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Sigma Assisted vs. Unassisted Pathways in the Ionization of Tertiary Cyclopropyl Triflates

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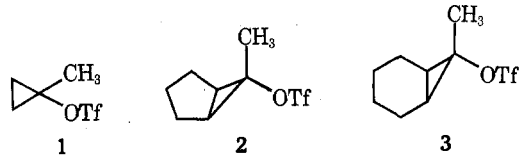
Synthetic schemes have been developed which allow the preparation of *endo*-6-methyl-*exo*-bicyclo[3.1.0]hex-6-yl triflate (**2**) and *endo*-7-methyl-*exo*-bicyclo[4.1.0]hept-7-yl triflate (**3**). Synthesis of the latter involved a copper-catalyzed addition of ethyl diazopropionate to cyclohexene which give principally the *exo*-carboethoxy cyclopropanation product **17**. Similar stereoselectivity was seen in the addition to cyclopentene. Solvolysis rates of 1-methyl cyclopropyl triflate, **1**, **2**, and **3** were rapid in acetic acid at room temperature. Relative rates were 0.95, 1.0, and 8.8, respectively. Solvolysis of **2** was suggested to involve the unopened 6-methylbicyclo[3.1.0]hex-6-yl cation, **25**, which rapidly rearranged to an allylic cation before capture of nucleophile could occur. α-Methyl/hydrogen rate ratios were smaller than expected in view of the stabilization demands of an unopened cyclopropyl cation. In contrast **3** gave unopened products on acetolysis. Product and rate data were interpreted in terms of a slightly opened allylic cation, **31**, with charge residing essentially at the 7 position. Triflate **1** gave only isobutylene on solvolysis in aqueous diglyme containing sodium borohydride.

Cyclopropyl substrates tend to undergo ionization with concerted ring opening to give allylic or partially opened allylic cationic systems.[1] Unopened cyclopropyl cations result only when groups capable of contributing greatly to cationic stability are present.[2] Recently[3] we have shown that concerted opening of cyclopropyl systems can be completely blocked in the ionization step by the incorporation of a bicyclo[2.2.1] system fused to the cyclopropyl system trans to the leaving group. Electrocyclic opening could also be prevented if olefinic or cyclopropyl participating groups were suitably positioned.[3,4] While the substitution products in these systems were completely in accordance with cationic rearrangement processes, the response of ionization rate to solvent ionizing power was quite small. Substrate m values[5] were in the range of the nucleophilic mechanism seen for primary substrates. The suggestion offered was that the low response to solvent ionizing power was in part due to the triflate leaving group and also reflected less than "normal" charge development in the transition state for ionization of cyclopropyl triflates.

In order to further support this suggestion, we sought to use the methyl group as a probe for charge development in developing cyclopropyl cations. We also sought to employ the methyl group as a neighboring group to evaluate its effectiveness in thwarting electrocyclic ring opening during ionization. We report here the results of these studies of α-methyl substitution in a series of cyclopropyl triflates.

