86, 478 (1964).
(9) R. A. Lee, C. Mc Andrews, K. Patel, and W. Reusch, *Tetrahedron Lett.*, 965 (1973).
(10) (a) D. H. R. Barton and C. H. Robinson, *J. Chem. Soc.*, 3045 (1954); (b) G. Stork and S. D. Darling, *J. Am. Chem. Soc.*, 86, 1761 (1964).
(11) C. B. C. Boyce and J. S. Whitehurst, *J. Chem. Soc.*, 2680 (1960); cf. V. Prelog and D. Zäch, *Helv. Chim. Acta*, **49**, 1862 (1959).
(12) G. Bauduin and Y. Pietrasanta, *Tetrahedron*, **29**, 4225 (1973).
(13) (a) A. J. Birch, E. Pride, and H. Smith, *J. Chem. Soc.*, 4688 (1958); (b) C. H. Heathcock, R. Ratcliffe, and J. Van, *J. Org. Chem.*, **37**, 1796 (1972).
(14) D. J. Pasto and C. R. Johnson, "Organic Structure Determination", Prentice-Hall, Englewood Cliffs, N.J., 1969, p 382.
(15) N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry", Holden-Day, San Francisco, Calif., 1964, Chapter 2.
(16) G. Stork, P. Rosen, N. Goldman, R. V. Coombs, and J. Tsuji, *J. Am. Chem. Soc.*, **87**, 275 (1965).
(17) For a general discussion of reduction potentials and empirical rules for their prediction see: H. O. House, L. E. Huber, and M. J. Umen, *J. Am. Chem. Soc.*, **94**, 8471 (1972).
(18) A. I. Scott, "Interpretation of the Ultraviolet Spectra of Natural Products", Pergamon Press, New York, N.Y., 1964.
(19) C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems", Marcel-Dekker, New York, N.Y., 1970.
(20) R. Ratcliffe and R. Rodehorst, *J. Org. Chem.*, **35**, 4000 (1970).
(21) H. Stetter and W. Dierich, *Chem. Ber.*, **85**, 1061 (1952).
(22) R. D. Clark, J. E. Ellis, and C. H. Heathcock, *Synth. Comm.*, **3**, 347 (1973).

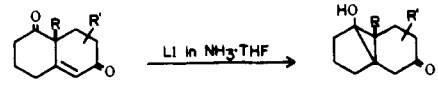
Transformations of Cyclopropanol Intermediates. 3. Ring-Opening Reactions of 6-Methyl-5-hydroxytricyclo[4.4.0.0^{1,5}]decan-9-one

William Reusch,* Kurt Grimm, Janice E. Karoglan, Jerrold Martin, K. P. Subrahamanian, P. S. Venkataramani, and John D. Yordy

Contribution from the Department of Chemistry, Michigan State University, East Lansing, Michigan 48824. *Received July 16, 1976*

Abstract: The tricyclic title compound (**1**) was transformed under a variety of acid- or base-catalyzed conditions to bicyclic isomers having spiro[5.4]decane (**2**), decalin (**3** and **4**), or perhydroindene (**5**) skeletons. Each of these isomeric classes could be favored by an appropriate choice of reaction conditions. Methanolic hydrochloric acid converted **1** to a mixture of isomeric cyclopropanol methyl ethers (**6** and **7**), which slowly reacted further to give ring-opened products. Acetate derivatives of the same isomeric cyclopropanols (**25** and **26**) were obtained when the conjugate base of **1** was quenched with acetic anhydride. Reactions of **1** with methanolic acid and base were compared with equivalent reactions of the corresponding diol, **19**, prepared by reduction of **1**. The dramatic influence of the carbonyl function in **1** on the cyclopropanol ring-opening reactions is clearly evident in the results. The ring-cleavage reactions of **19** were also compared with similar reactions of *endo*-7-hydroxybicyclo[4.1.0]-heptane (**22**) reported by Wharton and Bair.

Alkyl-substituted 5-hydroxytricyclo[4.4.0.0^{1,5}]decane derivatives are readily prepared by the reductive cyclization shown in eq 1.[1] Since these cyclopropanols are potentially

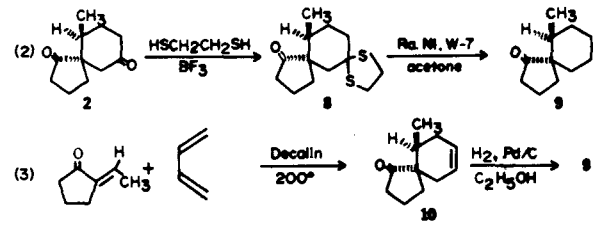


useful intermediates, we have studied their ring-opening reactions under a variety of acid- and base-catalyzed conditions. In this paper we discuss the behavior of cyclopropanol **1** derived from the Wieland–Miescher ketone (eq 1, R = CH_3, R′ = H), and shall endeavor to point out the ways in which its chemistry parallels or deviates from that of simpler analogues.

Results

The products obtained from the treatment of **1** with several different ring-opening reagents are listed in Table I. These reactions were monitored by a combination of TLC (silica gel) and GLC (QF-1), and pure samples of each major component were isolated by preparative GLC and/or crystallization. Identification of these compounds was achieved by a combination of mass spectrometric, infrared, and ^{1}H NMR measurements. The reactions were usually permitted to proceed to completion (TLC) before collecting the products, because unreacted **1** decomposes to several of the same compounds in the hot injection chamber of the gas chromatograph.

Authentic samples of *cis*- and *trans*-decalindiones **3** and **4** were prepared by established methods,[2] and their configurations were confirmed by the characteristic peak shapes of the angular methyl ^{1}H NMR signals.[3] The spirodiketone **2** was identified by its characteristic spectra (Experimental Section), and its conversion to spiroketone **9** (eq 2), which was independently synthesized by catalytic reduction of the Diels–Alder adduct from *trans*-2-ethylidenecyclopentanone[4] and 1,3-butadiene (eq 3).



Our elucidation of the structure of *trans*-1,6-dimethylbicyclo[4.3.0]nonane-2,7-dione (**5**) was accomplished in two independent stages. In the first, we effected a conversion of **5** to the saturated ketone **13** (eq 4), which was then compared

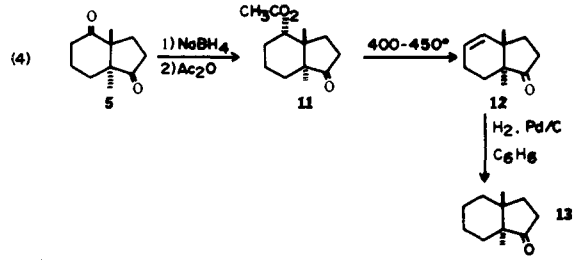
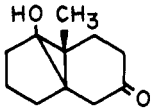
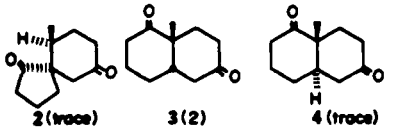
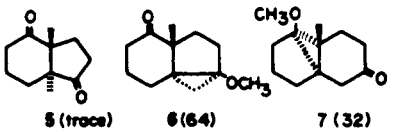
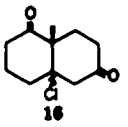
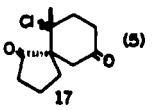


Table I. Ring Opening Reactions of

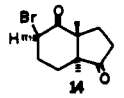


(1)

