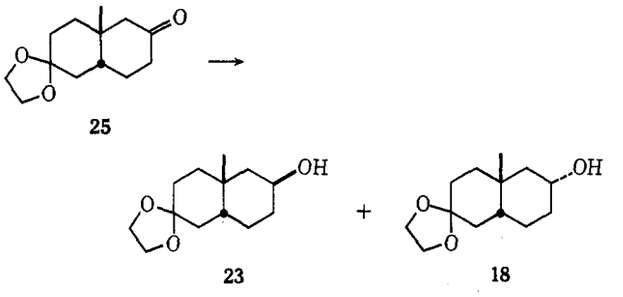
The remarkable selectivity observed in the oxymercuration of **17** is interesting, although we can offer no suitable explanation for it. Hydroboration, a reaction believed to be very sensitive to steric factors, converts olefin **17** into a mixture of three alcohols, **18**, **23**, and **24**. The highly selective hydroborating re-



17 18 23 24

agents disiamylborane[14] and 9-borabicyclo[3.3.1]-nonane[15] fail to react with compound **17**.

Oxidation of alcohol **18** with bispyridinechromium(VI) oxide in methylene chloride[16] affords the highly crystalline keto ketal **25**, previously synthesized by



25 23 18

ketone **25** to the desired alcohol **23**, we employed various Ireland using a different route.[17] In order to convert hydride reducing agents. All reagents studied give mixtures of **23** and **18**, with the former predominating in each case (see Table II). While lithium aluminum

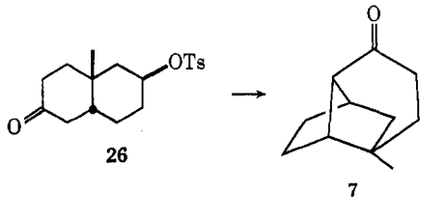
TABLE II
HYDRIDE REDUCTION OF KETO KETAL **25**

Reducing agent	Product composition, % Alcohol **23**	Alcohol **18**
$LiAlH_4$	54	46
Li(*tert*-BuO)$_3$AlH	70	30
Li(*tert*-AmO)$_3$AlH[a]	72	28
Li(Et$_3$CO)$_3$AlH[a]	71	29
Lithium perhydro-9b-boraphenalylhydride[b]	68	32

[a] H. C. Brown and R. F. McFarlin, *J. Amer. Chem. Soc.*, **80**, 5372 (1958). [b] H. C. Brown and W. C. Dickason, *ibid.*, **92**, 709 (1970).

hydride gives only a sight predominance of the axial alcohol, the more bulky reagent lithium tri-*tert*-butoxyaluminum hydride yields 70% of the axial alcohol. Increasing the bulk of the reducing agent still further has little effect on the product ratio.

The 70:30 mixture of epimeric alcohols **23** and **18** was deketalized and treated with *p*-toluenesulfonyl chloride in pyridine to afford the corresponding mixture of keto tosylates. The major keto tosylate (**26**) was obtained in pure form by fractional crystallization of the mixture of epimers. When keto tosylate **26** is treated with 1 equiv of potassium *tert*-butoxide in *tert*-butyl alcohol, it is cleanly converted into the tricyclic ketone **7** (91% yield), identical in all respects with the material obtained from rearrangement of ketone **5** (*vide supra*).



26 7

With the structures of the four rearrangement products rigorously established, we may now consider possible modes for their formation. A probable mechanism for formation of the tricyclic ketone **6** is outlined in Chart I. Ring expansion of the protonated ketone gives the secondary carbonium ion **27**, which undergoes a subsequent alkyl migration to ketone **6**. As seen in Table I, approximately 20% of ketone **5** reacts by this *ring expansion* route.

(10) H. C. Brown and P. Geohagen, Jr., *J. Amer. Chem. Soc.*, **89**, 1522 (1967).
(11) C. H. Heathcock, R. A. Badger, and J. W. Patterson, Jr., *ibid.*, **89**, 4133 (1967).
(12) E. J. Corey and M. Chaykovsky, *ibid.*, **87**, 1345 (1965).
(13) C. H. Heathcock and R. Ratcliffe, *J. Org. Chem.*, in press.
(14) H. C. Brown and A. W. Moerikofer, *J. Amer. Chem. Soc.*, **85**, 2063 (1963).
(15) E. F. Knights and H. C. Brown, *ibid.*, **90**, 5280, 5281 (1968).
(16) R. Ratcliffe and R. Rodehorst, *J. Org. Chem.*, **35**, 4000 (1970).
(17) R. F. Church, R. E. Ireland, and D. R. Shridhar, *ibid.*, **27**, 707 (1962).