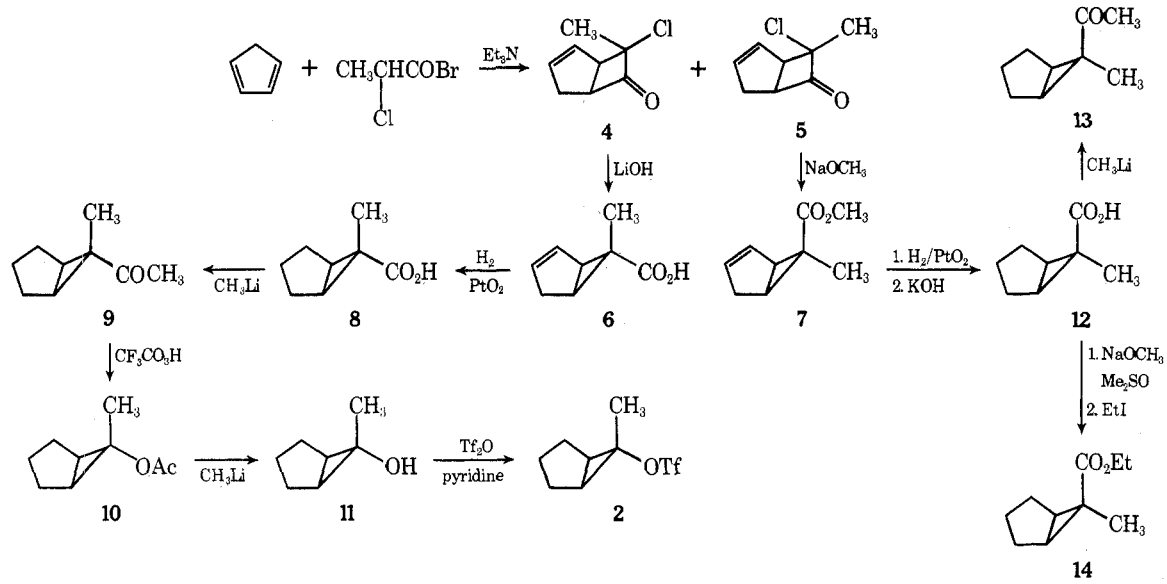
Synthetic Aspects. Of immediate interest was the preparation of triflates **1**, **2**, and **3**. The preparation of **1** has been previously described.[4] Triflate **2** was prepared as shown in Scheme I. The reaction of chloromethylketene, generated from 2-chloropropionyl bromide and triethylamine, and cyclopentadiene led to the known mixture of chloromethylbicyclo[3.2.0]heptenones, **4** and **5**.[6] Chloro ketone **4** was stereospecifically ring contracted with lithium hydroxide to *endo*-6-methyl-*exo*-bicyclo[3.1.0]hex-2-ene-6-carboxylic acid (**6**) using the procedure of Garin and Cammack.[7] Catalytic hydrogenation of the methyl ester of **6** or the unsaturated methyl ketone derived by treatment of **6** with methyllithium gave partial reduction of the cyclopropane ring along with the olefinic linkage. To avoid the cyclopropane bond reduction, it was necessary to carry out the hydrogenation on the free acid using platinum oxide as catalyst. Conversion of the saturated acid **8** to the corresponding methyl ketone **9** was accomplished by treatment with methyllithium. A primary side product of this transformation was the tertiary alcohol derived from addition of methyllithium to **9**. It has been suggested[8] that a major source of tertiary alcohol in the preparation of ketones from acids and organolithium reagents is the addition of unreacted excess organolithium reagent to the ketonic product during the hydrolysis of intermediate, $R_2C(OLi)_2$. In the preparation of **9**, and for many analogous transformations which we have carried out, this problem can be circumvented. Following the suggestion of Jorgenson,[8b] we have destroyed the excess methyllithium by the addition of ethyl acetate to the reaction mixture prior to the addition of water. With this procedure tertiary alcohol formation is negligible.

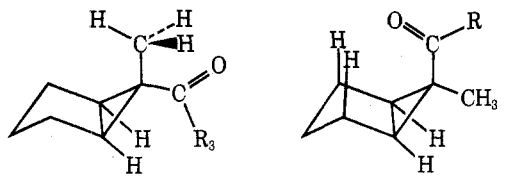
exo-Methyl ketone **9** shows a carbonyl stretching frequency of 1684 cm^{-1}. This compares to a value of 1702 cm^{-1} for the isomeric *endo*-methyl ketone **13**. These significant differences are in line with the decreased conjugation of the carbonyl group with the cyclopropyl system in **13**, and a resultant carbonyl shift to higher energy, as a result of steric factors. Ap-



1 2 3

Scheme I





9, R = CH_3
15, R = OEt

13, R = CH_3
14, R = OEt

parently conjugation in **13** is lessened owing to an unfavorable steric interaction of the *endo*-acetyl group with the fused ring system. Distortion from the preferred conformation necessary for maximal conjugation with the cyclopropyl system, as shown above, results in an increased carbonyl stretching frequency. Similar trends are seen in the ethyl esters **14** and **15** derived from the corresponding acids by alkylation of the carboxylate salts with ethyl iodide in dimethyl sulfoxide. Exo ester **15** has a carbonyl stretching frequency of 1717 cm^{-1} while the value for endo ester **14** is 1727 cm^{-1}.

The remainder of the synthetic sequence shown in Scheme I to triflate **2** was analogous to procedures previously described.

The approach to the synthesis of triflate **3** was undertaken in terms of a carboethoxymethylcarbene addition to cyclohexene. Singlet carboethoxymethylcarbene is expected to yield ethyl acrylate via simple intramolecular hydrogen transfer to the carbenic center. Hence the addition was attempted by way of the triplet state which is known to add to isobutylene to give cyclopropane derivatives.[9] Benzophenone-sensitized photolysis of ethyl diazopropionate in cyclohexene gave small amounts of the desired cyclopropanation product **17**. However, the major product was the radical dimer, **16**. Hydrogen atom abstraction from cyclohexene apparently occurs in preference to addition of triplet carboethoxymethylcarbene to cyclohexene. This approach to synthetically useful amounts of **17** was therefore abandoned.