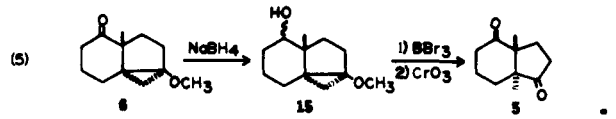
Reaction conditions	Products (% yield)
HCl, CH_3OH, 25 °C, 5 h	 2 (trace), 3 (2), 4 (trace)  5 (trace), 6 (64), 7 (32)
HCl, $CH_3OH + H_2O$, 25 °C, 10 h	2 (10), 3 (20), 5 (16), 6 (21), 7 (29)
HCl, glyme, 25 °C, 2 h	2 (11), 3 (80), 5 (9)
p-$C_7H_7SO_3H$, C_6H_6, 25 °C 20 h (0.15 equiv)	2 (32), 3 (18), 4 (6), 5 (44)
KOH, $CH_3OH + H_2O$, 25 °C, 3 h	2 (trace), 3 (20), 5 (80)
Guanidine, THF + HMPA, 25 °C, 10 h (0.01 equiv)	2 (76), 3 (8), 4 (15)
Guanidine, THF + HMPA, 25 °C, 10 h (20 equiv)	3 (20), 4 (trace), 5 (79)
1. NaH, C_6H_6 (slurry) 2. CH_3OH (rapid stirring)	2 (80), 3 (8), 4 (8)
$FeCl_3$, H_2O, 25 °C	 (>90).  (5)

with an authentic sample generously provided by Professor E. Wenkert.[5]

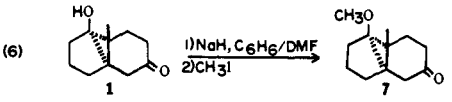
Since the melting points and ^1H NMR spectra of **13** and its 2,4-DNP derivative are similar to the corresponding properties of the cis-fused isomer, we felt that our long-range synthesis plans required an ironclad structure proof for the key intermediate **5**. To this end we undertook an x-ray structural analysis of the bromo derivative **14**,[6] and were pleased to find that this study confirmed our earlier assignment.[7]



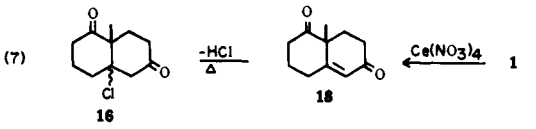
Methoxy ketone **6** was identified on the strength of its characteristic ^1H NMR, infrared, and mass spectra (Experimental Section) and its conversion to **5** by the sequence of reactions shown in eq 5.



The structure of isomer **7** is similarly supported by its spectroscopic properties. In addition, **7** was prepared independently from **1** by the alkylation procedure shown in eq 6.



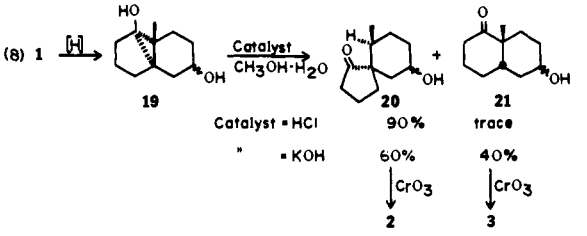
It has been established by deBoer and his co-workers[8] that tertiary cyclopropanols are readily oxidized by certain transition-metal cations (e.g., Fe^{3+} and Ce^{4+}). When ferric chloride is the oxidizing agent, β-chloro ketones are usually formed; however, in the case of **1** the major product (**16**) is unstable and undergoes rapid dehydrohalogenation on warming (eq 7).



Structure **17** is suggested for the minor product of the ferric chloride reaction.

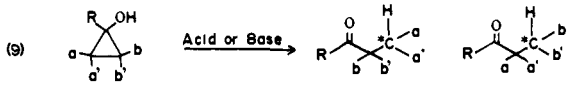
We find ceric nitrate oxidation of **1** to **18** to be a useful step in the workup of cyclopropanol reactions containing unreacted **1**, because it avoids the introduction of misleading products, such as those produced by GLC analysis of **1**.

In order to examine the influence of the carbonyl group in **1** on the course of cyclopropanol ring-opening reactions, we prepared the corresponding diol (**19**) by lithium in ammonia or sodium borohydride reduction of **1**. This largely equatorial mixture of epimeric alcohols was then subjected to some of the acid- and base-catalyzed reaction conditions that caused rearrangement of **1** (Table I). The results of this study are outlined in eq 8.

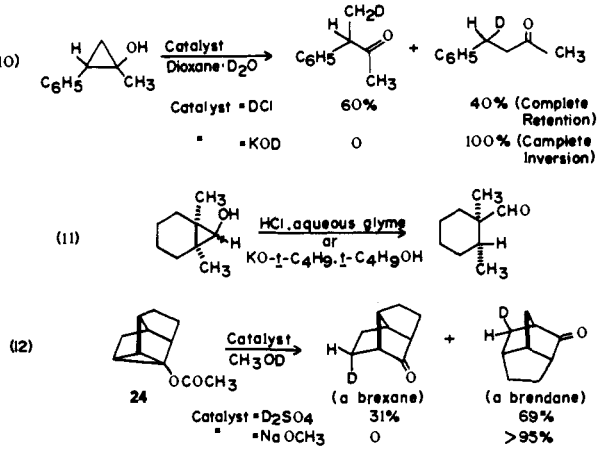


Discussion

The acid- and base-catalyzed transformations reported here for 6-methyl-5-hydroxytricyclo[4.4.0.0^{1,5}]decan-9-one (**1**) and the corresponding diol (**19**) should be viewed in the light of existing facts and principles concerning cyclopropanol ring-opening reactions.[9] Equation 9 illustrates two important aspects of such reactions. These are: (1) To what degree is the cleavage of the α bonds to the a and b sides regioselective? (2) What is the degree of stereoselectivity in the C-protonation step?



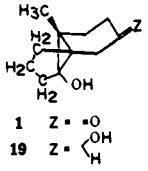
The results from previous studies suggest that proton-catalyzed ring-opening reactions often do not show high regioselectivity[10,11] (eq 10 and 12), but usually proceed with retention of configuration[10b,12] (eq 10 and 11). Steric hindrance to retention appears to shift the C-protonation to inversion[11]



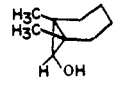
(eq 12); however, an extraordinary solvent effect on this protonation has been noted in one case.[12c]

Base-catalyzed cyclopropanol ring-opening reactions, on the other hand, generally proceed with high regioselectivity[10,13] (eq 10 and 12). Furthermore, the C-protonation step is usually characterized by inversion of configuration,[10b,12] although solvent perturbations of this stereochemistry may occur.[14]

Before extending our discussion to the results reported here, we should note the close structural similarity of our fused-ring cyclopropanols **1** and **19** to the *endo*-7-hydroxybicyclo[4.1.0]-heptane (**22**) studied by Wharton and Bair[12a] (eq 11). From the accompanying formulas we see that the key differences between these systems are the presence of a two-carbon ring segment in **1** and **19** and a carbonyl function in **1**.

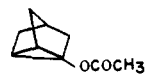


1 Z = =O
19 Z = OH, H

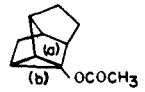


22

In order to isolate the influence of the asymmetrically positioned two-carbon bridge from that of the carbonyl group, we shall first confine our attention to comparable reactions of **19** and **22**. Furthermore, it will be instructive to contrast our findings with those from an earlier study by Nickon et al.[10d] (eq 12), in which a two-carbon bridge perturbs the symmetry of nortricyclyl acetate (**23**).



