1.66 (1 H, dd, J = 13, 9 Hz). Decoupling experiments in the presence of Eu(fod)$_3$ indicate the following coupling constant assignments: $J_{1,2\text{-exo}} = 4$, $J_{9,10\text{-exo}} = 4$, $J_{9,10\text{-endo}} < 1$, $J_{10\text{-exo},10\text{-endo}} = 19$ Hz.

Registry No.—**4b,** 61063-63-6; **8a,** 61063-55-6; **8b,** 61063-56-7; **8c,** 61063-57-8; **9b,** 61063-58-9; **9c,** 61063-59-0; **10a,** 61063-60-3; **10b,** 61063-61-4; **10c,** 61116-91-4; **14,** 34817-42-0; **15,** 61063-62-5; **15** ketone derivative, 57261-23-1; **16** 9-ene, 61063-64-7; **16** 10-ene, 61092-33-9; **17,** 61092-34-0; **19,** 61063-65-8; **21,** 61063-66-9; **22,** 61063-67-0; **23,** 61116-92-5; **25,** 61063-68-1; **27,** 61063-69-2; **29,** 61063-70-5; **30,** 61063-71-6; **32,** 61063-72-7; **33,** 61063-73-8; *tert*-butyl chloroacetate, 107-59-5; diethyl malonate, 105-53-3; *tert*-butyl ethyl 2-carboethoxysuccinate, 61063-74-7; monoethyl(2-carboethoxy) succinate, 61063-75-0; cycloheptatrienyl fluoroborate, 61063-76-1; 3,3-dicarboethoxy-3-(7-cyclohepta-1,3,5-trienyl)propionic acid, 61063-77-2; 2-carboethoxysuccinic acid, 61063-78-3; 3-carboethoxy-3-(7-cycloheptatrienyl)propionic acid, 61063-79-4; piperidine, 110-89-4; 3,3-dicarboethoxy-3-(7-cyclohepta-1,3,5-trienyl)propionic acid piperidine, 61063-80-7; 3,3-dicarboethoxy-3-(7-cyclohepta-1,3,5-trienyl)propionyl chloride, 61063-81-8; dicyclohexylamine, 101-83-7; 3-carboethoxy-3-(7-cyclohepta-1,3,5-trienyl)propionic acid dicyclohexylamine salt, 61063-82-9; diazomethane, 334-88-3; 3-carboethoxy-3-(7-cyclohepta-1,3,5-trienyl)propionyl chloride, 61063-83-0; cycloheptatrienylacetic acid diazo ketone, 61063-84-1; 3-(7-cyclohepta-1,3,5-trienyl)propionic acid, 61063-85-2; dicyclohexylammonium 3-(7-cyclohepta-1,3,5-trienyl)propionate, 61063-86-3; 3-(7-cycloheptatrienyl)propionyl chloride, 61063-87-4; spiro[6,4]-undeca-6,8,10-trien-2-one, 61063-88-5; bicyclo[3.2.2]non-6-ene-8-*syn*,9-*syn*-dicarboxylic anhydride, 29577-71-7; ethyl bicyclo-[3.2.2]non-6-ene-8-*syn*,9-*syn*-dicarboxylic acid, 61063-89-6; dicyclohexylammonium ethyl bicyclo[3.2.2]non-6-ene-8-*syn*,9-*syn*-dicarboxylic acid, 61116-93-6; bicyclo[3.2.2]non-6-ene-8-*syn*-carboxylic acid 9-*syn*-carbonyl chloride, 61063-91-0; ethyl tetracyclo-[5.4.0.0^{2,11}.0^{3,9}]undecan-10-one-8-carboxylate, 61063-90-9; ethyl tetracyclo[5.4.0.0^{2,11}.0^{3,9}]undecan-10-ol-8-carboxylate, 61092-35-1.

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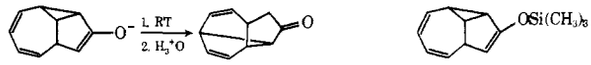

ii iii iv

of ii at room temperature. The same ketone iii is also obtained from the enol silane iv (20 h, room temperature). Attempted rearrangement of the enolate derived from **9b** at room temperature resulted in degradation.

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Protolytic and Pyrolytic Rearrangements of Polycyclic Methyl Cyclopropyl Ketones

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Certain methyl cyclopropyl ketones containing methylated tricyclo[3.2.1.0^{2,4}] nuclei undergo rapid rearrangement in dilute trifluoroacetic acid to give α,β-unsaturated ketones and cyclic enol ethers. The mechanism is discussed in terms of the cyclopropyl carbinyl to homoallylic rearrangement. Release of strain and stability of the cationic intermediates are thought to contribute to the ease of the rearrangement. Methyl migration appears to be slower than hydride transfer to the initial cationic center. When migration cannot readily occur, internal enol capture results leading to enol ethers. The related thermal rearrangement of these ketones at temperatures greater than 200 °C provides a route to certain γ,δ-unsaturated ketones.

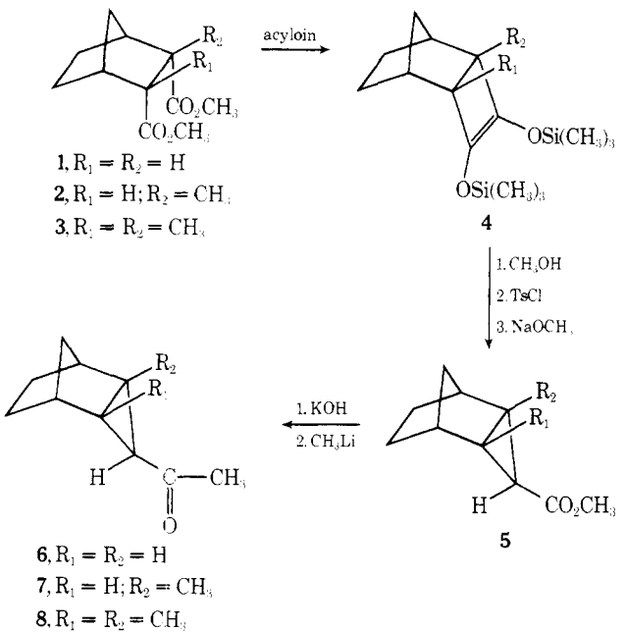
As part of a study of mechanistic pathways by which cyclopropyl systems undergo substitution reactions, we had use for a variety of cyclopropyl containing substrates. As precursors for the preparation of compounds that would undergo substitution reactions, we have developed methods for the formation of certain methyl substituted cyclopropyl ketones.