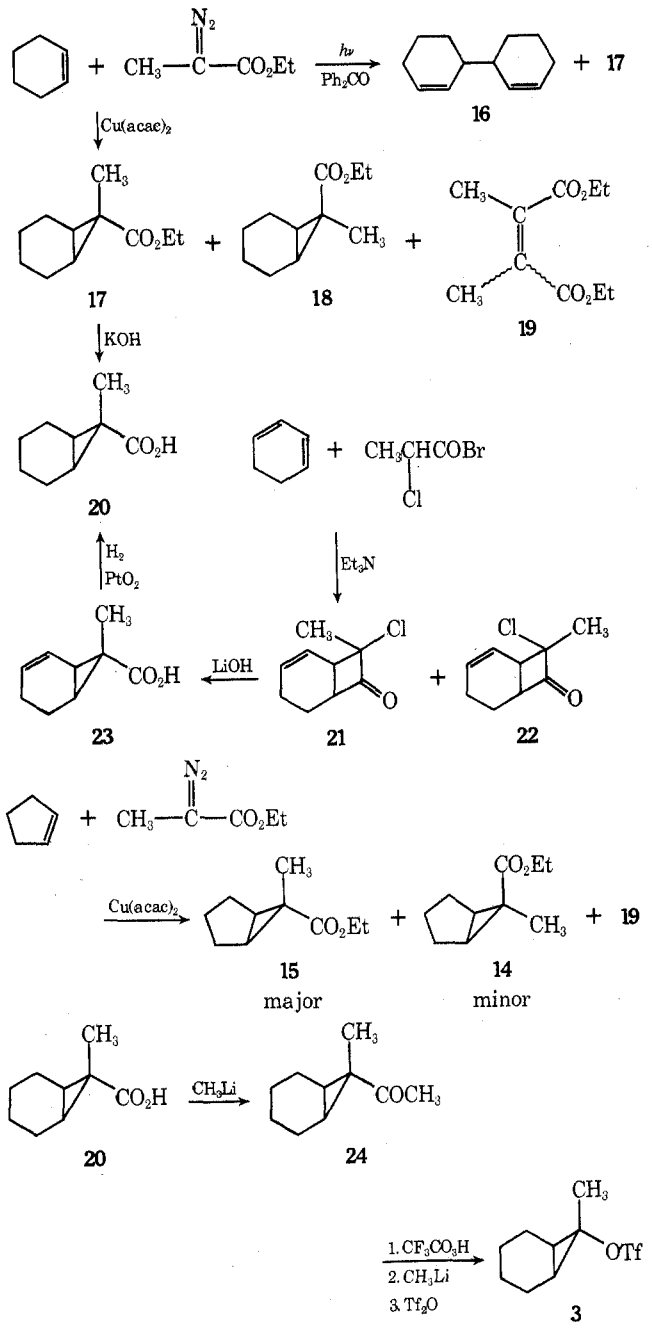
The copper-catalyzed addition of ethyl diazoacetate to cyclohexene has been thoroughly investigated and found to give a predominance of *exo*-7-carboethoxybicyclo[4.1.0]-heptane.[10] We have found that the copper acetylacetonate catalyzed addition of ethyl diazopropionate to cyclohexene gives cyclopropanation products **17** and **18** along with larger amounts of the formal carbene dimers **19**. The *exo*-carboethoxy adduct **17** was the predominant isomer. The stereochemistry of this cyclopropanation product was suggested by the analogous reaction of cyclopentene. The copper acetylacetonate catalyzed reaction of ethyl diazopropionate with cyclopentene gave a 6:1 mixture of *exo*- and *endo*-6-carboethoxy-6-methylbicyclo[3.1.0]hexane (**15** and **14**). Product identification in this case was made by spectral comparison with authentic samples independently prepared as shown in Scheme I. The predominance of the *exo*-carboethoxy isomer **15** in the reaction with cyclopentene suggested a similar stereochemical pathway for cyclohexene.

Proof of the stereochemistry of **17** was accomplished by saponification to give *endo*-7-methyl-*exo*-bicyclo[4.1.0]heptane-7-carboxylic acid (**20**), which could be prepared independently as shown in Scheme II. The known addition of chloromethylketene to 1,3-cyclohexadiene gave a mixture of cycloadducts **21** and **23**.[11] Chloroketene **21** was separated and stereospecifically ring contracted with lithium hydroxide to give the unsaturated acid **23**. This acid could be hydrogenated to give a product identical with that obtained by saponification of **17**.