CHART I

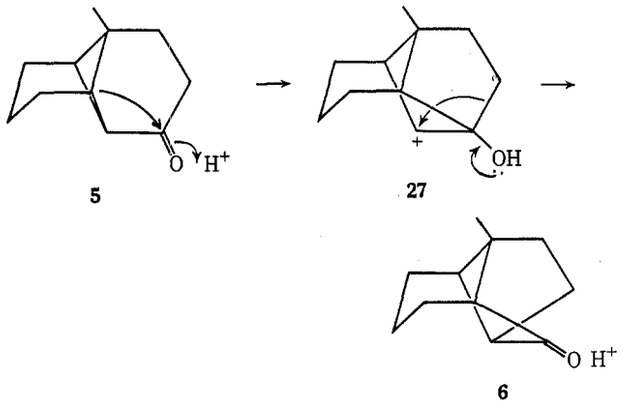
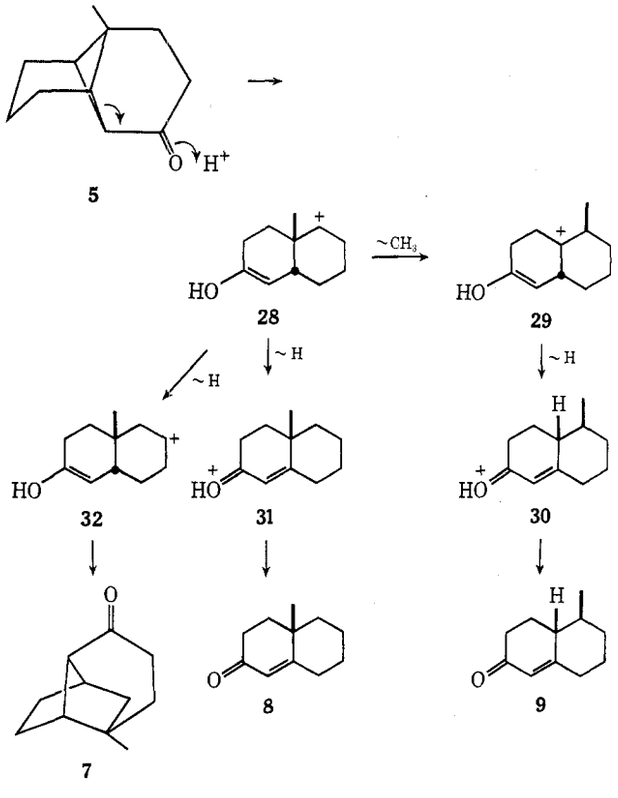


CHART II



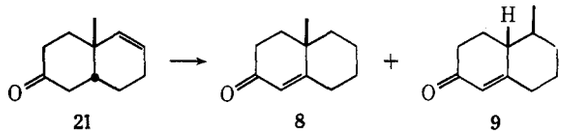
The remaining three products can be rationalized by a route involving *ring opening* of ketone **5** (Chart II). The initially formed cation **28** can undergo 1,2-methide migration to ion **29**, followed by 1,2-hydride migration to yield oxomium ion **30**.[18] Deprotonation of **30** then yields octalone **9**. Alternatively, ion **28** may undergo 1,3-hydride shift, producing oxonium ion **31**. Subsequent deprotonation of this species yields octalone **8**. When ion **28** undergoes 1,2-hydride shift to ion **32**, the positive charge may be immediately discharged by intramolecular alkylation of the enol grouping. The resulting product is tricyclic ketone **7**. Precedent for such a reaction has been provided by Stork and Grieco.[19] The scheme outlined in Chart II may well be a greatly oversimplified version of what actually transpires. We have neglected the possibility of intermediate sulfates and olefins and the keto forms of ions **28**, **29**, and **32**.

(18) Oxonium ion **30** may also be formed from **29** by a deprotonation–reprotonation mechanism.

(19) G. Stork and P. A. Grieco, *J. Amer. Chem. Soc.*, **91**, 2407 (1969).

Approximately 80% of ketone **5** apparently reacts by this ring-opening route.

In an experiment designed to shed further light on the hypothetical genesis of products **7**, **8**, and **9**, octalone **21**[11] was treated with concentrated sulfuric acid. In



this reaction, octalones **8** and **9** are produced in a ratio of 48:52. None of the tricyclic ketone **7** is formed. In this case reaction probably occurs by way of keto carbonium ions, rather than by way of enolic cations **28**, **29**, and **32**.

Experimental Section

Melting points (Pyrex capillary) and boiling points are uncorrected. Infrared spectra (ir) were recorded on Perkin-Elmer 137 and 237 spectrophotometers. Proton magnetic resonance spectra (pmr) were reported on Varian A-60 and T-60 spectrometers. Line positions are given in the δ scale, with internal tetramethylsilane as standard. The multiplicity, peak areas, coupling constants, and proton assignments are given in parentheses. Ultraviolet spectra (uv) were measured on a Perkin-Elmer 202 spectrophotometer. Consolidated 21-103c and Varian M-66 mass spectrometers provided the mass spectra. High-resolution molecular weight determinations were obtained on a Consolidated 21-110 spectrometer.

Gas liquid partition chromatography (glpc) analyses were performed on Aerograph Models 204B, A90-P, and A90-P3 instruments. Silica Gel G was used for thin layer chromatography (tlc) and Silica Gel PF_{254} for preparative tlc. Elemental analyses were performed by the Microanalytical Laboratory, operated by the Department of Chemistry, University of California, Berkeley, Calif.

Acid-Catalyzed Rearrangement of Ketone 5. A. Analytical Runs.—In a typical run, 1.64 g of ketone **5**[11] was dissolved in 4 ml of concentrated sulfuric acid. The resulting dark red solution was placed in a stoppered flask and stirred at room temperature for 1 week. At the end of this time, the solution was pured into 25 ml of water and the aqueous mixture was extracted with ether (2 × 25 ml). The ethereal solution was washed with 1 *N* NaOH (2 × 20 ml), dried, and evaporated to yield 1.40 g of product as a pale yellow oil. The product was analyzed by glpc (6 ft × 0.25 in 10% FFAP on Chromosorb W at 180°). Four volatile products were present: 19% **6** (retention time 6.9 min), 33% **7** (9.6 min), 10% **8** (12.9 min), and 38% **9** (14.1 min). Similar runs were done for periods of 2 hr, 2 days, and 2 weeks. The results are collected in Table I.