In our attempts to analyze and convert these ketones to suitable derivatives, we have found that in some cases, acid-catalyzed rearrangements occur with extreme ease. We report here the results of these protolytic rearrangements and also some related thermal rearrangements of some methyl cyclopropyl ketones.

Results and Discussion

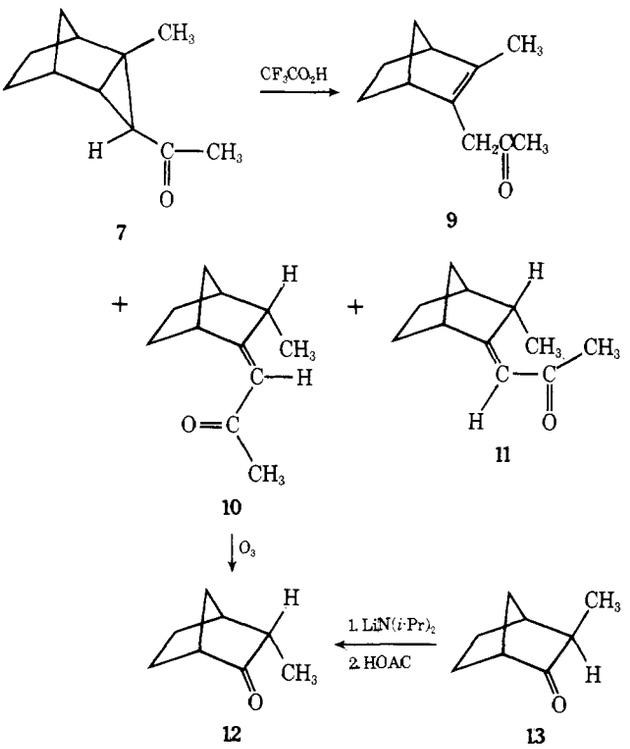
The general procedure outlined in Scheme I has been used to prepare cyclopropyl ketones **6, 7,** and **8.** Acyloin condensation of the appropriate diester followed by methanolysis, tosylate (or mesylate) formation, and Favorskii rearrangement gave the cyclopropyl derivatives **5.** Saponification followed by treatment of the corresponding acid with methyllithium gave methyl ketones **6, 7,** and **8.** We have previously reported on the Baeyer–Villiger oxidation of **6** with peroxytrifluoroacetic acid which gave a high yield of the corresponding acetate.[2] While the preparation of ketones **7** and **8** was straightforward, these ketones appeared to be unstable to gas chromatographic conditions. Additionally, attempted Baeyer–Villiger oxidation with peroxytrifluoroacetic acid gave extremely complex product mixtures. In order to determine the reasons for the unsuccessful peracid oxidation, ketone **7** was treated with dilute trifluoroacetic acid in methylene chloride at room temperature. A rapid exothermic reaction ensued. The products were an isomeric ketone mixture in 93% yield which consisted of trace amounts of ketone **9** and α,β-unsaturated ketones **10** and **11** in a ratio of 5.8:1. A control experiment showed these products to be stable under the reaction conditions.

Scheme I



The structure of the major ketone product **10** was assigned on spectral evidence as well as chemical degradation. Mass spectral data showed the rearrangement products to be isomeric. Infrared and ultraviolet spectral data showed that the two major products, **10** and **11,** were α,β-unsaturated ketones. Ketone **10** showed a single proton resonance at δ 3.92 in the NMR spectrum attributed to the allylic bridgehead proton. The larger than normal downfield shift of this bridgehead proton is attributed to the proximity of the acetyl group in this stereoisomer. The methyl group stereochemistry of **10** was assigned on the basis of ozonolysis, which gave, upon a reductive workup, *endo*-3-methylbicyclo[2.2.1]heptan-2-one (**12**). This ketone could be prepared independently by the formation of the enolate from *exo*-3-methylbicyclo[2.2.1]-heptan-2-one (**13**) with lithium diisopropylamide followed by quenching with acetic acid.[3] The product mixture after protonation consisted of a 3.5:1 mixture of ketones **12** and **13** with **12** predominating.

Scheme II

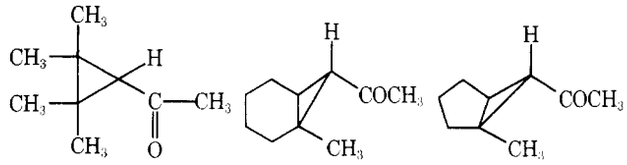


The stereochemistry of the minor α,β-unsaturated ketone **11** is based on mechanistic considerations to be discussed. The allylic bridgehead proton of **11** is not shifted downfield to any unusual extent and suggests an acetyl configuration anti to the bridgehead proton. Unfortunately, ozonolysis of **11** gave a complex product mixture and assignment of the methyl group stereochemistry could not be made in this manner.

The structure of ketone **9,** produced in minor amounts, was based on the fact that this isomeric ketone was not α,β-unsaturated. Catalytic hydrogenation gave the same product as hydrogenation of **10.** Spectral comparison and gas chromatographic retention time ruled out isomeric ketone **30** as being involved in the trifluoroacetic acid catalyzed rearrangement of **7.** Hence the most probable structure of the minor rearrangement product is given by **9.**[4]

These trifluoroacetic acid catalyzed rearrangement products offer an explanation for the unsuccessful attempt to oxidize **7** with peroxytrifluoroacetic acid. Apparently the trifluoroacetic acid produced in the formation of peracid from hydrogen peroxide and trifluoroacetic anhydride and as a by-product of oxidation processes catalyzes the rearrangement of **7.** These rearrangements are apparently faster than Baeyer–Villiger oxidation despite the presence of large amounts of potassium dihydrogen phosphate in the reaction medium.