The stereochemical results of the copper-catalyzed addition of ethyl diazopropionate to cyclopentene and cyclohexene were unexpected in view of the steric requirements of a methyl group vs. the carboethoxy group. Conformational equilibria suggest that a methyl group is sterically more bulky than the carboethoxy group. On this basis, the conclusion must be that some feature other than steric bulk of the two groups controls the stereochemical outcome of the copper complexed carboethoxymethylcarbene addition to cyclopentene and cyclohexene. This stereoselectivity, which is not in accord with steric factors, is not unprecedented. Endo (syn) stereoselectivity is seen in the addition of phenylcarbene,[12] chlorocarbene,[13] and phenylthiocarbene[14] (or carbenoid species), among others, to olefins. Electronic factors in the transition state, which outweigh steric factors, are suggested to account for some cases of syn stereoselectivity.[12] Opposing electronic factors, and not solely steric effects, may control both carboethoxycarbene and carboethoxymethylcarbene (as copper complexes) addition to olefins giving exo (anti) stereoselectivity. The remainder of the synthetic sequence to triflate **3** is shown in Scheme II.

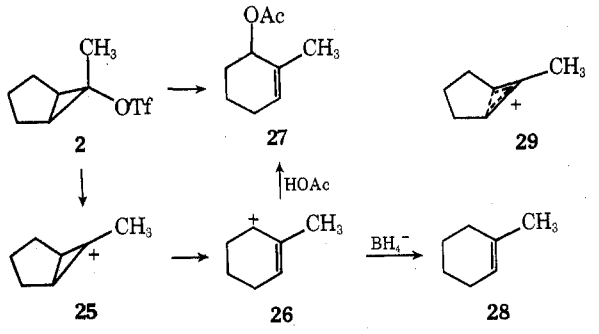
Solvolytic Studies. Triflates **1**, **2**, and **3** proved to be quite reactive. Solvolytic studies were carried out at room temperature in acetic acid. Rate data are given in Table I. In acetic acid, triflate **2** gave 2-methylcyclohex-2-enyl acetate (**27**) as the only product. Even the very nucleophilic borohydride anion cannot intercept structurally unrearranged products. Solvolysis in aqueous diglyme containing sodium borohydride

Scheme II



gave 1-methylcyclohexene (28) as the only product. The mechanistic scheme suggested involves formation of the unopened tertiary cyclopropyl cation **25** as the first intermediate. The products suggest that rearrangement of **25** to allylic cation **26** occurs.

A potential intermediate that must be considered is a partially opened allylic cation such as **29**. Schleyer[1] has postulated



that analogous intermediates intervene in the solvolysis of *exo*-bicyclo[3.1.0]hex-6-yl triflate and *exo*-bicyclo[4.1.0]-hept-7-yl tosylate. Rate and product data were completely in line with neither trans allylic cations nor cyclopropyl cation intermediates. To account for rate data and products of retained ring structure and stereochemistry, partially opened allylic cation intermediates were suggested. Theoretical calculations also support the viability of such intermediates.[1c]

None of the retained acetate **10**, which would be expected from a partially opened allylic cation such as **29**, is observed. Apparently opening of **25** by the allowed disrotatory mode to give **26** is the most rapid process even in the presence of borohydride anion.[15] While solvolysis of *exo*-bicyclo[3.1.0]hex-6-yl triflate is suggested to occur via a partially opened allylic cation,[1a] the methyl group appears to be completely effective in blocking the analogous partial opening of triflate **2** during the ionization process.

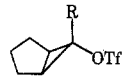
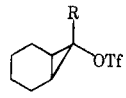
As a sidelight to this investigation, it was found that while borohydride cannot successfully intercept cation **25**, it does succeed in capturing the 1-phenylcyclopropyl cation. Previous studies[20] have shown that solvolysis of 1-phenylcyclopropyl tosylate in acetic acid gave only allylic products. These results can be interpreted in terms of a stepwise process leading to the 2-phenylallyl cation (via the 1-phenylcyclopropyl cation) or possibly a concerted pathway giving the allylic cation directly. We have found that solvolysis of 1-phenylcyclopropyl tosylate in aqueous diglyme containing sodium borohydride gives a hydrocarbon mixture consisting of α-methylstyrene (3.7 parts) and phenylcyclopropane (1 part). These results show that borohydride is nucleophilic enough to intercept some 1-phenylcyclopropyl cations before opening to the allylic cation can occur and provide strong evidence for the discrete intermediacy of the 1-phenylcyclopropyl cation.