B. Characterization of Products.—To 24.23 g of tricyclic ketone **5** in a 125-ml Erlenmeyer flask was added 50 ml of concentrated sulfuric acid. The flask was stoppered and the mixture was stirred for 65 hr at room temperature. The reaction mixture was poured into 350 ml of ice–water and extracted with ether (2 × 400 ml). The ether extracts were washed with 1 *N* sodium hydroxide and water, and dried over magnesium sulfate. The ether was removed by rotary evaporation to afford 19.98 g of brown oil. The oil was chromatographed on 1.75 kg of SilicAR CC-7 to which 10% water had been added. The column was eluted with mixtures of ether in pentane ranging from 2.5% ether to 8% ether. A total of 1496 fractions of 20 ml each were collected. Every tenth fraction was monitored by both tlc and glpc (150 ft × 0.01 in. SF-96 at 145°).

Fractions 397–416 were found to contain 1.069 g of a single compound, **6**. An analytical sample, mp 81–83°, was obtained after two sublimations at 40° (0.1 mm): ir (CCl_4) 1750, 1467, 1443, 1380, 1075 cm^{-1}; pmr (CCl_4) δ 1.17 (s, 3, bridgehead Me), 2.37 (d, 1, J = 4 Hz, bridgehead H).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.28; H, 9.79.

The 2,4-dinitrophenylhydrazone melts at 132–134° after two recrystallizations from 95% ethanol.

Fractions 558–652 were found to contain 2.073 g of a single

compound, 7, by glpc. This material was distilled through a short-path microstill to give 7 as a water-white, low-melting solid, bp 50° (0.3 mm). The analytical sample was obtained as colorless plates, mp 35–36°, after sublimation at 40° (0.65 mm): ir (CCl_4) 1706, 1475, 1450, 1410, 1375, 1284, 1257, 1078, 1029, 971 cm^{-1}; pmr (CCl_4) δ 1.12 (s, 3, bridgehead Me).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.20; H, 9.64.

The 2,4-dinitrophenylhydrazone was obtained as brilliant orange plates, mp 205–208°, after two recrystallizations from ethanol–ethyl acetate.

Anal. Calcd for $C_{17}H_{20}N_4O_4$: C, 59.29; H, 5.85; N, 16.27. Found: C, 59.15; H, 5.86; N, 16.46.

Fractions 703–1004 were found to contain 5.025 g of a 40:60 mixture of 8 and 9. Analytical samples of 8 and 9 were obtained by preparative glpc (10 ft × 0.25 in. 4% FFAP on Chromosorb G at 180°). The ir and pmr spectra of compound 8 were identical with the corresponding spectra of the known octalone 8.[2]

Compound 9 exhibited the following properties: ir (CCl_4) 3050, 1680, 1629, 1447, 1376, 1351, 1326, 1255, 1209, 1120, 959, 886, 862 cm^{-1}; pmr (CCl_4) δ 1.07 (broad s, 3, $W_{1/2}$ = 5 Hz, Me), 5.65 (broad s, 1, $W_{1/2}$ = 4 Hz, olefinic H); uv (95% EtOH) λ_{max} 238 mμ (ϵ_a 12,200).

Anal. Calcd for $C_{11}H_{16}O$: mol wt, 164.1201. Found: mol wt, 164.1196 (high-resolution mass spectroscopy).

Fractions 1005–1180 were composed primarily of compound 9 along with a complex mixture of more polar substances. The remaining fractions (1181–1496) contained an unidentifiable mixture of products in trace amounts.

Treatment of Ketones 6–9 with Sulfuric Acid.—In order to check the stability of the rearrangement products, each was subjected to the above reaction conditions. A typical procedure follows. A mixture of 61 mg of tricyclic ketone 6 in 1 ml of concentrated sulfuric acid was kept at room temperature for 46 hr. The solution was then poured into 10 ml of water and worked up in the normal manner. The crystalline product (51.6 mg) was shown to be unreacted ketone 6 by pmr and glpc (6 ft × 0.25 in. FFAP at 180°). Similar experiments were carried out on ketones 7, 8, and 9. In each case, the starting ketone was recovered unchanged in at least 89% yield.

Base-Catalyzed Rearrangement of Tricyclic Ketone 6.—A mixture of 105 mg of tricyclic ketone 6 (0.64 mmol), 140 mg of potassium *tert*-butoxide (1.25 mmol), and 3 ml of *tert*-butyl alcohol was vacuum sealed in a thick-walled Pyrex tube and heated for 1 week at 185°.[8] The tube was opened after cooling and the contents were washed into a separatory funnel with pentane. The pentane layer was washed three times with water and dried over magnesium sulfate. The solvent was removed by rotary evaporation to afford 86.2 mg (82%) of semicrystalline solid. The spectral and chromatographic properties of this material were identical with those of tricyclic ketone 13, prepared as previously described.[1]

Deuteration of α,β-Unsaturated Ketone 9.—The deuterated enone was obtained by preparative glpc (6 ft × 0.25 in. 10% KOD, 20% Carbowax on Chromosorb W 60/80 at 180°). The deuterated sample was analyzed for deuterium content by mass spectroscopy, which showed 2.3% $C_{11}H_{13}D_3O$, 10.8% $C_{11}H_{12}D_4O$, 34.9% $C_{11}H_{11}D_5O$, and 51.2% $C_{11}H_{10}D_6O$.