Acids are known to catalyze rearrangement of cyclopropyl ketones.[5] However, the conditions required to promote these rearrangements are generally quite strenuous. We were therefore surprised at the ease with which rearrangement of **7** occurred. Under the same conditions, no rearrangement of **6, 14, 15,** or **16** occurred. Treatment of **6** with toluenesulfonic acid in refluxing chloroform does not even promote rearrangement. Yet **7** rearranges in 0.1 M trifluoroacetic acid at room temperature. The facile rearrangement of **7** is apparently a result of two factors: the stability of the cation initially

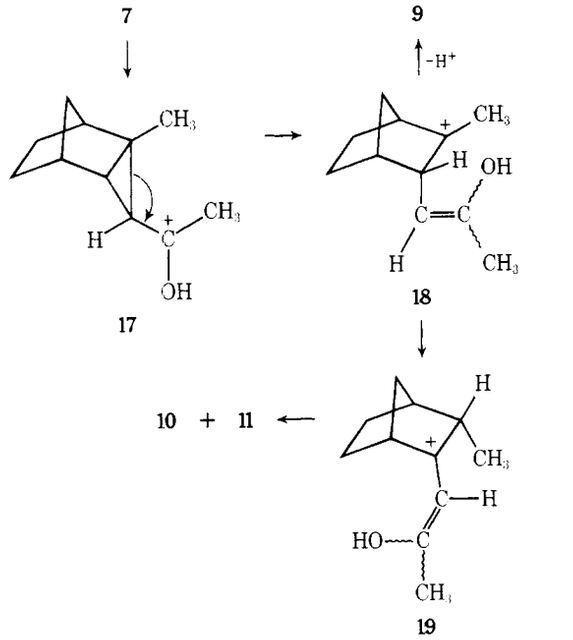


14 15 16

produced and the strain relieved in rearrangement of this system. Lack of rearrangement of **6** illustrates this first factor. Lack of rearrangement of the less strained cyclopropyl ketones **14, 15,** and **16** demonstrates the importance of the latter strain factor. The strain energies of **15** and **16** may be approximated by those of bicyclo[4.1.0]heptane and bicyclo[3.1.0]hexane, which are 30 and 34 kcal/mol, respectively.[5d] Although there are no theoretical estimates or experimental values for the strain energy associated with the *endo*-tricyclo[3.2.1.$0^{2,4}$]octyl system, the value is expected to be *greater* than that of the former two systems. The fusion of the norbornyl system (17 kcal/mol strain energy) to the cyclopropyl ring should result in a strain energy of **7** between that of **16** and a bicyclo[2.1.0]-pentyl system (57 kcal/mol).[5d] The extra ground state strain associated with the cyclopropyl ring of **7** provides a rationale for its more rapid acid-catalyzed rearrangement.

The mechanistic pathway shown in Scheme III illustrates some interesting features of the rearrangement. The cyclo-

Scheme III



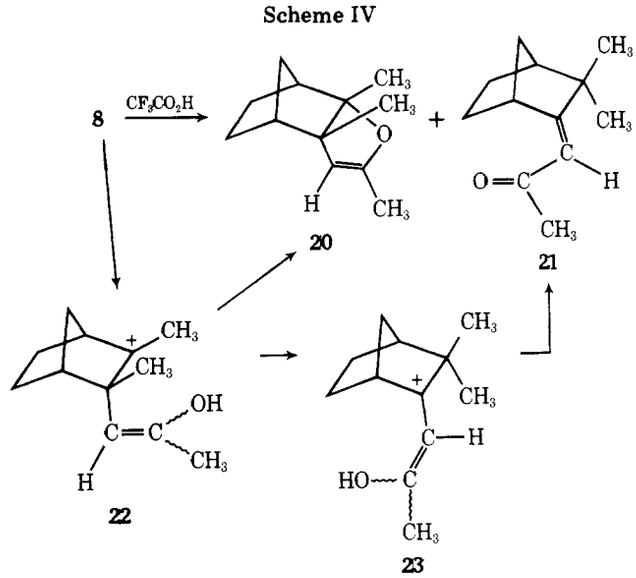
17 18 19

propyl carbinyl, homoallylic rearrangement of the protonated ketone **17** gives cation **18.** Exo hydride migration to give allylic cation **19** is apparently the major fate of **18,** and consistent with the expected facile exo 2,3-hydride shift in norbornyl cations.[6] This exo hydride shift accounts for the observed endo methyl stereochemistry in the major rearrangement product, **10,** and strongly suggests a similar methyl stereochemistry in **11.** Apparently methyl substitution at carbon 3 results in allylic cation **19** being produced in preference to the isomer with the larger group syn to the endo methyl group.[7] Deprotonation of **19** results in **10** while deprotonation of the isomeric allylic cation yields the minor isomeric α,β-unsaturated ketone **11.**[8]

Ketone **8** also rearranges rapidly in dilute trifluoroacetic acid solution. In this case the products obtained were enol ether **20** and α,β-unsaturated ketone **21** in a ratio of 1:2.6, respectively.

The structure of ketone **21** was based on its infrared and

Scheme IV



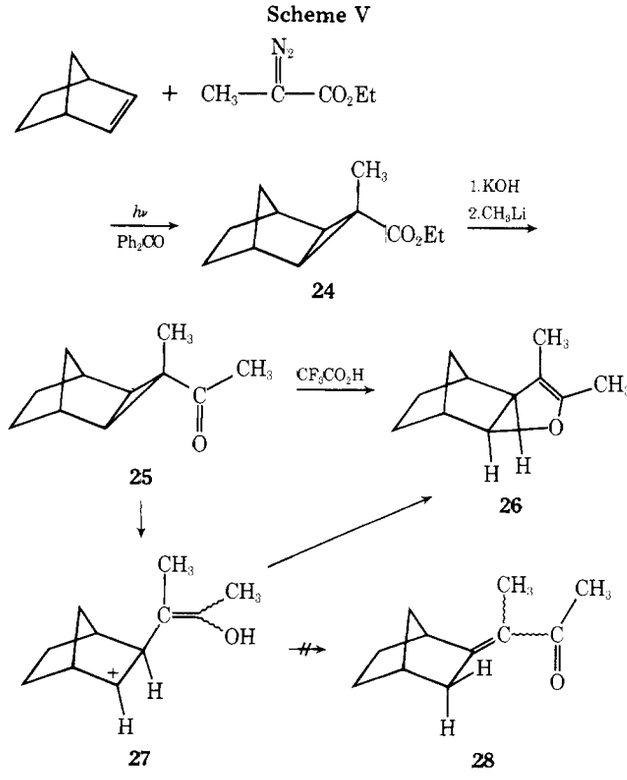
20 21 22 23

NMR spectral properties. The NMR spectrum showed an olefinic proton singlet at δ 5.78, a single proton multiplet at δ 3.95, attributed to the allylic bridgehead proton, and methyl singlets at δ 2.09 and δ 1.06. Apparently the geminal dimethyl substitution at carbon 3 results in formation of ketone **21** with the exclusion of the isomeric α,β-unsaturated ketone.