23



24

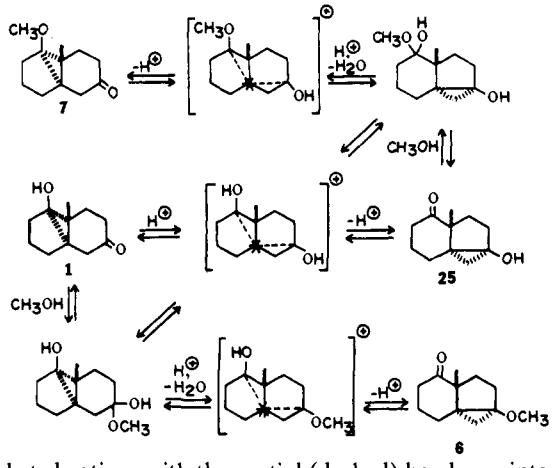
Acid- and base-catalyzed ring-opening reactions of **24** showed moderate to high regioselectivity favoring cleavage of bond (a), and the authors point out that this leads to the more stable brendane ring system. The exclusive inversion of configuration observed for C-protonation in the brendane product was attributed to steric hindrance by the bridging chain.

Our studies with compound **19** (eq 8) show that acid-catalyzed isomerization proceeds with high regio- and stereoselectivity to **20**. The retention of configuration observed in the C-protonation step parallels the findings of Wharton and Bair for the symmetrical analogue (eq 11). Interestingly, **20** is a derivative of the least stable bicyclic ring system that could result from cleavage of one of the two α carbon–carbon bonds in **19**. Heat of combustion measurements indicate that spiro[5.4]decane is less stable than either *cis*- or *trans*-decalin by 4.5–7.0 kcal/mol, respectively,[15] and aluminum chloride induced isomerization of the former to the latter has been reported.[16]

In contrast, the base-catalyzed isomerization of **19** is poorly regioselective and proceeds with opposite stereoselectivity in the formation of the two products **20** and **21** (the former is generated with retention of configuration and the latter with inversion). Since a molecular model (Dreiding) of **19** does not disclose any obvious steric hindrance associated with the bridging chain, we believe that these results may reflect rather subtle distortions of the bicyclo[4.1.0]heptane skeleton induced by the three-carbon bridge. The secondary hydroxyl function in **19** does not appear to be positioned in a manner that would allow it to effect an intramolecular protonation in the course of the ring cleavage.

From the data in Table I we conclude that the carbonyl function and the three-membered ring in **1** interact in a distinctive manner. This interaction is evident, for example, in the rapid formation of methoxy ketone **6** on treatment of **1** with methanolic hydrochloric acid. In order to rationalize the results of several related experiments of this kind, we shall find it helpful to consider the equilibrium shown in Scheme I. The

Scheme I

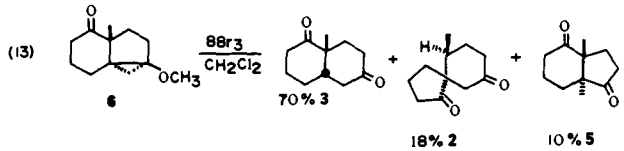


bracketed cations with the partial (dashed) bonds are intended to represent either a dynamic bond-switching interconversion of oxycarbonium ions or a nonclassical delocalized cation. In either case the carbon atom designated by an asterisk undergoes an inversion during the bond switching.

On treatment with cold (0 °C) methanolic hydrochloric acid for 1 h, **1** was partially converted (ca. 50%) to **6**, this being the only significant product other than **1**. After 5 h, **6** was still the major product, but substantial amounts of the isomer **7** were also obtained. More vigorous reaction conditions (25 °C, longer reaction times) not only gave roughly equivalent amounts of **6** and **7**, but also yielded increased quantities of ring-cleavage products such as **2**, **3**, and **5**. These results point to a very rapid hemiketalization reaction followed by a slower isomerization of the three-membered ring (via the bracketed cations?) and an even slower ring cleavage of the stable methoxy derivatives **6** and **7**.

Reaction of **1** with a saturated solution of hydrogen chloride in glyme (1,2-dimethoxyethane) provides a striking contrast to the reactions in methanol. Since hemiketal formation is no longer possible in glyme, only the equilibria shown in the central horizontal row of Scheme I can take place. In this case the products consisted exclusively of ring-cleavage isomers (predominantly **3**), and were formed much more rapidly than the cleavage products from the methanol reaction. This enhanced reactivity in the glyme reaction is consistent with an observation of DePuy and Van Lanen:[10c] "... cyclopropyl methyl ethers are significantly less reactive toward cleavage with acid than the corresponding alcohols."

We have not been able to isolate or observe the isomeric cyclopropanol **25**; however, methyl ether and acetate derivatives of **25** have been made and are stable. The majority of the cleavage products from these reactions appear to derive from **1** rather than **25**, since acid-catalyzed cleavage of a derivative of **6**, lacking the neighboring carbonyl function, gave only perhydroindene products (eq 5). The occurrence of acid-catalyzed isomerization of **25** to **1** was established by an equivalent reaction of **6** itself (eq 13), which led to a mixture of products similar to those obtained from **1** in glyme.



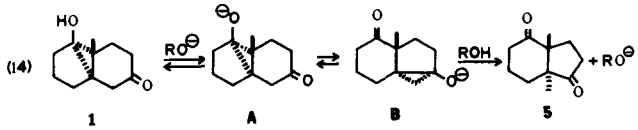
(13)

6 → BBr_3, CH_2Cl_2 → 70% **3** + 18% **2** + 10% **5**

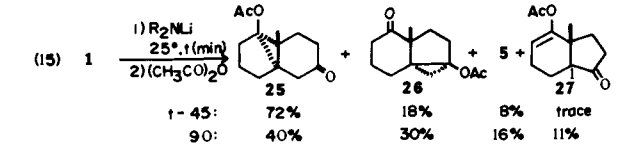
Our present understanding of these acid-catalyzed reactions does not yet provide a convincing explanation for the influence of the carbonyl function in **1** on the regioselectivity of cyclopropanol ring cleavage. Thus, the rearrangement products

from **1** consist chiefly of *cis*-decalindione **3** (formed with inversion of configuration), whereas the corresponding reaction of **19** favors the spirodecane ketol **20** (formed with retention of configuration). In addition, we have observed an interesting solvent effect in the reaction of **1** with small amounts (0.15 equiv) of *p*-toluenesulfonic acid in benzene or glyme solution. After 12 h at 25 °C, the reaction in benzene showed complete rearrangement of **1**, the major products being **5** (44%) and **2** (32%). In contrast, the reaction in glyme solution was only 35% complete after 16 h, and the major product was **3** (50%) accompanied by **5** (32%) and **2** (15%). An important factor here may be the 1000-fold decrease in acid strength that results from conversion of the sulfonic acid to an oxonium conjugate acid in glyme.[17]

Base-catalyzed rearrangement of **1** under conditions equivalent to those used for the cyclopropanol ring cleavage of **19** (eq 8) demonstrates again the remarkable influence of the carbonyl function. Perhydroindene **5** proved to be the major product from the reaction of **1** with methanolic base, whereas spirodecane **2** accounted for <1% of the total products. The formation of **5** in this reaction is best rationalized by rearrangement of the initial conjugate base A to the isomeric base B, as shown in eq 14, followed by cleavage of B at the less-substituted β-carbon atom.