5β-Methyl-3,4,4aβ,5,6,7,8,8aβ-Octahydronaphthalen-2(1*H*)-one (10).—A mixture of 15 mg of 10% palladium on carbon and 1 ml of ethyl acetate was placed in a 10-ml round-bottom flask equipped with a magnetic stirrer and a sidearm fitted with a serum cap. The catalyst was prereduced on a low-pressure hydrogenation apparatus, and a solution of 75 mg of enone 9 in 2 ml of ethyl acetate was added by syringe. The reaction mixture was stirred at room temperature until hydrogen uptake ceased. The catalyst was filtered and washed with a few milliliters of ethyl acetate. The filtrate was evaporated at reduced pressure to afford 69 mg of ketone 10 as a colorless liquid. An analytical sample was obtained by preparative glpc (6 ft × 0.25 in. 10% FFAP at 160°); ir (CCl_4) 1716, 1449, 1376, 1263, 1224, 1155 cm^{-1}; pmr (CCl_4) δ 0.98 (d, 3, J = 6 Hz, Me).

Anal. Calcd for $C_{11}H_{18}O$: mol wt, 166.1357. Found: mol wt, 166.1353 (high-resolution mass spectroscopy).

Preparative glpc gave the deuterated ketone (6 ft × 0.25 in. 10% KOD, 20% Carbowax 20M on Chromosorb W 60/80 at 180°). Mass spectral analysis showed that the sample contained 5.9% $C_{11}H_{16}D_2O$, 17.8% $C_{11}H_{15}D_3O$, and 76.3% $C_{11}H_{14}D_4O$.

7β-Methyl-4,4aβ,5,6,7,8-hexahydronaphthalen-2(3*H*)-one (11) and 5β-Methyl-4,4aβ,5,6,7,8-hexahydronaphthalen-2(3*H*)-one (9).—A solution of 22.4 g (0.2 mol) of 3-methylcyclohexanone in 70 ml of ether was placed in a 200-ml three-neck flask equipped with magnetic stirrer, condenser, and dropping funnel. The solution was cooled to 0° on an ice bath, and a solution of 2.3 g of potassium hydroxide in 7 ml of 95% ethanol was added with stirring, followed by the dropwise addition of 7.009 g (0.1 mol) of freshly distilled methyl vinyl ketone in 45 ml of ether over a period of 1.5 hr. The ice bath was removed and the reaction mixture was stirred for an additional 12 hr at room temperature. The mixture was washed with water (3 × 50 ml) and dried over magnesium sulfate. The solvent was removed by rotary evaporation, and the residue was distilled through a 4-*in.* Vigreux to afford 5.12 g of 3-methylcyclohexanone, bp 26–31° (1.5 mm), 6.71 g of clear liquid, bp 90–94° (0.5 mm), and 7.73 g of yellow oil, bp 144° (0.5 mm).

The fraction boiling at 90–94° (0.5 mm) was analyzed by glpc (10 ft × 0.25 in. 4% FFAP on Chromosorb G at 180°), and was found to contain three components in the ratio of 13:67:20 with retention times of 12.3, 22.5, and 24.3 min, respectively.

The major component was identified as compound 11: ir (CCl_4) 3040, 1680, 1630, 1452, 1376, 1325, 1253, 1208, 914, 899, 854 cm^{-1}; pmr (CCl_4) δ 1.00 (unresolved d, 3, Me), 5.68 (broad s, 1, $W_{1/2}$ = 4 Hz, olefinic H).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.28; H, 9.64.

The component with a retention time of 24.3 min was identical with α,β-unsaturated ketone 9 isolated from the rearrangement of ketone 5 (*vide supra*). This material was also identical with a sample of ketone 9 prepared by another route.[7]

6α-Hydroxy-4aβ-methyl-3,4,4a,5,6,7,8,8aβ-octahydronaphthalen-2(1*H*)-one Ethylene Ketal (18).—In a 500-ml Erlenmeyer flask equipped with magnetic stirrer were placed 23.9 g (0.075 mol) of mercuric acetate, 75 ml of water, 75 ml of tetrahydrofuran, and 10.4 g (0.05 mol) of unsaturated ketal 17.[11] The mixture was stirred at room temperature for 27 hr, during which time the bright yellow complex turned colorless. To the mixture was added 75 ml of 3 *N* sodium hydroxide, followed by 75 ml of 0.5 *N* sodium borohydride in 3 *N* sodium hydroxide. Demercuration was instantaneous. The aqueous layer was extracted with 250 ml of ether. The combined organic layers were washed with water (200 ml) and brine and dried over magnesium sulfate. The solvent was removed by rotary evaporation to afford 10.10 g of crude ketal alcohol 18 as a clear viscous oil. An analytical sample was obtained by preparative glpc (5 ft × 0.25 in. 20% Carbowax 20M at 195°): ir (CCl_4) 3400 (broad), 1445, 1350, 1089 cm^{-1}; pmr (CCl_4) δ 0.97 (s, 3, angular Me).

Anal. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 68.87; H, 9.58.