Comparison of the rate of solvolysis of *endo*-6-methyl-*exo*-bicyclo[3.1.0]hex-6-yl triflate (**2**) with *exo*-bicyclo[3.1.0]hex-6-yl triflate gives an α-methyl/hydrogen ratio of $10^{7.56}$. This compares to a value of 10^8 suggested by Schleyer[16] as a standard value for secondary substrates. This value is slightly less than the suggested "normal" value. What is the origin of this slight discrepancy? The rationale that immediately comes to mind is the fact that solvolysis of *exo*-bicyclo[3.1.0]hex-6-yl triflate is σ assisted by partial fragmentation of the internal cyclopropane bond, yielding a partially opened allylic cation as the initial intermediate. This fact should result in a less than normal α-methyl/hydrogen rate ratio.

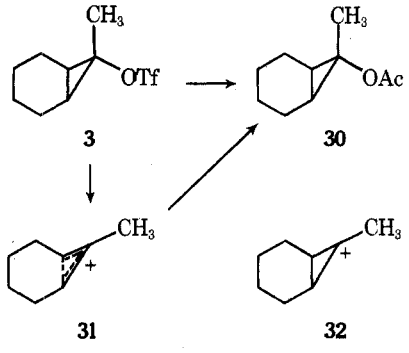
The observed α-methyl/hydrogen ratio of $10^{7.56}$ is also not out of line with the suggestion that transition state charge development in the ionization of cyclopropyl triflates is less than normal.[18] The demand for stabilization on an α-methyl group should be enormous in the extremely unstable cyclopropyl cation. As such, the suggested α-methyl/hydrogen ratio of 10^8 may not reflect the true demand of an unopened cyclopropyl cation. It would not be unreasonable to expect an α-methyl/hydrogen ratio of *greater than* 10^8 owing to this larger than normal demand for stabilization in the unopened cyclopropyl cation. The observed value of $10^{7.56}$ may reflect an early transition state as well as the σ-assisted solvolysis of *exo*-bicyclo[3.1.0]hex-6-yl triflate.

Consider next the acetolysis of *endo*-7-methyl-*exo*-bicyclo[4.1.0]hept-7-yl triflate (**3**). The rate of acetolysis is only slightly faster (8.8 times) than that of **2**. This compares to a rate difference of greater than 5000 for the unmethylated analogues.[4,18] However, a product study shows that only *endo*-7-methyl-*exo*-bicyclo[4.1.0]hept-7-yl acetate (**30**) is produced from **3** in acetic acid. We prefer the mechanistic scheme shown involving partially opened allylic cation **31** as the key intermediate. If tertiary cyclopropyl cation **32** were involved, rapid opening to give an allylic cation, and hence an

Table I. Rates of Solvolysis in Acetic Acid–0.1 M Sodium Acetate

Registry no.	Compd	$k^{25°}$, s^{-1}	k_{rel}	$k_{R=CH_3}/k_{R=H}$
				
60153-71-1	R = CH_3	$(5.82 \pm 0.01) \times 10^{-5}$	1.0	$10^{7.6}$
25327-17-7	R = H	1.61×10^{-12} *a,b*		
				
60153-72-2	R = CH_3	$(5.11 \pm 0.00) \times 10^{-4}$	8.8	$10^{3.9}$
60153-73-3	R = H	6.32×10^{-8} *a,c*		
				
60153-74-4	R = CH_3	$(5.52 \pm 0.04) \times 10^{-5}$	0.95	$10^{3.1}$
25324-42-1	R = H	4.35×10^{-8} *a,b*		$(10^{3.0})^d$

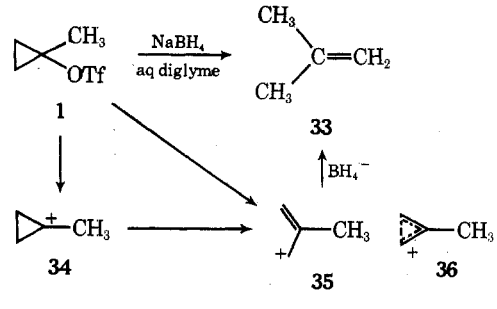
a Extrapolated value. *b* Reference 17. *c* Reference 4. *d* For tosylates; ref 1a.



allylic acetate product, would be expected. The opening of **32** might not be as rapid as the comparable opening of **25**, which even the nucleophilic borohydride cannot intercept. However, opening of **32** should be faster than solvent capture by the relatively nonnucleophilic (vs. borohydride) acetic acid solvent.