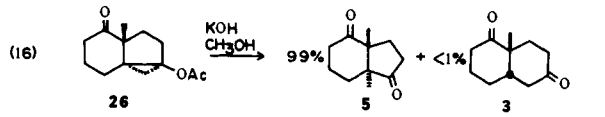


Since no products incorporating the tricyclic skeleton of B were obtained, we sought independent support for this mechanism by trapping the conjugate bases A and B in an aprotic medium. Treatment of an ice cold solution of **1** in glyme with 1 equiv of lithium diisopropylamide gave, after rapid quenching with excess acetic anhydride, an oil which proved to be chiefly (97%) the corresponding acetate **25.** When this experiment was repeated at room temperature in a mixed solvent consisting of glyme, hexamethylphosphoramide (HMPA), and tetramethylethylenediamine (TMEDA), the products were **25,** the isomeric acetate **26,** a small amount of **5,** and an enol acetate tentatively identified as **27** (eq 15). Furthermore, from the time



dependency of the **25**:**26** ratio, we conclude that the rearrangement of A to B under these conditions is moderately slow.

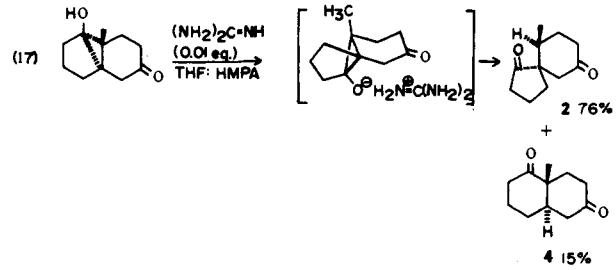
The question of whether conjugate base B rearranges back to A was explored by saponifying the acetate derivative **26** with methanolic potassium hydroxide. Since **5** was the sole product from this reaction (eq 16), it appears that B undergoes ring-



opening protonation faster than it isomerizes to A. This result also clarifies another facet of the base-catalyzed rearrangement of **1**; namely, that the *cis*-decalin **3** which is also formed in this reaction (Table I) comes from ring opening of A (with inversion of configuration) and not from B (with retention of configuration).

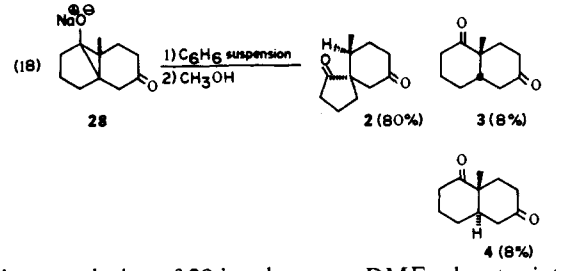
The conversion of **1** to **5** in 80% yield on treatment with methanolic base completes a convenient two-step synthesis of this potentially useful intermediate from the Wieland–Miescher ketone. Purification of **5** is facilitated by the fact that **3** forms a bisulfite addition complex, whereas **5** does not. Various modifications of this rearrangement have been examined in an effort to improve the yield of **5**. Since the unwanted **3** comes from A and the isomerization of A to B is slow, we concluded that a decrease in the rate at which A is converted to **3** should result in an increased yield of **5** (assuming that conversion of B to **5** is faster than A to **3**). To put this strategy into practice we treated **1** with a cold (15 °C) solution of potassium *tert*-butoxide in Me_2SO. After 3 h, the only material detected by GLC analysis was **5** (< 1% **3** was present); however, the isolated yield of **5** was inferior to our original procedure. Apparently higher molecular weight condensation products are formed along with **5** in this approach.

Two other base-induced rearrangements of **1** merit comment. In the first case we find that a catalytic amount of guanidine influences the stereochemistry of protonation in a dramatic way (eq 17).



Not only does the less stable spiro[5.4]decane isomer (**2**) predominate in this reaction, but both major products are formed with retention of configuration at the protonation sites, in contrast to the inversion that normally characterizes the decalin product (eq 8 and Table I). This stereochemistry undoubtedly reflects the fact that the guanidinium cation, formed as a result of proton abstraction from the cyclopropanol, is the only proton source for the ring-opening step and is necessarily oriented beneath the six-membered ring.[18] This is the only base-catalyzed rearrangement of **1** in which significant amounts of **4** are produced. Treatment of **1** with a large excess of guanidine gave a product mixture similar to that obtained from methanolic base.

The second noteworthy example is what we believe to be a heterogenous protonation of the sodium salt of **1**. A vigorously stirred dispersion of sodium hydride in benzene reacts with **1** to give a finely divided suspension of the corresponding sodium salt. Decomposition of this salt (**28**) with methanol gave high yields of the spirodiketone **2** accompanied by small amounts of *cis*- and *trans*-decalindiones (eq 18).



Since a solution of **28** in a benzene–DMF solvent mixture reacts with methyl iodide to give **7** (eq 6) and with methanol to give **5** by way of regenerated **1**, we suggest that the exceptional behavior in benzene alone is a direct consequence of the heterogeneity of this reaction. A similar heterogeneity effect has been noted in the alkylation of phenols.[19]

Experimental Section

Melting points were determined in capillaries or on a Kofler hot stage and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 237B grating spectrophotometer. Proton magnetic resonance spectra were obtained with either a Varian T-60 or a Varian

HA-100 spectrometer, using tetramethylsilane as an internal standard. Mass spectra were obtained with an Hitachi RMU-6 mass spectrometer. All reactions involving alkaline conditions were carried out under dry N_2 or Ar, using solvents freshly purified by distillation from suitable drying agents. Microanalyses were performed by Spang Microanalytical Labs, Ann Arbor, Mich.

Acid- and base-catalyzed rearrangements of (1*R**,5α,6β)-5-hydroxy-6-methyltricyclo[4.4.0.0^{1,5}]decan-9-one (**1**) are outlined in Table I. Specific conditions for these reactions are given in the following accounts, along with evidence for the structure assignments of the major products.

Reaction of 1 with Methanolic Potassium Hydroxide. To a cold solution of potassium hydroxide (0.35 g, 6.3 mmol) in 8 mL of a deoxygenated mixture of methanol and water (1:1) was added 1.02 g (5.7 mmol) of cyclopropanol **1**. This solution was stirred for 2 h at 0 °C and then overnight at room temperature. The organic phase obtained by dilution of the reaction mixture with water and extraction with benzene was washed and dried. Evaporation of the solvent gave a solid which, on crystallization from ether, yielded 0.6 g of *trans*-1,6-dimethylbicyclo[4.3.0]nonane-2,7-dione, **5**, mp 167–168 °C. Extraction of an ether solution of the mother liquors with 20% sodium bisulfite solution (freshly prepared) removed isomers **2** and **3**, and permitted an additional 0.2 g of **5** to be obtained, for a total yield of 0.8 g (80%). Spectroscopic evidence supporting the assigned structure for **5** includes IR (KBr) 1735, 1705 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.92 (s, 3 H), 1.17 (s, 3 H), 1.32–2.90 (m, 10 H); and mass spectrometry (70 eV) *m/e* (rel abundance) 180 (59), 165 (55), 152 (4), 136 (24), 124 (45), 109 (100), 94 (57), 82 (51), 67 (50).

Anal. ($C_{11}H_{16}O_2$) C, H.

Analysis (GLC) of the organic material recovered from the bisulfite extract showed it to be largely the *cis*-decalin **3** (ca. 19%) accompanied by a trace of the spirodiketone **2**.