4aβ-Methyl-6α-toluenesulfonyloxy-3,4,4a,5,6,7,8,8aβ-octahydronaphthalen-2(1*H*)-one Ethylene Ketal (19).—To a 50-ml Erlenmeyer flask equipped with a magnetic stirrer was added a solution of 2.815 g (12.45 mmol) of crude ketal alcohol 18 in 13 ml of anhydrous pyridine, followed by a solution of 2.44 g (12.8 mmol) of *p*-toluenesulfonyl chloride in 8 ml of anhydrous pyridine. The solution was allowed to stand at room temperature for 101 hr. The reaction mixture was poured onto 60 ml of ice–water and extracted with methylene chloride (25 ml, 3 × 12 ml). The combined organic extracts were washed with 10% sulfuric acid (4 × 25 ml), water (12 ml), and brine (12 ml), and dried over magnesium sulfate. The solvent was removed by rotary evaporation to afford 5.208 g (80%) of crude ketal tosylate 19 as a crystalline white solid. The crude material was recrystallized from ethyl acetate–hexane to afford 3.562 g of white crystals: mp 113.5–115.0°; ir (CCl_4) 1358, 1188, 1175, 1095, 945, 934, 880, 850, 815 cm^{-1}; pmr (CCl_4) δ 0.99 (s, 3, angular Me), 2.47 (s, 3, aryl Me), 3.85 (s, 4, ketal ethylene), 4.65 (broad m, 1, $W_{1/2}$ = 18 Hz, C-6 H), 7.55 (A_2B_2 with δ_A 7.78 and δ_B 7.34, 4, J_{AB} = 8 Hz, aryl H's).

Anal. Calcd for $C_{20}H_{28}O_5S$: C, 63.10; H, 7.42; S, 8.43. Found: C, 62.86; H, 7.02; S, 8.34.

4aβ-Methyl-3,4,4a,5,6,7,8,8aβ-octahydronaphth-6α-ol-2(1*H*)-one *p*-Toluenesulfonate (20).—A solution of 0.4 ml of concentrated sulfuric acid and 3.6 ml of water was added to a solution of 2.128 g of ketal tosylate 19 in 20 ml of acetone at 50°. The colorless solution was stirred at 50° for 45 min, cooled to room temperature, and concentrated to approximately 6 ml by rotary evaporation. The viscous liquid remaining was dissolved in ether, washed with 5% sodium bicarbonate and brine, and dried over magnesium sulfate. The solvent was removed by rotary evaporation to afford 1.834 g of semicrystalline material. Re-

crystallization from ethyl acetate–hexane yielded 1.442 g of keto tosylate **20** as white clusters: mp 77.3–78.0°; ir (CCl_4) 1718, 1600, 1366, 1190, 1180, 1100, 940, 856, 820 cm^{-1}; pmr (CCl_4) δ 1.09 (s, 3, angular Me), 2.48 (s, 3, aryl Me), 4.72 (broad m, 1, $W_{1/2}$ = 17 Hz, C-6 H), 7.57 (A_2B_2 with δ_A 7.79 and δ_B 7.34, 4, J_{AB} = 8 Hz, aryl H's).

Anal. Calcd for $C_{18}H_{24}O_4S$: C, 64.26; H, 7.19; S, 9.53. Found: C, 64.43; H, 7.06; S, 9.33.

A 0.5 *M* solution of methylsulfinyl carbanion in dimethyl sulfoxide was prepared according to the procedure of Corey.[12] This solution (4 ml) was added to a solution of 672.4 mg (2.0 mmol) of keto tosylate **20** in 4 ml of dimethyl sulfoxide under nitrogen, and the resulting solution was stirred at 60° for 2 hr. The reaction mixture was cooled, diluted with 15 ml of water, and extracted with ether (3 × 10 ml). The combined ether extracts were washed with water (10 ml) and brine (10 ml) and dried over magnesium sulfate. Removal of the solvent by rotary evaporation afforded 315.4 mg of yellow oil. Analysis by glpc (10 ft × 0.25 in. 4% FFAP on Chromosorb G at 180°) showed the product to be a 60:40 mixture of octalones **21** and **22** by coinjection with authentic samples.[13]

4aβ-Methyl-3,4,4a,5,8,8aβ-hexahydronaphthalen-2(1*H*),6-(7*H*)-dione 2-Ethylene Ketal (25).—To a 1-l. round-bottom flask equipped with magnetic stirrer and drying tube was added 42.0 g (0.531 mol) of anhydrous pyridine and 480 ml of anhydrous methylene chloride. The solution was stirred on an ice bath and 26.5 g (0.265 mol) of chromium trioxide was added all at once.[16] The orange-brown solution was stirred for 75 min, during which time the solution warmed to room temperature. A solution of 9.984 g (0.0442 mol) of crude ketal alcohol **18** dissolved in 80 ml of anhydrous methylene chloride was added, and stirring was continued for 45 min at room temperature. The methylene chloride solution was decanted from the black tarry residue and the residue was washed with ether (3 × 200 ml). The combined organics were washed with 5% sodium hydroxide (2 × 300 ml), water (300 ml), 5% hydrochloric acid (2 × 300 ml), 5% sodium bicarbonate (300 ml), and brine (300 ml) and dried over magnesium sulfate. The solvent was removed by rotary evaporation to afford 8.48 g of crude keto ketal **25** as a yellow oil. The crude product was dissolved in 5 ml of ether, and 20 ml of petroleum ether (bp 30–75°) was added. After standing in the refrigerator overnight, 6.59 g of white crystalline material was collected. Two additional crops yielded a total of 7.77 g, mp 76–78°. The analytical sample melts at 79–80° (lit.[17] mp 79.5–80.5°) after two recrystallizations from ether–petroleum ether: ir (CCl_4) 1715, 1445, 1362, 1229, 1153, 1094, 943, 872 cm^{-1}; pmr (CCl_4) δ 0.94 (s, 3, angular Me), 3.84 (s, 4, ketal ethylene).

Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.37; H, 8.77.

Hydride Reduction of Ketone 25. A. With Lithium Aluminum Hydride.—In a 25-ml flask equipped with magnetic stirrer, reflux condenser, and drying tube was placed a mixture of 51 mg (1.34 mmol) of lithium aluminum hydride and 10 ml of anhydrous ether. To the stirring mixture was added 100 mg (0.446 mmol) of crystalline ketone **25**. After stirring for 3 hr at room temperature, excess hydride was decomposed by the careful addition of 5% potassium hydroxide. The white precipitate was filtered and washed with ether. The filtrate was dried over magnesium sulfate and evaporated to afford 96 mg of clear liquid. The pmr spectrum showed the product to be a 46:54 mixture of the epimeric alcohols **18** and **23**.

B. With Lithium Tri-*tert*-butoxyaluminum Hydride.—To a 10-ml Erlenmeyer flask equipped with magnetic stirrer was added a solution of 100 mg (0.446 mmol) of compound **25** in 2 ml of anhydrous tetrahydrofuran. The solution was cooled in an ice bath and 200 mg (0.76 mmol) of lithium tri-*tert*-butoxyaluminum hydride in 2 ml of anhydrous tetrahydrofuran was added. The reaction mixture was stirred for 3.5 hr, during which time the mixture was allowed to warm to room temperature. Excess hydride was destroyed by careful addition of 5% potassium hydroxide. The white precipitate was filtered, and the filtrate was dried over magnesium sulfate. Evaporation of the solvent afforded 104.7 mg of clear liquid. The pmr spectrum showed the product to be a 29.5:70.5 mixture of the epimeric alcohols **18** and **23**.

C. With Lithium Tri-*tert*-amyloxyaluminum Hydride.—To a 10-ml Erlenmeyer flask equipped with magnetic stirrer was added a solution of 100 mg (0.446 mmol) of keto ketal **25** in 2 ml of anhydrous tetrahydrofuran. The solution was cooled to 0° on an ice bath and 250 mg (0.844 mmol) of lithium tri-*tert*-amyloxyaluminum hydride in 2 ml of anhydrous tetrahydrofuran was added. The reaction mixture was stirred overnight, during which time it was allowed to warm to room temperature. Excess hydride was destroyed by careful addition of 5% potassium hydroxide. The white precipitate was filtered and washed with a few milliliters of tetrahydrofuran. The filtrate was dried over magnesium sulfate and evaporated at reduced pressure to afford 87.7 mg of viscous, clear liquid. The pmr spectrum indicated the product to be a 28:72 mixture of alcohols **18** and **23**.

D. With Lithium Tri(3-ethyl-3-pentoxy)aluminum Hydride.—To a 10-ml Erlenmeyer flask equipped with magnetic stirrer was added a solution of 100 mg (0.446 mmol) of keto ketal **25** in 2 ml of anhydrous tetrahydrofuran. The solution was cooled in an ice bath and 300 mg (0.788 mmol) of lithium tri(3-ethyl-3-pentoxy)aluminum hydride in 3 ml of anhydrous tetrahydrofuran was added. The reaction mixture was stirred for 70 hr at room temperature. Excess hydride was destroyed by careful addition of 5% potassium hydroxide. The white precipitate was filtered and washed with tetrahydrofuran. The filtrate was dried over magnesium sulfate and evaporated at reduced pressure to afford 294.2 mg of yellowish liquid. The crude product was chromatographed on basic alumina (Woelm, activity I), eluting with ether–benzene mixtures. There was obtained 90.7 mg of clear liquid, whose pmr spectrum showed a 29:71 mixture of alcohols **18** and **23**.

E. With Lithium Perhydro-9b-boraphenalylhydride.—To a 50-ml three-neck flask equipped with magnetic stirrer, reflux condenser, nitrogen inlet, and rubber serum cap was added 13 ml of a 0.575 *M* (7.5 mmol) solution of lithium perhydro-9b-boraphenalylhydride in tetrahydrofuran followed by 1.12 g (5 mmol) of keto ketal **25** in 2 ml of tetrahydrofuran. The solution was stirred at room temperature in a nitrogen atmosphere for 16 hr, and 3.75 ml of 3 *N* sodium hydroxide was added followed by 3.75 ml of 30% hydrogen peroxide. The organic layer was separated and washed with 5 ml of solvent which was removed at the rotary evaporator. Addition of ether to the crude product resulted in the precipitation of a yellow solid, which was filtered. The filtrate was evaporated to afford 0.972 g of viscous liquid, whose pmr spectrum showed it to be a 32:68 mixture of alcohols **18** and **23**.