The small rate enhancement, relative to **2**, seen in the acetolysis of **3** is also consistent with a small amount of σ assistance. In the intermediate partially opened cation **31**, charge should reside essentially at the tertiary center. Internal bond fragmentation should be minimal, but enough to prevent disrotatory opening to give an allylic cation. This is borne out by the formation of only acetate **30** in which configuration is maintained and no diacetate products analogous to those produced in the acetolysis of *exo*-bicyclo[4.1.0]hept-7-yl tosylate. While methyl substitution can completely offset σ participation in the *exo*-bicyclo[3.1.0]hex-6-yl system, similar substitution is apparently not sufficient to offset the larger amount of σ assistance in bicyclo[4.1.0]hept-7-yl substrates.

Interpretation of rate and product data in the solvolysis of 1-methylcyclopropyl triflate (**1**) is less straightforward. Solvolysis in aqueous diglyme containing sodium borohydride gave isobutylene (**33**) as the sole product. Either a stepwise



formation of allylic cation **35** or a concerted ionization–ring opening is consistent with formation of this product. Borohydride may not be nucleophilic enough to trap unrearranged cation **34** or **34** may be completely bypassed in favor of **35**. As in the case of cyclopropyl tosylate, product analysis does not allow a distinction.

In terms of rate, 1-methylcyclopropyl triflate (**1**) solvolyses at the same rate as *endo*-6-methylbicyclo[3.1.0]hex-6-yl triflate (**2**). Triflate **2** is suggested to give a completely unopened tertiary cyclopropyl cation. A similar postulate that unopened cation **34** is involved in solvolysis of **1** may seem compelling. The α-methyl group can offset all of the σ participation in **2** and most of such participation in **3**. It is not unreasonable to expect that all or most of the σ participation in **1** should also be offset by α-methyl substitution. However, we cannot use solely rate data to implicate **34** and to rule out **35** as being formed directly from **1**. Steric rate acceleration in solvolysis of **2** may be involved along with a σ-assisted solvolysis of **1** (via transition state **36**). The equal solvolysis rates could therefore be fortuitous. The first intermediate in solvolysis of **1** could be allylic cation **35**. In any case, there should be less demand for σ participation in solvolysis of **1** than in unsubstituted cyclopropyl triflate. It would therefore not be unreasonable to expect that the transition state for ionization of **1** should have less cyclopropane bond fragmentation than in solvolysis of unsubstituted cyclopropyl triflate. The negligible rate difference between **1** and **2**, as compared to a 3×10^4 difference between cyclopropyl triflate and bicyclo[3.1.0]hex-6-yl triflate, bears this out.

Experimental Section

NMR spectra were recorded on a Varian A-60A spectrometer. Mass spectra were recorded on an AEI Scientific Apparatus MS 902 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 457 spectrometer or a Perkin-Elmer Infracord spectrometer.

1-Methylcyclopropyl Triflate (1). Triflate **1** was prepared as previously described.[4]

***endo*-6-Methyl-*exo*-bicyclo[3.1.0]hexane-6-carboxylic Acid (8).** Unsaturated acid **6** (3.0 g) was added to a mixture of 100 mg of platinum oxide (previously reduced by shaking with hydrogen at 50 psi) and 25 ml of absolute ether. The mixture was hydrogenated (Parr hydrogenator) at 36 psi for 90 min and filtered through Celite and the solvent was removed by rotary evaporator. The yield of crude acid was 2.95 g (98%): mp 70–75 °C; NMR (CCl_4) δ 2.2–1.4 (8 H, m), 1.14 (3 H, s); mass spectroscopic molecular weight, 140.0841 (calcd for $C_8H_{12}O_2$, 140.0837).

***exo*-6-Acetyl-*endo*-6-methylbicyclo[3.1.0]hexane (9).** Carboxylic acid **8** (2.5 g) was dissolved in 12 ml of ether and the solution was cooled to 0 °C. Methyllithium (17.5 ml of a 2.06 M solution) was diluted with 20 ml of absolute ether and added dropwise over a 15-min

period to the cooled solution. The mixture was then refluxed for 70 min and 2 g of ethyl acetate was carefully added. The mixture was then poured into water and the organic phase separated, washed with 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 through a short-path condenser to give 2.346 g (95%) of ketone **9**: bp 69–71 °C (2.8 mm); NMR (CCl_4) δ 2.01 (3 H, s), 2.0–1.3 (8 H, m), 1.17 (3 H, s); mass spectroscopic molecular weight, 138.1046 (calcd for $C_9H_{14}O$, 138.1045).