Reaction of 1 with Guanidine. Treatment of a suspension of guanidine carbonate in ethanol with an equivalent amount of sodium ethoxide, followed by filtration of the insoluble sodium carbonate and evaporation of the solvent, gave crude guanidine. Residual ethanol was removed by repetitive shaking with anhydrous THF, in which guanidine is relatively insoluble. The resulting anhydrous guanidine was a colorless solid, mp ca. 50 °C. A stock solution of 0.01 M guanidine in 1:1 THF/HMPA was prepared, and 0.5 mL of this solution was added to a solution of **1** (90 mg, 0.5 mmol) in 10 mL of THF/HMPA. After 10 h at room temperature, the reaction mixture was quenched in ice water, acidified with dilute HCl, and extracted with ether. The ether extracts yielded 90 mg of an oil, which proved to be a mixture of **2** (76%), **3** (8%), and **4** (15%) by GLC analysis (4% QF-1, 160 °C). The major product (**2**) was isolated by preparative GLC, and proved to be identical (mp, IR, ^{1}H NMR) with the major product from heterogeneous protonation of the sodium salt of **1**. Compounds **3** and **4** were identified by spiking the GLC analysis with authentic samples.[2]

When the guanidine/cyclopropanol molar ratio was increased to 20:1, the above reaction yielded a mixture of **3** (20%), **4** (trace), and **5** (79%) in good yield. Only a trace of **2** was observed.

Heterogeneous Quenching of the Sodium Salt of 1. To a vigorously stirred suspension of sodium hydride (0.96 g, 40 mmol) in 300 mL of dry benzene was added dropwise a solution of cyclopropanol **1** (4.0 g, 22.3 mmol) in 100 mL of benzene. Following 4.5 h of stirring at ambient temperature, the salt suspension was cooled and carefully decomposed by the addition of excess methanol (ca. 5 mL). The light brown mixture resulting from quenching the reaction mixture with 200 mL of ice water was allowed to separate, and the aqueous layer was extracted three times with ether. The combined organic layers were washed (water and brine), dried, and concentrated. The crude product solidified on cooling and, after sublimation (65 °C (0.075 Torr)) and recrystallization from pentane, yielded 3.22 g (80.4%) of pure spirodione **2**, mp 60–62 °C. Spectroscopic evidence supporting the assigned structure includes IR ($CHCl_3$) 2961, 2872, 1735, 1705 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.85 (d, J = 6.5 Hz, 3 H), 1.30–2.70 (m, 3 H); and mass spectrometry (70 eV) parent ion at *m/e* 180.

Anal. ($C_{11}H_{16}O_2$) C, H.

Reaction of 1 with Methanolic Hydrogen Chloride. A solution of cyclopropanol **1** (60 mg, 0.33 mmol) in 10 mL of methanol was cooled to 0 °C and treated with six drops of concentrated hydrochloric acid. The reaction mixture was permitted to warm to room temperature, while being monitored by TLC. After 4 h at room temperature, the starting material was consumed and the reaction was quenched in aqueous bicarbonate solution. Removal of the methanol at reduced pressure followed by extraction with ether yielded 50 mg of an oil, which proved to be a mixture of **6** (64%) and **7** (32%), along with traces of **2, 3, 4,** and **5** (GLC analysis, 4% QF-1, 160 °C). Analytical samples of **6** and **7** were obtained by preparative GLC and characterized by the following measurements.

6, (1*S**,3α,6α)-3-methoxy-6-methyltricyclo[4.4.0.0^{1,3}]decan-7-one: IR (film) 1705, 1439, 1234, 1045 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.34 (d, J = 5.5 Hz, 1 H), 0.74 (d, J = 5.5 Hz, 1 H), 1.32 (s, 3 H), 1.36–2.80 (m, 10 H), 3.37 (s, 3 H); mass spectrum (70 eV) *m/e* (rel abundance) 194 (14), 179 (100), 151 (26), 138 (27), 123 (80), 110 (35), 91 (36).

Anal. ($C_{12}H_{18}O_2$) C, H.

7, (1*R**,5α,6β)-5-methoxy-6-methyltricyclo[4.4.0.0^{1,5}]decan-9-one: IR (film) 1710 cm^{-1}; ^{1}H NMR ($CDCl_3$) 1.12 (s, 3 H), 1.20–2.80 (m, 12 H), 3.37 (s, 3 H); mass spectrum (70 eV) *m/e* (rel abundance) 194 (12), 179 (100), 151 (15), 137 (88), 123 (31), 105 (34), 93 (38), 91 (50).

Anal. ($C_{12}H_{18}O_2$) C, H.

Compound **7** was also prepared by methylation of the conjugate base of **1**. Reaction of 1.0 g (5.6 mmol) of **1** with a suspension of 0.24 g of sodium hydride in a 1:1 mixture of benzene and DMF (940 mL total volume) gave, after quenching with 3 g (21 mmol) of methyl iodide and conventional workup, 0.6 g of an oil. Analysis by GLC indicated this material to be chiefly compound **7**, and the ^{1}H NMR spectrum supported this conclusion. A semicarbazone derivative was prepared, mp 212–213 °C.

Anal. ($C_{13}H_{21}N_3O_2$) C, H, N.

A similar reaction of 90 mg (0.5 mmol) of **1** in 10 mL of methanol/water (1:1) containing six drops of concentrated hydrochloric acid for 10 h at room temperature yielded 87 mg of an oil, which proved to be a mixture of **2** (10%), **3** (20%), **4** (4%), **5** (16%), **6** (21%), and **7** (29%) by GLC analysis.

Reaction of 1 with *p*-Toluenesulfonic Acid in Benzene. To a solution of **1** (180 mg, 1 mmol) in 10 mL of dry benzene was added a small amount (25 mg) of *p*-toluenesulfonic acid. After 20 h at room temperature, TLC analysis of the reaction mixture indicated that the starting material had been completely transformed. The benzene solution was washed with dilute bicarbonate solution, dried, and concentrated to 180 mg of a colorless oil. Analysis by GLC (QF-1, 160 °C) demonstrated this to be a mixture of spirodiketone **2** (32%), *cis*-decalin **3** (18%), *trans*-decalin **4** (6%), and perhydroindene **5** (44%).

Reaction of 1 with Hydrogen Chloride in Glyme. Anhydrous hydrogen chloride was bubbled into freshly distilled glyme for 2 min. A 50-mg sample of cyclopropanol **1** (0.28 mmol) was then dissolved in a 2-mL portion of the acidified glyme, and the resulting reaction was monitored by TLC. Reaction was complete after 2 h at room temperature, and the reaction mixture was quenched in a cold mixture of benzene and dilute bicarbonate solution. After the benzene extract was washed and dried, it yielded ca. 45 mg of an oil which proved to be a mixture of spirodiketone **2** (11%), perhydroindene **5** (9%) and *cis*-decalin **3** (80%). The latter component was confirmed by a mixture melting point with authentic **3** (mp 65 °C).[21]

Reaction of 1 with Aqueous Ferric Chloride. A 1-g sample of cyclopropanol **1** (5.5 mmol) was added in one portion to a stirred solution of ferric chloride (4 g) in 25 mL of water. The yellow color of the solution lightened perceptibly as the cyclopropanol dissolved, and over a 10-min period a crystalline material slowly deposited. This substance, which was assumed to be chiefly the chlorodiketone **16**, was washed and dried, but could not be recrystallized because of its tendency to decompose on heating or on standing in moist air. A mass spectrum (70 eV) of this crude material showed parent ions at *m/e* 216 and 214 (relative abundances 1:2.8), in agreement with the formula $C_{11}H_{15}O_2Cl$.

When heated on a steam bath for 1 h, compound **16** decomposed with the loss of HCl, leaving a light yellow oil which was taken up in ether so that residual acid could be washed away. Analysis of the resulting oil (GLC) showed it to be 90% the Wieland–Miescher ketone and 10% a minor component, which was partially purified by chromatography. Since an infrared spectrum of this enriched material showed a carbonyl absorption at 1735 cm^{-1} in addition to those expected from the major product, we tentatively assign structure **17** to the minor product.