The structure of enol ether **20** was based on mass spectral, infrared, and NMR data. The mass spectrum showed that the product is isomeric with ketone **8** while the infrared spectrum showed the presence of a carbon–carbon double bond at 5.97 μ. The NMR spectrum showed an olefinic proton at δ 4.12, a methyl doublet at δ 1.70, and methyl singlets at δ 1.17 and 0.98. The unusual formation of enol ether **20** is in line with a lower propensity for exo methyl migration (relative to hydride) in this norbornyl system.[9] Competing with methyl migration in cation **22** is intramolecular cyclization to give **20.** This product is formally the result of a carbonyl analogue of the vinylcyclopropane to cyclopentene rearrangement.[10]

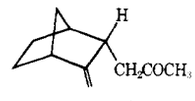
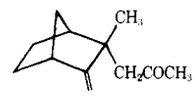
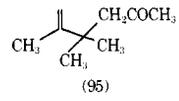
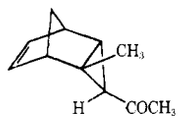
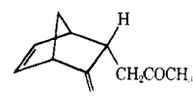
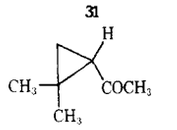
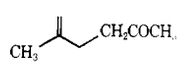
Ketone **25**[11] can be prepared, as shown in Scheme V, via

Scheme V



24 25 26 27 28

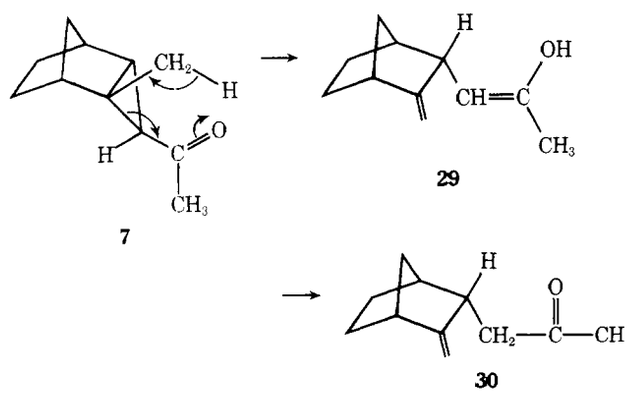
Table I. Rates of Rearrangement in *n*-Dodecane at 210 °C

Registry no.	Ketone	Half-life, h	Product (%)[c]
42856-13-3	7	1.5	 (83)
60802-85-9	8	0.13	 (94)
60802-86-0	14	1.2	 (95)
28465-15-8	 31	2.3[a]	 (84)
872-75-3	 32	0.11[b]	

[a] See ref 15. [b] Calculated from data of Roberts, ref 14. [c] Pyrolysis of neat ketone; isolated yield after distillation.

ester **24**, produced in the benzophenone sensitized addition of ethyl diazopropionate to norbornene.[12] In this system, we sought to determine the effect of increased steric strain due to an unfavorable interaction of the 3-methyl group with the methylene bridge. We also wanted to evaluate the effectiveness of potential endo hydride migration.[13] Slightly more strenuous conditions are required to promote rearrangement of **25**. Refluxing in 0.4 M trifluoroacetic acid in methylene chloride promoted rearrangement despite the necessity of involving a relatively unstable secondary cation, **27**. A low yield of enol ether **26** was produced as the sole isolable product. No α,β-unsaturated ketones, **28**, which would be a result of endo hydride migration, are observed. These observations reinforce the belief that endo hydride migration in norbornyl systems is a relatively slow process.[6,9]

In addition to undergoing facile acid-catalyzed rearrangements, ketones **7** and **8** are also thermally labile as is ketone **14**. At temperatures above 200 °C, we have observed rearrangements yielding γ,δ-unsaturated ketones. This process has been discussed by Roberts[14] and is considered to be a concerted thermal process giving products analogous to the Norrish type II photochemical process. Rearrangement of **7** gave ketone **30** via **29**. It is interesting to note that none of this ketone is produced in the acid-catalyzed rearrangement



process. Table I gives rates of this rearrangement and analogous processes in *n*-dodecane solvent as monitored by NMR spectroscopy. Rates of thermal rearrangement are all comparable, differing only by a factor of 20. Reasons for the slightly more facile rearrangements of **8** and **32** are not well understood. Statistical correction of the rate constants for **8** and **14** does not further simplify the data. However, the general rearrangement appears to be applicable for the preparation of the γ,δ class of unsaturated ketones.

Experimental Section

Acyloin Condensation of *endo*-2,3-Dicarbomethoxy-2-methylbicyclo[2.2.1]heptane. Sodium metal (23 g) was dispersed in 1 l. of dry, refluxing toluene in a Morton flask and 103.4 g of chlorotrimethylsilane was added. A solution of 45.1 g of *endo*-2,3-dicarbomethoxy-2-methylbicyclo[2.2.1]heptane (from hydrogenation, esterification of the methyl maleic anhydride, cyclopentadiene adduct) in 530 ml of toluene was added dropwise using a Hirsch dropping funnel over a 15-h period. Refluxing was continued for 1 h and the mixture was then filtered through Celite. Solvents were removed by distillation at reduced pressure. The crude product was distilled through a Vigreux column to give 53.7 g (73%) of the corresponding bis(trimethylsilyl) ether: bp 65–80 °C (0.15 mm); NMR (CCl_4) δ 2.15 (2 H, m), 1.9–1.4 (3 H, m), 1.3 (4 H, m), 1.12 (3 H, s), 0.10 (18 H, d).