4aβ-Methyl-3,4,4a,5,6,7,8,8aβ-octahydronaphth-6β-ol-2(1*H*)-one p-Toluenesulfonate (26).—A solution of 917 mg of a 70:30 mixture of ketal alcohols **23** and **18** in 20 ml of acetone was heated to 50°. A solution of 0.4 ml of concentrated sulfuric acid in 3.6 ml of water was added and the clear solution was kept at 50° for 45 min. The reaction mixture was cooled to room temperature and concentrated to approximately 5 ml by rotary evaporation. The concentrate was dissolved in ether and washed with 5% sodium bicarbonate and brine. After drying over magnesium sulfate, the solvent was removed by rotary evaporation to afford 411.3 mg of a mixture of keto alcohols. This material was dissolved in 2.5 ml of anhydrous pyridine and added to a solution of 475 mg of *p*-toluenesulfonyl chloride. The mixture was stirred to make it homogeneous and allowed to stand for 134 hr at room temperature. The reaction mixture was poured into 15 ml of water and extracted with chloroform (10 ml, 3 × 5 ml). The combined organic extracts were washed with 10% sulfuric acid (4 × 5 ml), water (5 ml), and brine (5 ml), and dried over magnesium sulfate. Evaporation of the solvent at reduced pressure afforded 576 mg of viscous liquid. This material was induced to crystallize from ethyl acetate–hexane to yield 203 mg of white crystalline keto tosylate **26**. An analytical sample was obtained by recrystallization from ethyl acetate–hexane to give white clusters: mp 105–107°; ir (CCl_4) 1718, 1603, 1453, 1364, 1190, 1178, 1099, 958, 950, 919, 857 cm^{-1}; pmr (CCl_4) δ 1.26 (s, 3, angular Me), 2.45 (s, 3, aryl Me), 4.57 (broad m, 1, $W_{1/2}$ = 18 Hz, C-6 H), 7.51 (A_2B_2 with δ_A 7.72 and δ_B 7.31, 4, J_{AB} = 8.5 Hz, aryl H's).

Anal. Calcd for $C_{18}H_{24}O_4S$: C, 64.26; H, 7.19; S, 9.53. Found: C, 64.07; H, 6.99; S, 9.40.

6-Methyltricyclo[4.4.0.0^{2,8}]decan-3-one (7).—To a solution of 28.1 mg (0.25 mmol) of potassium *tert*-butoxide in 1 ml of anhydrous *tert*-butyl alcohol was added 90 mg (0.268 mmol) of crystalline keto tosylate **26**. The mixture was refluxed under nitrogen for 3 hr and poured into 3 ml of ice-cold water. The resulting mixture was extracted with ether (2 × 2 ml). The combined ether extracts were washed with water (3 × 1 ml) and dried over magnesium sulfate. The solvent was removed by rotary evaporation to afford 40 mg (91%) of crude tricyclic ketone **7** as an orange-tinted semisolid. An analytical sample was obtained

by preparative glpc (10 ft × 0.25 in. 10% SE-30 at 170°). The spectral properties of this material were identical in all respects to those of the material isolated from the acid-catalyzed rearrangement of tricyclic ketone **5** (*vide supra*).

Acid-Catalyzed Rearrangement of Octalone 21.—To 821.4 mg of octalone **21**[11] in a 10-ml Erlenmeyer flask was added 2 ml of concentrated sulfuric acid. The flask was stoppered and the brown mixture was stirred for 2 days at room temperature. The mixture was poured into 15 ml of ice–water and extracted with ether (2 × 15 ml). The combined extracts were washed with 20 ml of 1 *N* sodium hydroxide and dried over magnesium sulfate. The solvent was evaporated to afford 646.8 mg of yellow oil. Glpc analysis of the product (6 ft × 0.25 in. 10% FFAP at 180°) revealed the presence of two components in a ratio of 48:52. The two components were identified as the α,β-unsaturated ketones **8** and **9**, respectively, by comparison of their spectra with those of authentic samples.

Registry No.—**5**, 17159-66-9; **6**, 18503-74-7; **6** 2,4-DNP, 18503-75-8; **7**, 33830-72-7; **7** 2,4-DNP, 33830-73-8; **9**, 33835-42-6; **10**, 33835-43-7; **11**, 33835-44-8; **18**, 25826-87-3; **19**, 33835-46-0; **20**, 33835-47-1; **25**, 33835-48-2; **26**, 33835-49-3.

Acknowledgments.—We thank the National Science Foundation and the Alfred P. Sloan Foundation for financial support.

Strained Ring Systems. XI.[1a] The Synthesis of Benzobicyclo[2.2.0]hexa-2,5-diene, Benzobicyclo[2.2.0]hex-2-ene, and Benzobicyclo[2.2.0]hex-5-en-*exo*-2-ol[1b]

RICHARD N. McDONALD,* D. G. FRICKEY,[1c] AND GARY M. MUSCHIK[1c]

Department of Chemistry, Kansas State University, Manhattan, Kansas 66502

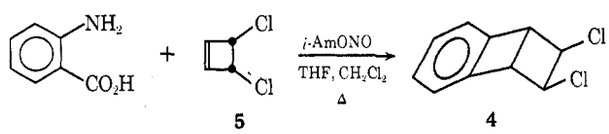
Received October 4, 1971

This paper describes the cycloaddition of benzyne with *cis*-3,4-dichlorocyclobutene to give *exo,cis*-5,6-dichlorobenzobicyclo[2.2.0]hex-2-ene (**4**), the disodium–phenanthrene dechlorination of **4** to benzobicyclo[2.2.0]-hexa-2,5-diene (**2**), the diimide reduction of **2** to benzobicyclo[2.2.0]hex-2-ene (**3**), and the hydroboration of **2** to benzobicyclo[2.2.0]hex-5-en-*exo*-2-ol (**8**). Some of the spectral features of these compounds are discussed.