(1α,3α,6β)-3-Bromo-1,6-dimethylbicyclo[4.3.0]nonane-2,7-dione (14). A solution of 1.42 g (7.90 mmol) of perhydroindene **5** in 50 mL

of dry carbon tetrachloride was allowed to react with 4.40 g (9.59 mmol) of 2-pyrrolidone hydrotribromide[20] in the dark for 20 h at room temperature. Unreacted reagent and other solids were removed by filtration, and the resulting clear solution was concentrated and taken up in ether. Following bicarbonate, water, and brine washes, the dried ether solution was evaporated and the residue crystallized from ether to give 1.7 g (84%) of pure **14**: mp 144–147 °C; IR (KBr) 1740, 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.95 (s, 3 H), 1.49 (s, 3 H), 1.60–3.04 (m, 8 H), 4.43 (dd, J = 4.0 Hz, J' = 6.8 Hz, 1 H); mass spectrum (70 eV) parent ions at *m/e* 260 and 258 (equal intensity).

Anal. ($C_{11}H_{15}O_2Br$) C, H.

***trans*-10-Methylspiro[4.5]decane-1,7-dione 7-Ethylenethioketal (8).** A solution of 1.24 g (6.92 mmol) of **2** in hot glacial acetic acid was treated with 2.23 g (24.7 mmol) of ethanedithiol followed by 2 mL of boron trifluoride etherate. After this hot solution had cooled (ca. 3 h) it was washed with sodium carbonate solution, water, and brine. The yellow oil obtained by concentrating the organic layer was chromatographed on silica gel, and the chief component was crystallized from pentane to give 1.45 g (82%) of thioketal **8**, mp 92.5–94 °C. The structural assignment of this compound was supported by spectroscopy: IR (CCl_4) 1733 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.75 (d, J = 6.0 Hz, 3 H), 1.4–2.5 (m, 13 H), 3.27 (s, 4 H); mass spectrum (70 eV) parent ion at *m/e* 256; and analysis.

Anal. ($C_{13}H_{20}OS_2$) C, H, S.

***trans*-10-Methylspiro[4.5]dec-7-en-1-one (10).** A solution of *trans*-2-ethylidenecyclopentanone[4] (2.76 g, 25.1 mmol) and excess 1,3-butadiene (ca. 20 g) in decalin was heated to 200 °C for 7.5 h in a sealed tube. The resulting gelatinous product mixture was partitioned in a methylene chloride–water mixture, and the dried organic phase was concentrated at reduced pressure. Decalin was removed by passing a hexane solution of this material through a silica gel column, the Diels–Alder adduct then being eluted by a chloroform–ether mixture (85:15). Distillation of the crude adduct gave 1.1 g (28%) of **10**: bp 63–66 °C (0.05 Torr); IR (film) 3017, 1736, 1736, 660 cm^{-1}; ^1H NMR (CCl_4) δ 0.73 (d, J = 6.0 Hz, 3 H), 1.5–2.7 (m, 11 H), 5.53 (br s, 2 H); mass spectrum (70 eV) parent ion at *m/e* 164.

***trans*-6-Methylspiro[4.5]decan-1-one (9). (A) From 8.** A solution of 0.788 g (3.08 mmol) of thioketal **8** in 1-propanol (10 mL) was added to a rapidly stirred suspension of W-7 Raney Nickel (deactivated by refluxing acetone for 1 h) in 75 mL of 1-propanol. After refluxing for 59 h (the reaction was monitored by TLC) the mixture was cooled and filtered through Celite. The Celite filter cake was washed several times with propanol and ether, and the combined organic solutions were concentrated at reduced pressure. Distillation of the crude product yielded 0.47 g of a clear liquid, bp 135–138 °C (25 mm), which was reduced with hydrogen in the presence of a palladium catalyst in order to remove olefinic by-products. The resulting saturated ketone was distilled, bp 150–158 °C (25 mm), to give 0.32 g (62%) of **9**: IR (film) 1733 cm^{-1}; ^1H NMR (CCl_4) δ 0.66 (d, J = 6.5 Hz, 3 H), 1.13–2.2 (m, 15 H); mass spectrum (70 eV) *m/e* (rel abundance) 166 (65), 111 (90), 97 (75), 95 (100), 81 (85), 67 (75).

(B) From 10. A solution of 0.85 g (5.19 mmol) of **10** in 20 mL of absolute ethanol containing 102 mg of 10% Pd/C was stirred under a hydrogen atmosphere until the hydrogen uptake ceased (a total of 128.6 mL of hydrogen was consumed). The crude product obtained by filtration and solvent removal proved to be chiefly (>95%) a single compound, having a GLC retention time (4% QF-1, 125 °C) identical with the reduction product from **8** (part A). Purification by preparative GLC yielded 0.76 g (88%) of pure **9**, having IR, ^1H NMR, and mass spectra identical with those obtained for the product from part A.

Anal. ($C_{11}H_{18}O$) C, H.

1β,6α-Dimethyl-2α-acetoxybicyclo[4.3.0]nonan-7-one (11). A solution of perhydroindene **5** (27.0 g, 0.15 mol) in 1350 mL of ethanol was cooled to 0 °C, while a solution of sodium borohydride (6.45 g, 0.17 mol) and sodium hydroxide (23.2 g, 0.58mol) in 100 mL of ethanol and 50 mL of water was added dropwise with stirring. The diketone **5** was completely reduced (GLC analysis) after 3.5 h at 0 °C, at which time the ethanol was removed by evaporation and the aqueous slush taken up in a mixture of water and ether. The aqueous phase was extracted with ether, and the combined extracts were washed and dried. The crude ketol (26.6 g, 97%) may be used as is for the acetylation, or may be purified by sublimation: mp 179–180 °C (sealed tube); IR ($CDCl_3$) 3590, 3450, 1735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.9 (s, 3 H), 1.25 (s, 3 H), 1.3–2.7 (m, 11 H), 3.8 (m, 1 H); mass spectrum (70 eV) *m/e* (rel abundance) 182 (41), 167 (15), 154 (5), 149 (8), 138 (10), 122 (40), 111 (100), 109 (85), 96 (64).

Anal. ($C_{11}H_{18}O_2$) C, H.

A 1-g sample (5.5 mmol) of this ketol in 50 mL of dry pyridine was treated with 10 mL of freshly purified acetic anhydride. After standing at room temperature overnight, the reaction mixture was poured into 50 mL of ice water and extracted with ether. The ether extracts were then washed with cold 5% hydrochloric acid and twice with water. The residue remaining after evaporation of the solvent was crystallized from light petroleum ether, yielding 1.2 g of low-melting crystals. A second crystallization from a small volume of ether gave pure keto acetate **11**: mp 50–52 °C; IR ($CHCl_3$) 1710–1735, 1240 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.95 (s, 3 H), 1.2 (s, 3 H), 1.3–2.6 (m, 10 H), 2.1 (s, 3 H), 4.9 (m, 1 H); mass spectrum (70 eV) parent ion *m/e* 224.

Anal. ($C_{13}H_{20}O_3$) C, H.