Anal. Calcd for $C_{16}H_{30}O_2Si_2$: C, 61.87; H, 9.74. Found: C, 61.79; H, 9.75.

Preparation of *exo*-2-Methyl-3-carbomethoxytricyclo[3.2.1.$0^{2,4}$]octane. A solution of 20.4 g of the bis(trimethylsilyl) ether prepared above in 100 ml of methanol was refluxed for 10 h. The methanol was removed at reduced pressure. The NMR spectrum of the crude α-hydroxy ketone showed a mixture of isomers. The major isomer (approximately 2 parts) showed a carbinyl proton doublet at δ 4.91, J = 9 Hz, and is presumed to be *endo*-3-hydroxy-5-methyltricyclo[4.2.1.$0^{2,5}$]nonan-4-one on the basis of this coupling constant. The minor isomer (approximately 1 part) shows a carbinyl proton doublet at δ 4.47, J = 4 Hz, and is presumably *endo*-3-hydroxy-2-methyltricyclo[4.2.1.$0^{2,5}$]nonan-4-one on the basis of the smaller coupling constant. The crude mixture of hydroxy ketones was converted directly to a tosylate mixture by treatment with 14.2 g of tosyl chloride in 90 ml of pyridine for 2 days at −5 °C. The pyridine solution was taken up into ether and water and the organic extract was washed with dilute hydrochloric acid to remove the pyridine. After drying, the solvent was removed by rotary evaporator. The NMR of the crude oil showed a mixture of tosylate (doublets at δ 5.36, J = 9 Hz, and 4.90, J = 3 Hz).

The crude tosylate mixture was dissolved in 40 ml of methanol and added to a solution of sodium methoxide prepared from 15.7 g of sodium in 240 ml of methanol at room temperature. The solution was slowly brought to reflux and reflux was continued for 2.5 h. The mixture was then cooled and taken up into ether and water containing 40 ml of acetic acid. The ether extract was washed with water and saturated sodium chloride solution and dried over anhydrous sodium sulfate. The solvent was removed by distillation through a Vigreux column and the residue was distilled to give 6.86 g [58% based on bis(trimethylsilyl) ether] of ring contracted ester: bp 65 °C (0.15 mm); NMR (CCl_4) δ 3.63 (3 H, s), 2.6–1.2 (9 H, m), 1.27 (3 H, s); mass spectroscopic molecular weight, 180.1156 (calcd for $C_{11}H_{16}O_2$, 180.1150).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.42; H, 9.02.

Preparation of *exo*-2-Methyltricyclo[3.2.1.$0^{2,4}$]octane-3-carboxylic Acid. A mixture of 4.85 g of 86% potassium hydroxide, 30 ml of water, 30 ml of methanol, and 6.86 g of *exo*-2-methyl-3-carbomethoxytricyclo[3.2.1.$0^{2,4}$]octane was refluxed for 2 h. Approximately 40 ml of the solvent was removed by distillation and the residue was added dropwise with stirring to a cold solution of 16 ml of concentrated hydrochloric acid in 150 ml of water. The precipitated acid was collected on a Buchner funnel and air dried to give 5.71 g (90%) of carboxylic acid: mp 139–144 °C; mass spectroscopic molecular weight 166.0990 (calcd for $C_{10}H_{14}O_2$, 166.0994).

Preparation of 7. Methyllithium (8 ml of a 1.7 M solution in ether) was diluted to 15 ml with ether and added dropwise to a solution of 1.00 g of *exo*-2-methyltricyclo[3.2.1.$0^{2,4}$]octane-3-carboxylic acid in 10 ml of ether at 0 °C. The mixture was brought to reflux for 1 h and cooled to room temperature and excess ethyl acetate was added dropwise to destroy excess methyllithium. Water was then added, the organic phase was separated and dried over anhydrous sodium sulfate, and the solvent was removed by distillation through a Vigreux column.

The residue was distilled to give 0.851 g (86%) of ketone **7**: bp 65–68 °C (0.8 mm); NMR (CCl_4) δ 2.6–1.0 (broad multiplets) with sharp singlets at 2.15 and 1.13; mass spectroscopic molecular weight, 164.1215 (calcd for $C_{11}H_{16}O$, 164.1201).

Preparation of *endo*-2,3-Dicarbomethoxy-2,3-dimethylbicyclo[2.2.1]heptane. Lithium diisopropylamide was prepared from 44.5 g of diisopropylamine and 184 ml of 2.4 M butyllithium in hexane. The solvent was removed under vacuum and the solid residue was dissolved in 250 ml of tetrahydrofuran under nitrogen. The mixture was cooled to −78 °C and a solution of 76 g of *endo*-2,3-dicarbomethoxy-2-methylbicyclo[2.2.1.]heptane in 150 ml of tetrahydrofuran was added dropwise. After stirring for 4 h at −78 °C, a solution of 124 g of methyl iodide in 420 ml of dimethyl sulfoxide was added while warming to room temperature. After stirring at room temperature for 4 h, the entire mixture was taken up into ether and water. The aqueous phase was extracted with an additional portion of ether and the combined ether extracts were washed with dilute hydrochloric acid to remove the amine. After washing with 2 portions of water and saturated sodium chloride solution, the organic phase was dried over anhydrous sodium sulfate and the solvent was removed by rotary evaporator. Gas chromatographic analysis indicated about 80% conversion to the alkylated diester. The mixture was recycled in portions to give samples of greater than 95% *endo*-2,3-dicarbomethoxy-2,3-dimethylbicyclo[2.2.1]heptane, bp 110–115 °C (0.6 mm), with traces of unalkylated diester as the only impurity: NMR (CCl_4) δ 3.53 (6 H, s), 2.2–1.0 (8 H, m), 1.23 (6 H, s).