***endo*-6-Methyl-*exo*-bicyclo[3.1.0]hex-6-yl Acetate (10).** Peroxytrifluoroacetic acid, prepared from 0.79 g of 90% hydrogen peroxide and 7.4 g of trifluoroacetic anhydride in 8 ml of methylene chloride, was added dropwise over a 10-min period to a stirred mixture of 1.62 g of ketone **9**, 21 g of dibasic potassium phosphate, and 25 ml of methylene chloride. The mixture was refluxed for 1 h and stirred at room temperature for 3 h. The mixture was then taken up into ether and water. The organic phase was washed with dilute potassium carbonate solution and dried over sodium sulfate. Solvents were removed by distillation through a Vigreux column and the residue was distilled through a short-path condenser to give 1.607 g (89%) of acetate **10**: bp 56–64 °C (3.1 mm); NMR (CCl_4) δ 1.88 (3 H, s), 2.0–1.3 (8 H, m), 1.30 (3 H, s); mass spectroscopic molecular weight, 154.0986 (calcd for $C_9H_{14}O_2$, 154.0994).

***endo*-6-Methyl-*exo*-bicyclo[3.1.0]hex-6-yl Triflate (2).** A mixture of 1.365 g of acetate **10** and 10 ml of ether was cooled to 0 °C as 10 ml of 2.3 M methyllithium was added dropwise. After 15 min, excess ethyl acetate was then added to the mixture. The mixture was then cooled to −78 °C and water was added dropwise. After warming to about 10 °C, the organic phase was separated, washed with saturated sodium chloride solution, and dried over sodium sulfate. Solvents were removed by water aspirator. The crude alcohol **11**, 0.88 g (88%), was used directly in the next step.

A solution of 3.75 g of trifluoromethanesulfonic anhydride in 15 ml of pyridine was cooled to −5 °C and a solution of alcohol **11** (0.88 g) in 5 ml of ether was added dropwise with stirring. After storing at −10 °C for 4.25 h, the mixture was rapidly taken up into cold water and ether. The ether extract was rapidly washed in succession with cold water, cold dilute hydrochloric acid, and cold saturated sodium chloride solution. After drying over anhydrous sodium sulfate, solvents were removed by distillation through a Vigreux column. Care was taken so that the temperature of the solution did not exceed 50 °C. The residue was distilled to give 1.483 g (77% based on crude alcohol **11**) of triflate **2**: bp 41–42 °C (0.35 mm); NMR (CCl_4) δ 2.1–1.6 (8 H, m), 1.63 (3 H, s).

***endo*-6-Carbomethoxy-*exo*-6-methylbicyclo[3.1.0]hex-2-ene (7).** Sodium methoxide was prepared from 5.2 g of sodium and 120 ml of absolute methanol. Chloro ketone **5**[6] (7.11 g), which was separated from the isomeric chloro ketone **4** by fractional distillation, was added to the solution cooled to 0 °C. The mixture was brought to reflux for 2.5 h, cooled, and taken up into ether and water. The organic extract was separated and the aqueous phase was extracted with another portion of ether. The combined ether extracts were washed with water 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 6.35 g (92%) of ester **7**, bp 60–62 °C (5 mm) [lit.[19] bp 60–62 °C (2 mm)].

***exo*-6-Methylbicyclo[3.1.0]hexane-*endo*-6-carboxylic Acid (12).** A mixture of 120 mg of platinum oxide, 50 ml of ether, and 6.25 g of unsaturated ester **7** was hydrogenated (Parr hydrogenator) at 40 psi for 2 h. After filtering through Celite, solvents were removed by distillation through a Vigreux column. The residue was distilled to give 6.20 g (99%) of the saturated methyl ester: bp 55–57 °C (3.5 mm); NMR (CCl_4) δ 3.58 (3 H, s), 2.10–1.25 (8 H, m), 1.18 (3 H, s).

A solution of 5.4 g of potassium hydroxide, 30 ml of water, 30 ml of methanol, and 6.1 g of the saturated methyl ester prepared above was refluxed for 6 h. Most of the methanol was removed by distillation. The aqueous solution was extracted with pentane and then added to a solution of 8 ml of concentrated hydrochloric acid in 20 ml of water. The precipitate was collected on a Buchner funnel and dried under vacuum to give 3.86 g (70%) of saturated acid **12**: mp 76–78 °C; NMR (CCl_4) δ 12.33 (1 H, s), 2.2–1.35 (8 H, m), 1.25 (3 H, s); mass spectroscopic molecular weight, 140.0846 (calcd for $C_8H_{12}O_2$, 140.0837).