***trans*-1,6-Dimethylbicyclo[4.3.0]non-2-en-7-one (12).** A solution of keto acetate **11** (1.5 g, 6.7 mmol) in degassed cyclohexane (15 mL) was slowly added (1 drop/s) at the top of a 25-cm pyrolysis column packed with Pyrex glass beads and heated to 450 °C. The pyrolysis column was swept by dry nitrogen at a rate of 6 L/h during the addition. The effluent from the column was collected in a dry ice-cooled flask, washed with bicarbonate solution, dried, and concentrated. The resulting colorless solid (ca. 1.1 g) proved to be mainly one component (97% by GLC analysis), and was crystallized from pentane to give pure **12**: mp 62–65 °C; IR ($CDCl_3$) 1735 (br), 1605 cm^{-1}; ^1H NMR (CCl_4) δ 0.85 and 0.9 (overlapping s, 6 H), 1.3–3.0 (m, 8 H), 5.0–6.0 (m, 2 H); mass spectrum (70 eV) *m/e* (rel abundance) 164 (43), 149 (40), 107 (100), 93 (86).

***trans*-1,6-Dimethylbicyclo[4.3.0]nonan-7-one (13).** A solution of **12** (176 mg, 1.1 mmol) in 20 mL of dry benzene, containing 27 mg of 10% Pd/C catalyst, was hydrogenated at atmospheric pressure. A total of 1.05 equiv of hydrogen was taken up over a 24-h period, and the resulting mixture was then filtered and evaporated to yield 175 mg of a colorless solid. This crude **13** was purified by sublimation: mp 110–111 °C (sealed capillary); ^1H NMR ($CDCl_3$) δ 0.93 (s, 3 H), 1.05 (s, 3 H); ^1H NMR (C_6H_6) δ 0.35 (s, 3 H), 0.45 (s, 3 H), 1.0–2.5 (m, 12 H); mass spectrum (70 eV) *m/e* (rel abundance) 166 (53), 151 (12), 124 (30), 110 (90), 109 (68), 95 (100), 81 (62). A 2,4-DNP derivative of **13** was prepared and crystallized twice from ethanol: mp 137–138 °C; ^1H NMR ($CDCl_3$) δ 0.88 (s, 3 H), 1.10 (s, 3 H).

The properties noted here for **13** and its 2,4-DNP derivative correspond very closely to those communicated to us by Professor E. Wenkert for the same compound prepared by a different route. We are indebted to Professor Wenkert for this information.

Acid-Catalyzed Cleavage of (1S*,3α,6α)-3-Methoxy-6-methyltricyclo[4.4.0.0^{1,3}]decan-7-one (6) and its Reduced Derivative (15). (A) To a solution of 75 mg (0.38 mmol) of **6** in 5 mL of methylene chloride at −78 °C was added 0.3 mL (3.2 mmol) of boron tribromide. After 2 h at −78 °C, GLC analysis indicated that all the starting material had been transformed, and the reaction was quenched by mixing with a cold ammonium chloride–ammonium carbonate buffer solution. Extraction with methylene chloride yielded 70 mg of a mixture, which GLC analysis showed to be spirodiketone **2** (18%), *cis*-decalin **3** (70%), and perhydroindene **5** (10%).

(B) A solution of **6** (130 mg, 0.67 mmol) in 5 mL of absolute ethanol was reduced at 0 °C by the addition of 25 mg (0.66 mmol) of sodium borohydride. After stirring for 1 h, the reaction was quenched with a few drops of acetic acid, the solvent was removed at reduced pressure, and an ether solution of the residue was washed and dried. The oily mixture of **15** epimers was dissolved in 5 mL of dry methylene chloride, cooled to −78 °C, and treated with 0.2 mL (2.1 mmol) of boron tribromide. Following a 1-h reaction period, the mixture was worked up as in part **A** and the residue was oxidized by the Jones procedure.[22] The product consisted chiefly (72%) of the perhydroindene **5**, the remaining 28% being unchanged **6**. Compound **5** was identified by its IR and ^1H NMR spectra as well as a mixture melting point with authentic material.

(C) A similar acid-catalyzed transformation of **15**, effected in absolute methanol saturated with anhydrous hydrogen chloride, gave diketone **5** in good yield after the usual workup and Jones oxidation. Isomers **2** and **3** were not observed among the products by GLC analysis.

Reduction of (1R*,5α,6β)-5-Hydroxy-6-methyltricyclo[4.4.0.0^{1,5}]decan-9-one (1) to Epimeric Diols (19). The carbonyl function of **1** is readily reduced by sodium borohydride or lithium in ammonia; however, the epimeric alcohol products are unstable and are best characterized by acid-catalyzed rearrangement.

(**A**) A solution of cyclopropanol **1** (50 mg, 0.28 mmol) in 9 mL of methanol was treated with 32.6 mg (16 mequiv) of sodium borohydride at −44 °C. After 3.5 h the reaction was quenched with a few drops of acetic acid and permitted to warm to room temperature. This solution of **19** epimers was then treated with aqueous hydrochloric acid (0.5 mL of concentrated HCl in 4 mL of water) overnight. Extraction with benzene yielded, after appropriate washing, ca. 45 mg of an oil which GLC analysis (QF-1, 185 °C) indicated to be a 94:6 mixture of two components. Jones oxidation of this mixture gave spirodiketone **2** in 94% yield. Less than 1% **3** and **5** were present in the oxidation mixture. Identification of **2** as the major product was achieved by a comparison of chromatographic retention times and infrared spectrum with an authentic sample.

(**B**) A solution of cyclopropanol **1** (360 mg, 2 mmol) in 50 mL of THF was added to a solution of lithium (ca. 3 mmol) in 50 mL of freshly distilled ammonia cooled to −78 °C. Following a 2-h period, during which the temperature of the reaction mixture increased to the point of reflux, the remaining lithium was quenched by a few drops of ethylene dibromide (blue color is discharged). Workup in the usual fashion yielded 350 mg of **19** epimers, portions of which were subjected to acid- and base-catalyzed ring cleavage. Thus, a 170-mg portion, on treatment overnight with methanolic hydrochloric acid, gave a 65:35 mixture of isomeric ketols. Oxidation of this mixture with Jones reagent yielded 160 mg of spirodiketone **2**, containing no discernible amounts of **3** or **5** (GLC analysis).

Base-Catalyzed Reaction of Epimeric Diols 19. A 300-mg sample of **19** (1.6 mmol), prepared by sodium borohydride reduction of **1**, was dissolved in 15 mL of methanol containing sufficient potassium hydroxide to raise the pH >13. After an overnight reaction period at room temperature, the mixture was diluted with water and extracted with benzene. The residue from the benzene extracts was oxidized by Jones reagent and worked up in the usual fashion. Analysis of the crude product by GLC (QF-1, 185 °C) demonstrated it to be a 58:42 mixture of spirodiketone **2** and *cis*-decalin **3**. These products were separated and identified by their characteristic spectra and appropriate mixture melting point measurements.

Rearrangement and Acetylation of the Conjugate Base of 1. A solution of 0.18 mL (1.22 mmol) of diisopropylamine in 0.6 mL of HMPA at 0 °C was treated with 0.70 mL (1.33 mmol) of 1.9 M *n*-BuLi, and stirred for 15 min. To the resulting lithium amide was added 200 mg (1.11 mmol) of cyclopropanol **1** in 1.2 mL of DME followed by the addition of 0.7 mL of TMEDA. Following a 1.5-h reaction period, during which time the solution gradually warmed to room temperature, the reaction was quenched with 6 mL of acetic anhydride and stirred for an additional 15 min. This mixture was poured into ice water saturated with $NaHCO_3$, stirred for 1 h, and then extracted with ether. The combined ether extracts yielded an oil which was analyzed by GLC, using a combination of 4% QF-1 and 4% SE-30 columns. The following four components were isolated by preparative GLC:

(**A**) (1*R**,5α,6β)-5-Acetoxy-6-methyltricyclo[4.4.0.0^{1,5}]decan-9-one (**25**) was formed in 40% yield and identified by its characteristic properties: IR (film) 1745, 1715, 1265, 1215 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.17 (s, 3 H), 2.05 (s, 3 H), 1.21–2.70 (m, 12 H); mass spectrum (70 eV) *m/e* (rel abundance) 222 (2), 180 (31), 162 (48), 137 (49), 43 (100).