Acyloin Condensation of *endo*-2,3-Dicarbomethoxy-2,3-dimethylbicyclo[2.2.1]heptane. Sodium metal (14 g) was dispersed in 600 ml of refluxing toluene and 62 g of chlorotrimethylsilane was added followed by a solution of 28.5 g of diester in 330 ml of toluene over a 9-h period. Reflux was continued for 13 h. The workup was identical with that previously described. After removal of the toluene by distillation at reduced pressure, the product was distilled to give 31.2 g (81%) of the corresponding bis(trimethylsilyl) ether: bp 78–90 °C (0.15 mm); NMR (CCl_4) δ 1.9–1.2 (8 H, m), 1.02 (6 H, s), 0.18 (18 H, s).

Anal. Calcd for $C_{17}H_{32}O_2Si_2$: C, 62.90; H, 9.94. Found: C, 63.14; H, 9.83.

Preparation of *exo*-2,4-Dimethyl-3-carbomethoxytricyclo[3.2.1.0^{2,4}]octane. A solution of 15.4 g of the bis(trimethylsilyl) ether prepared above and 75 ml of methanol was refluxed for 8 h and the solvent was removed under vacuum. The clear oil was converted directly to the tosylate by treatment with 11.73 g of *p*-toluenesulfonyl chloride in 70 ml of pyridine at 0 °C. After 3 days the entire mixture was taken up into ether and water. The ether extract was washed with hydrochloric acid to remove pyridine and dried in the usual manner. Solvent was removed by rotary evaporator. The crystalline product was washed with low-boiling petroleum ether and collected on a Buchner funnel. The yield of tosylate was 10.92 g (68%), mp 92–93 °C.

A solution of sodium methoxide was prepared from 9.2 g of sodium and 130 ml of methanol. The crude tosylate obtained above was added to the cold solution which was gradually brought to reflux. Reflux was continued for 2.5 h. The mixture was taken up into water and ether containing 24 ml of acetic acid. After a standard aqueous workup, the ether solvent was removed by distillation through a Vigreux column. The residue was distilled to give 3.78 g (59%) of ring contracted ester: bp 73 °C (0.15 mm); NMR (CCl_4) δ 3.53 (3 H, s), 2.09 (2 H, m), 1.9–1.1 (7 H, m), 1.20 (6 H, s). The mass spectrum showed a molecular ion at *m/e* 194.

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.57; H, 9.30.

Preparation of *exo*-2,4-Dimethyltricyclo[3.2.1.0^{2,4}]octane-3-carboxylic Acid. The procedure was analogous to that previously described for the monomethylated carboxylic acid. Saponification of 2.24 g of ester with 1.3 g of potassium hydroxide in 6 ml of methanol and 8 ml of water gave 2.06 g (99%) of *exo*-2,4-dimethyltricyclo[3.2.1.0^{2,4}]octane-3-carboxylic acid: mp 162–164 °C; mass spectroscopic molecular weight, 180.1153 (calcd for $C_{11}H_{16}O_2$, 180.1150).

Preparation of 8. A solution of 1.2 g of *exo*-2,4-dimethyl-3-carbomethoxytricyclo[3.2.1.0^{2,4}]octane in 15 ml of ether was cooled in ice as 9 ml of 1.8 M methyllithium, diluted with 10 ml of ether, was added dropwise. The mixture was refluxed for 1.5 h and ethyl acetate was added to destroy excess methyllithium. Water was added and a standard aqueous workup followed. Solvent was removed by distillation through a Vigreux column. The residue was distilled to give 1.06 g (89%) of ketone **8**: bp 55–56 °C (0.15 mm); NMR (CCl_4) δ 2.11 (3 H, s), 2.05–1.15 (8 H, m), 1.16 (6 H, s). The mass spectrum of **8** showed a molecular ion at *m/e* 178.

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.58; H, 10.47.

Acid-Catalyzed Rearrangement of 7. Ketone **7** (114 mg) was stirred at room temperature for 15 min with 6 ml of 0.4 M trifluoroacetic acid in methylene chloride. The mixture was then taken up into ether and water, washed with potassium carbonate solution and saturated sodium chloride solution, and dried over anhydrous sodium sulfate. Solvents were removed by distillation through a Vigreux column. The residue was distilled to give 106 mg (93%) of a mixture of ketones **9, 10,** and **11.** Samples of all three ketones were isolated by preparative gas chromatography using a 6-ft, 15% Carbowax 20M on Chromosorb P column at 145 °C. The major product of longest retention time, ketone **10,** had the following NMR spectrum (CCl_4): δ 5.81 (1 H, d, J = 2 Hz), 3.92 (1 H, m), 2.7–1.2 (11 H, m with sharp singlet at 2.07), 1.04 (3 H, d, J = 6.5 Hz). The UV spectrum showed λ_{max} at 248 nm (ε 13 400); IR $\nu_{C=O}$ and $\nu_{C=C}$ complex with absorptions at 5.91, 6.02, and 6.17 μ. The mass spectrum of **10** showed a molecular ion at *m/e* 164.

The product of intermediate retention time, ketone **11,** had the following NMR spectrum (CCl_4): δ 6.03 (1 H, d, J = 2.5 Hz), 2.9–1.2 (12 H, m with sharp singlet at 2.06), 1.08 (3 H, d, J = 7 Hz); IR $\nu_{C=O}$ and $\nu_{C=C}$ at 5.93 and 6.17 μ. The UV spectrum of an equimolar mixture of **11** and i showed λ_{max} at 247 nm (ε 10 400). The mass spectrum of **11** showed a molecular ion at *m/e* 164.

The product of shortest retention time, ketone **9,** showed a molecular ion at *m/e* 164 in the mass spectrum. The infrared showed $\nu_{C=O}$ at 5.82 μ. Ketone **9** was produced in only trace amounts. The ratio of **10** to **11** was 5.8:1 as determined by NMR of the product mixture. A control experiment showed that separate treatment of each of the products with 0.4 M trifluoroacetic acid in methylene chloride at room temperature for 15 min did not result in their interconversion. The rearrangement of **7** was also found to occur rapidly in 0.1 M trifluoroacetic acid in methylene chloride at room temperature.