When Dewar in 1867[2] reported his results from the oxidation of phenol, he suggested the use of a model by which he could construct the various structural isomers of a given molecular formula. For the formula C_6H_6, one of the structures written was that of bicyclo[2.2.0]-hexa-2,5-diene (**1**), which has become known as "Dewar benzene." Nearly 100 years later, van Tamelen and Pappas[3] reported the successful synthesis of **1**. Since that report various syntheses and studies of the chemistry of derivatives of **1** have been reported.

In our continuing program of the chemistry of molecules incorporating the [2.2.0] system, we felt that it would be most useful to develop a synthesis of benzobicyclo[2.2.0]hexa-1,5-diene ("hemi Dewar naphthalene")[4] (**2**) which might also be applicable to the preparation of 1-substituted derivatives of benzobicyclo[2.2.0]hex-2-ene (**3**). Since **2** should be convertible to 5-substituted derivatives of **3**, this approach would make available this set of compounds for further study. Such a synthetic approach has been achieved and is the subject of this paper.

Synthesis.—Conceptually, the approach was to prepare *cis*-5,6-dichlorobenzobicyclo[2.2.0]hex-2-ene (**4**) by the cycloaddition of benzyne and *cis*-3,4-



5 **4**

dichlorocyclobutene[7] (**5**) and then to seek methods for dechlorination of **4** to **2**. Two methods were carried out for the cycloaddition reaction. One involved the *in situ* generation of the benzyne precursor and benzyne itself;[8a] only 0.1% of **4** was obtained. The second method involved isolation of the benzyne precursor, benzenediazonium-2-carboxylate (**6**),[8b] and allowing it to decompose thermally in the presence of **5**. Yields of **4** ranging from 2.4 to 11.3% were obtained depending on the ratio of **5**:**6** used. The impurities in the crude reaction mixture appeared to be largely aromatic from the nmr spectrum; one of these was benzoic acid. Chromatography on basic, activity I alumina and elution with carbon tetrachloride gave quite pure **4** in the first few fractions. The infrared spectrum of **4** was fairly simple, indicating a high degree of symmetry in the tricyclic structure.

The nmr spectrum (CCl_4, internal TMS) of **4** exhibited absorptions centered at τ 2.80 (m, 4), 5.55 (m, J = 0.9 Hz, 2), and 5.92 (m, J = 0.8 Hz, 2). The aromatic hydrogens were assigned to the finely split multiplet at τ 2.80 which is only 0.2 ppm lower field than the center of the aromatic proton multiplet of benzocyclobutene (τ 3.01).[9] Irrespective of how we wish to rationalize the assignments[10] of the latter two absorptions (C_1, C_4 bridgehead *vs.* C_5, C_6 methine protons), the fact that the coupling constants are so small

(1) (a) Paper X: R. N. McDonald and E. P. Lyznicki, *J. Amer. Chem. Soc.*, **93**, 5920 (1971). (b) Part of this research was communicated in R. N. McDonald and D. G. Frickey, *ibid.*, **90**, 5315 (1968). (c) Taken from the M.S. thesis of D. G. Frickey, 1968, and the Ph.D. thesis of G. M. Muschik, 1972.

(2) (a) J. Dewar, *Proc. Roy. Soc. Edinburgh*, 84 (1866); (b) W. Baker, *Chem. Brit.*, **1**, 191 (1965), discusses Dewar's paper, and some of the efforts to synthesize **1** and its various derivatives.

(3) E. E. van Tamelen and S. P. Pappas, *J. Amer. Chem. Soc.*, **85**, 3297 (1963).

(4) We are aware of only two other literature entries into this family of compounds which incorporate two of the classically considered structures of benzene fused into a single molecule; one is a bridged "Dewar anthracene" reported by Applequist and Searle,[5a] and the second is a report of the 1,2-dimethyl and 1,2,3,4-tetramethyl derivatives of **2**.[5b] The preparation of "hemi Dewar biphenyl," a compound in which the moieties are joined but not fused, has been described by Burt and Pettit.[6]

(5) (a) D. E. Applequist and R. Searle, *J. Amer. Chem. Soc.*, **86**, 1389 (1964); (b) D. T. Carty, *Tetrahedron Lett.*, 4753 (1969).

(6) G. D. Burt and R. Pettit, *Chem. Commun.*, 517 (1965).

(7) M. Avram, I. Dinulescu, M. Elian, M. Farcasiu, E. Marica, G. Mateescu, and C. D. Nenitzescu, *Chem. Ber.*, **97**, 372 (1964).

(8) (a) L. Friedman and F. M. Logullo, *J. Amer. Chem. Soc.*, **85**, 1549 (1963); (b) M. Stiles, R. G. Miller, and U. Burkhardt, *ibid.*, **85**, 1792 (1963).

(9) G. Fraenkel, Y. Asahi, M. J. Mitchell, and M. P. Cava, *Tetrahedron*, **20**, 1179 (1965).

(10) See S. J. Cristol and G. W. Nachtigall, *J. Org. Chem.*, **32**, 3738 (1967), for the assigned nmr spectrum of the related *exo,cis*-5,6-dichlorobicyclo-[2.2.1]hept-2-ene.