Anal. ($C_{13}H_{18}O_3$) C, H.

(**B**) (1*S**,3α,6α)-3-Acetoxy-6-methyltricyclo[4.4.0.0^{1,3}]decan-7-one (**26**) was formed in 30% yield and identified by its characteristic properties: IR (film) 1750, 1708, 1213 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.37 (d, J = 5.5 Hz, 1 H), 0.95 (d, J = 5.5 Hz, 1 H), 1.45 (s, 3 H), 2.07 (s, 3 H), 1.1–2.9 (m, 10 H); mass spectrum (70 eV) *m/e* (rel abundance) 222 (1), 180 (22), 147 (62), 43 (100).

Anal. ($C_{13}H_{18}O_3$) C, H.

(**C**) *trans*-1,6-Dimethylbicyclo[4.3.0]nona-2,7-dione (**5**) was formed in 16% yield and identified by GLC retention time and ^{1}H NMR spectrum.

(**D**) A fourth compound, isolated in 11% yield, was identified as 2-acetoxy-*trans*-1,6-dimethylbicyclo[4.3.0]non-2-en-7-one on the strength of its ^{1}H NMR and mass spectra: ^{1}H NMR ($CDCl_3$) δ 1.11 (s, 3 H), 1.38 (s, 3 H), 2.15 (s, 3 H), 5.29 (m, 1 H), and a methylene envelope (ca. 8 H); mass spectrum (70 eV) *m/e* (rel abundance) 222 (1), 180 (86), 165 (54), 162 (41), 43 (100).

Base-Catalyzed Rearrangement of Keto Acetate 26. Rearrangement of **26** (1 mg) in 8 drops of methanol containing 2 drops of 0.43 M methanolic potassium hydroxide was monitored by GLC analysis, using a 4% SE-30 column. Reaction was complete in a few minutes and the sole observable product was the perhydroindene **5** (small amounts of isomers **2** and **3** could have been detected if present).

Acknowledgment. We thank the National Institutes of Health for their support of this work (Grant R01 AM 10849) and Mrs. Lorraine Guile for her assistance in obtaining mass spectra.

References and Notes

(1) W. Reusch, K. Grimm, J. Karoglan, J. Martin, K. Subrahamanian, Y-C Toong, P. S. Venkataramani, J. Yordy, and P. Zoutendam, *J. Am. Chem. Soc.*, preceding paper in this issue.
(2) (a) I. N. Nazarov, S. I. Zavyalov, M. S. Burmistrova, I. A. Gurvich, and L. I. Shmonina, *J. Gen. Chem. USSR*, **26**, 465 (1956); (b) A. J. Birch, E. Pride, and H. Smith, *J. Chem. Soc.*, 4688 (1958); (c) C. H. Heathcock, R. Ratcliffe, and J. Van, *J. Org. Chem.*, **37**, 1796 (1972).
(3) K. L. Williamson, T. Howell, and T. A. Spencer, *J. Am. Chem. Soc.*, **88**, 325 (1966).
(4) L. Birkofer, S. M. Kim, and H. D. Engles, *Chem. Ber.*, **95**, 1495 (1962).
(5) We are indebted to Professor E. Wenkert for information regarding **13**, its cis isomer, and the corresponding 2,4-DNP derivatives: E. Wenkert, J. Zylber, E. Kariv, and K. Kavkova, unpublished work; E. Kariv, Ph.D. Dissertation, Weizmann Institute of Science, Rehovoth, Israel, 1967; J. Yoder, Ph.D. Dissertation, Indiana University, Indianapolis, Indiana, 1969.
(6) J. D. Yordy and M. A. Neuman, *J. Cryst. Mol. Struct.*, **4**, 121 (1974).
(7) Some of our early findings in this study have been communicated to this journal: (a) P. S. Venkataramani, J. E. Karoglan, and W. Reusch, *J. Am. Chem. Soc.*, **93**, 269 (1971); (b) K. Grimm, P. S. Venkataramani, and W. Reusch, *ibid.*, **93**, 270 (1971).
(8) S. E. Schaafsma, H. Steinberg, and Th. J. deBoer, *Recl. Trav. Chim. Pays-Bas*, **85**, 73 (1966).
(9) A comprehensive review of such reactions is available: D. H. Gibson and C. H. DePuy, *Chem. Rev.*, **74**, 605 (1974).
(10) (a) A. deBoer and C. H. DePuy, *J. Am. Chem. Soc.*, **92**, 4008 (1970); (b) C. H. DePuy, F. W. Breitbeil, and K. DeBruin, *ibid.*, **88**, 3347 (1966); (c) C. H. DePuy and R. Van Lanen, *J. Org. Chem.*, **39**, 3360 (1974); (d) A. Nickon, D. F. Covey, G. D. Pandit, and J. J. Frank, *Tetrahedron Lett.*, 3681 (1975).
(11) Z. J. Barneis, R. J. Warnet, D. M. S. Wheeler, M. G. Waite, and G. A. Sim, *Tetrahedron*, **28**, 4683 (1972).
(12) (a) P. S. Wharton and T. I. Bair, *J. Org. Chem.*, **31**, 2480 (1966); (b) A. Nickon, J. J. Frank, D. F. Covey, and Y. Lin, *J. Am. Chem. Soc.*, **96**, 7574 (1974); (c) A. Nickon and J. J. Frank, *Tetrahedron Lett.*, 4335 (1975).
(13) C. H. DePuy, N. C. Arney, Jr., and D. H. Gibson, *J. Am. Chem. Soc.*, **90**, 1830 (1968).
(14) D. J. Cram, "Fundamentals of Carbanion Chemistry", Academic Press, New York, N.Y., 1965.
(15) (a) M. P. Kozina, A. K. Mirzawa, I. E. Sosnina, N. V. Elagina, and S. M. Skuratov, *Dokl. Akad. Nauk SSSR*, **155**, 1123 (1964); *Chem. Abstr.*, **61**, 2540d (1964); (b) D. M. Speros and F. D. Rossini, *J. Phys. Chem.*, **64**, 1723 (1960).
(16) M. B. Turova-Pollak, I. E. Sosnina, and T. P. Yudkina, *Zh. Obschch. Khim.*, **27**, 586 (1957); *J. Gen. Chem. USSR*, (*Engl. Trans.*), **27**, 817 (1957).
(17) (a) R. P. Bell, "The Proton in Chemistry", 2nd ed. Cornell University Press, Ithaca, N.Y., 1966; (b) N. C. Deno and J. O. Turner, *J. Org. Chem.*, **31**, 1969 (1966).
(18) Reference 14, p 88.
(19) N. Kornblum and A. P. Lurie, *J. Am. Chem. Soc.*, **81**, 2705 (1959).
(20) (a) W. E. Daniels, M. E. Chiddix, and S. A. Glickman, *J. Org. Chem.*, **28**, 573 (1963); (b) D. V. C. Awang and S. Wolfe, *Can. J. Chem.*, **47**, 706 (1969).
(21) V. Kucherov and T. A. Gurvich, *J. Gen. Chem. USSR*, **31**, 731 (1961).
(22) G. Büchi and B. Egger, *J. Org. Chem.*, **36**, 2021 (1971).