Ozonolysis of 10. A 74-mg sample of ketone **10,** isolated by preparative gas chromatography, in 3 ml of methanol was cooled to −78 °C and ozonized exhaustively. A solution of sodium iodide and sodium thiosulfate was added and the mixture was taken up into ether and water. Gas chromatographic analysis of the mixture on a 6-ft, 10% XE 60 on Chromosorb P column showed three minor products of shorter retention time than the major product, ketone **12.** Ketone **12** was isolated by preparative gas chromatography and identified by infrared spectral comparison with an authentic sample prepared as described below. The major impurity is a methyl ester, with a molecular ion at *m/e* 156, which is formally a result of addition of methanol across the 2,3 bond of **12.**

Preparation of 12 from *exo*-3-Methylbicyclo[2.2.1]heptan-2-one (13). A solution of 0.5 g of *exo*-3-methylbicyclo[2.2.1]heptan-2-one (**13**) (prepared by methylation of the enolate anion derived from norcamphor with methyl iodide) in 3 ml of tetrahydrofuran was added dropwise to a solution at −78 °C of lithium diisopropylamide in tetrahydrofuran prepared from 0.69 g of diisopropylamine and 3.1 ml of 2.17 M butyllithium in hexane. The solution was allowed to warm to approximately −40 °C for 20 min and recooled to −78 °C. A solution of 0.6 g of acetic acid in ether was then added dropwise. The mixture was warmed to room temperature and taken up into ether and water and the ether extract was washed with dilute hydrochloric acid. The organic phase was then washed with saturated sodium chloride solution and dried over sodium sulfate. Gas chromatographic analysis showed the appearance of a new product, ketone **12,** along with some unchanged **13.** A sample of **12** was isolated by preparative gas chromatography and was identical with the ketone product produced in the ozonolysis of **10.** The ratio of **12** to **13** was 3.55:1 as determined by gas chromatography.

Acid-Catalyzed Rearrangement of 8. A mixture of 164 mg of ketone **8** and 8 ml of 0.2 M trifluoroacetic acid in methylene chloride was held at room temperature for 12 min and then taken up into ether and water. After washing with dilute potassium carbonate solution and drying, the solvents were removed by distillation through a Vigreux column. The residue was distilled to give 105 mg (65%) of a mixture of enol ether **20** and ketone **21.** Samples of each product were isolated by preparative gas chromatography on a 6-ft, 15% Carbowax on Chromosorb P column at 150 °C. The minor product of shorter retention time, **20,** had the following NMR spectrum (CCl_4): δ 4.10 (1 H, m), 2.05 (1 H, m), 1.83 (1 H, m), 1.71 (3 H, d, J = 1.3 Hz), 1.8–1.2 (6 H, m), 1.17 (3 H, s), 0.98 (3 H, s); IR $\nu_{C=C}$ 5.97 μ; mass spectroscopic molecular weight 178.

The major product of longest retention time, ketone **21,** had the following NMR spectrum (CCl_4): δ 5.78 (1 H, bs), 3.95 (1 H, m), 2.08 (3 H, s), 2.07–1.10 (7 H, m), 1.06 (6 H, s); IR $\nu_{C=O}$ and $\nu_{C=C}$ absorptions at 5.92, 6.02, and 6.61 μ. The ratio of ketone **21** to enol ether **20**

was 2.58:1 as determined by NMR.

Preparation of 24. A mixture of 0.54 g of ethyl diazopropionate, 0.87 g of benzophenone, 17.4 g of norbornene, and 2 ml of pentane was irradiated with a set of General Electric sun lamps for 6 h during which time the yellow color faded substantially. The norbornene was removed by distillation through a Vigreux column. The crude ester **24** was separated from benzophenone by distillation through a Vigreux column. The yield of ester **24** was 0.55 g (69%): bp 54–57 °C (0.08 mm); NMR (CCl_4) δ 4.01 (2 H, q, J = 7 Hz), 2.42 (2 H, m), 1.42 (3 H, s), 1.4–1.0 (7 H, m), 1.20 (3 H, t, J = Hz), 0.83–0.50 (1 H, m). The mass spectrum of **24** showed a molecular ion at m/e 194.

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.42; H, 9.29.

Saponification of 24. A mixture of 1.11 g of ester **24**, 0.78 g of potassium hydroxide, 6 ml of water, and 6 ml of methanol was refluxed for 3.5 h. The remainder of the procedure was analogous to that previously described. The yield of crude acid was 0.70 g (74%): mp 131–133 °C; NMR (CCl_4) δ 12.38 (1 H, bs), 2.44 (2 H, m), 1.7–1.2 (11 H, m with sharp singlet at 1.43), 0.9–0.5 (1 H, m); mass spectroscopic molecular weight, 166.0992 (calcd for $C_{10}H_{14}O_2$, 166.0994).

Preparation of 25. The same general procedure was followed as described for the preparation of **7** and **8** from the corresponding acids. Reaction of 0.72 g of carboxylic acid in 15 ml of ether with 5.6 ml of 1.8 M methyllithium in ether gave 0.64 g (91%) of ketone **25**: bp 66–68 °C (0.3 mm); NMR (CCl_4) δ 2.44 (2 H, m), 2.02 (3 H, s), 1.7–1.0 (11 H, m with a sharp singlet at 1.44), 0.90–0.55 (1 H, m); mass spectroscopic molecular weight, 164.1194 (calcd for $C_{11}H_{16}O$, 164.1201).

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

Acid-Catalyzed Rearrangement of 25. A solution of 300 mg of ketone **25** in 8 ml of 0.4 M trifluoroacetic acid in methylene chloride was refluxed for 15 min and then worked up in the manner previously described. Gas chromatographic analysis revealed the presence of a single product and no starting ketone. The product, enol ether **26**, was isolated by preparative gas chromatography using a 6-ft, 15% Carbowax 20M on Chromosorb P column at 140 °C and had the following NMR spectrum (CCl_4): δ 4.17 (1 H, d, J = 8 Hz), 2.7–1.9 (3 H, m), 1.60 (3 H, m), 1.48 (3 H, m), 1.5–0.8 (6 H, m); IR $\nu_{C=C}$ at 5.87 μ. The mass spectrum showed a molecular ion at m/e 164.

Thermal Rearrangement of Methyl Cyclopropyl Ketones. In a typical procedure, 92 mg of ketone **7** and 21 mg of biphenyl (internal standard) were dissolved in n-dodecane and sealed in an NMR tube under nitrogen. The tube was immersed in an oil bath at 210 ± 1 °C. In all cases rates were monitored by following the appearance of the olefinic protons as a function of time. Thermal rearrangements in which products were isolated were carried out on the neat liquids in sealed tubes at 220 °C.

Registry No.—**2**, 60802-87-1; **3**, 60802-88-2; **4** (R_1 = H; R_2 = CH_3), 60802-89-3; **4** (R_1 = R_2 = CH_3), 60802-90-6; **5** (R_1 = H; R_2 = Me), 60802-91-7; **5** (R_1 = R_2 = CH_3), 60802-92-8; **9**, 60802-93-9; **10**, 60802-94-0; **11**, 60828-27-5; **20**, 17812-18-9; **21**, 60802-95-1; **24**, 60802-96-2; **24** free acid, 60802-97-3; **25**, 42856-10-0; **26**, 60802-98-4; i, 60828-28-6; *endo*-3-hydroxy-5-methyltricyclo[4.2.1.$0^{2,5}$]-nonan-4-one, 60802-99-5; *endo*-3-hydroxy-2-methyltricyclo-[4.2.1.$0^{2,5}$]nonan-4-one, 60803-00-1; *endo*-3-hydroxy-5-methyltricyclo[4.2.1.$0^{2,5}$]nonan-4-one tosylate, 60803-01-2; *endo*-3-hydroxy-2-methyltricyclo[4.2.1.$0^{2,5}$]nonan-4-one tosylate, 60803-02-3; *exo*-2-methyltricyclo[3.2.1.$0^{2,4}$]octane-3-carboxylic acid, 60803-03-4; *exo*-2,5-dimethyl-*endo*-3-hydroxytricyclo[4.2.1.$0^{2,5}$]nonan-4-one, 60803-04-5; *exo*-2,4-dimethyltricyclo[3.2.1.$0^{2,4}$]octane-3-carboxylic acid, 60803-05-6; ethyl diazopropionate, 6111-99-5; norbornene, 498-66-8; *exo*-2,5-dimethyl-*endo*-3-hydroxytricyclo[4.2.1.$0^{2,5}$]-nonan-4-one tosylate, 60803-06-7; chlorotrimethylsilane, 75-77-4; tosyl chloride, 98-59-9.

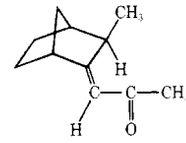
References and Notes

(1) NSF Undergraduate Research Participant, 1975–1976.

(2) X. Creary, *J. Org. Chem.*, **40**, 3326 (1975).

(3) For related examples of kinetic protonation from the less hindered side of enolate anions see (a) H. O. House, B. A. Tefertiller, and H. D. Olmstead, *J. Org. Chem.*, **33**, 935 (1968); (b) H. O. House and T. M. Bare, *ibid.*, **33**, 943 (1968); (c) F. Johnson and S. K. Malhotra, *J. Am. Chem. Soc.*, **87**, 5493, 5513 (1965).

(4) We have found that injection of **7** on a 15% Carbowax on Chromosorb P column at 150 °C also results in rearrangement of **7** to give **9**, **10**, and **11** in different ratios than the trifluoroacetic acid catalyzed rearrangement. A fourth ketone, i, is also produced in approximately the same amount as **11**. The structure of i is assigned on the basis of the NMR spectrum of the



i

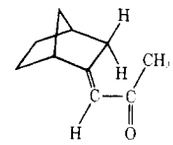
inseparable mixture of **11** and i, which shows a doublet (J = 7 Hz) at δ 1.00 and no unusual downfield shift of the allylic bridgehead proton. The origin of i is unclear as is the origin of the gas chromatographic rearrangement. A trace of "acid" on th column is a prime suspect.

(5) (a) H. M. Walborsky and L. Plonsker, *J. Am. Chem. Soc.*, **83**, 2138 (1961); (b) J. P. Freeman, *J. Org. Chem.*, **31**, 538 (1966); (c) G. Combaut and L. Giral, *Bull. Soc. Chim. Fr.*, 3258 (1969); (d) P. Schleyer, J. E. Williams, and K. R. Blanchard, *J. Am. Chem. Soc.*, **92**, 2377 (1970).

(6) G. D. Sargent in "Carbonium Ions", Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N.Y., 1972, p 1110.

(7) The rearrangements are suggested to proceed through enols **18** and **19**. Although we cannot eliminate the keto forms of these cations, we believe that one of the driving forces for hydride migration from the tertiary cationic center of **18** is the greater stability of allylic cation **19**.

(8) Ketone ii is produced from protonation of the corresponding enolate anion. Steric factors are probably responsible for the predominance of **10** and **21**, in which the acetyl stereochemistry is reversed, in the acid-catalyzed



ii

ketone rearrangement. See J. F. Bunnett, X. Creary, and J. E. Sundberg, *J. Org. Chem.*, **41**, 1707 (1976).

(9) For related rates of hydride and methyl migration under stable ion conditions, see (a) A. J. Jones, E. Huang, R. Haseltine, and T. S. Sorensen, *J. Am. Chem. Soc.*, **97**, 1133 (1975); (b) E. Huang, K. Ranganayakulu, and T. S. Sorensen, *ibid.*, **94**, 1780 (1972).

(10) For leading references see J. S. Swenton and A. Wexler, *J. Am. Chem. Soc.*, **93**, 3066 (1971).

(11) Ketone **25** has been prepared by a much more tedious route; see H. Monti and M. Bertrand, *Tetrahedron Lett.*, 2587 (1970).

(12) An analogous benzophenone sensitized addition to isobutylene has been reported. See M. B. Sohn and M. Jones, Jr., *J. Am. Chem. Soc.*, **94**, 8280 (1972).

(13) Such processes are generally quite unfavorable. See ref 6 and 9.

(14) R. M. Roberts, G. G. Landolt, R. N. Greene, and E. W. Heyer, *J. Am. Chem. Soc.*, **89**, 1404 (1967).

(15) Ketone **31** was prepared by a route analogous to the preparation of **7**. Monti and Bertrand[16] have previously reported the pyrolysis of **31** produced by an alternate method but give no kinetic data.

(16) H. Monti and M. Bertrand, *Tetrahedron Lett.*, 2591 (1970).