***endo*-6-Acetyl-*exo*-6-methylbicyclo[3.1.0]hexane (13).** The procedure was analogous to the preparation of the epimeric methyl ketone **9**. The yield of **13** obtained from 1.0 g of **12** and 10 ml of 2.06 M methyllithium was 0.741 g (75%): bp 70–73 °C (8 mm); NMR (CCl_4) δ 2.08 (3 H, s), 2.00–1.20 (8 H, m), 1.13 (3 H, s); mass spectroscopic molecular weight, 138.1046 (calcd for $C_9H_{14}O$, 138.1045).

***endo*-6-Carboethoxy-*exo*-6-methylbicyclo[3.1.0]hexane (14).** A solution of 0.25 g of acid **12** in 3 ml of Me_2SO was treated with 0.15 g of sodium methoxide followed by 0.7 g of ethyl iodide. The mixture was stirred at approximately 35 °C for 3 h. After an aqueous workup, distillation gave 0.277 g (92%) of ethyl ester **14**: bp 51–52 °C (1.1 mm); NMR (CCl_4) δ 4.06 (2 H, q, J = 7 Hz), 2.10–1.00 (14 H, m) with a triplet, J = 7 Hz, at δ 1.24 and a singlet at δ 1.17; mass spectroscopic molecular weight, 168.1154 (calcd for $C_{10}H_{16}O_2$, 168.1150).

***exo*-6-Carboethoxy-*endo*-6-methylbicyclo[3.1.0]hexane (15).** A solution of 0.23 g of acid **8** in 2.8 ml of Me_2SO was treated with 0.15 g of sodium methoxide followed by 0.7 g of ethyl iodide. The mixture was stirred at approximately 35 °C for 3 h. After an aqueous workup, distillation gave 0.239 g (87%) of ethyl ester **15**: bp 65–69 °C (1.1 mm); NMR (CCl_4) δ 3.96 (2 H, q, J = 7 Hz), 2.20–1.50 (8 H, m), 1.18 (3 H, t, J = 7 Hz), 1.08 (3 H, s): mass spectroscopic molecular weight, 168.1154 (calcd for $C_{10}H_{16}O_2$, 168.1150).

Copper Acetonylacetonate Catalyzed Addition of Ethyl Diazopropionate to Cyclohexene. Copper acetylacetonate (40 mg) was dissolved in 21 ml of refluxing cyclohexene. A solution of 2.1 g of ethyl diazopropionate in 10 ml of cyclohexene was added dropwise over a 1-h period. Nitrogen evolution was rapid after the solution color changed from blue to brown. Most of the cyclohexene was removed by distillation and the residue was taken up into ether and washed with dilute hydrochloric acid. After drying over anhydrous sodium sulfate, solvents were removed by distillation. The residue was distilled through a short-path condenser to give 0.97 g, bp 85–105 °C (1.7 mm). Gas chromatographic analysis on a 4-ft 10% SE-54 on Chromosorb P column at 140 °C showed four major products. A 0.83-g portion of the distillate was dissolved in 12 ml of methanol and ozonized exhaustively at −78 °C. A mixture of sodium iodide and sodium thiosulfate in water was then added. After stirring at room temperature for 5 min the mixture was extracted with ether. After drying, solvents were removed by distillation. The residue was distilled at 1.7 mm to give 0.291 g of products. Gas chromatographic analysis showed none of the two products of intermediate retention time. In a separate run, the products of intermediate retention time were isolated by preparative gas chromatography and shown to be ethyl esters of dimethylmaleic and dimethylfumaric acids (**19**). Samples of the two addition products, after ozonolysis, were isolated by preparative gas chromatography. Mass spectral analysis shows m/e 182 for both products. The ratio of **17** to **18** was approximately 7:1. Ester **17** had the following NMR (CCl_4): δ 4.00 (2 H, q, J = 7 Hz), 1.8–1.0 (16 H, m) with a triplet, J = 7 Hz, at δ 1.21 and a singlet at δ 1.17.

Copper Acetylacetonate Catalyzed Addition of Ethyl Diazopropionate to Cyclopentene. A 50-mg portion of copper acetylacetonate was partially dissolved in 21 ml of refluxing cyclopentene and a solution of 2.0 g of ethyl diazopropionate was added dropwise over a 6-h period of the refluxing mixture. After refluxing for 48 h, most of the cyclopentene was removed by distillation. The residue was distilled through a short-path condenser to give 0.85 g of a product mixture, bp 80–97 °C (1.1 mm). Gas chromatographic analysis showed four products. The products of longest retention time were ethyl esters of dimethylmaleic and dimethylfurmaric acids. A 200-mg sample of the product mixture was dissolved in 3.5 ml of methanol and ozonized exhaustively at −78 °C. The workup was the same as previously described. After removal of the solvents by distillation, samples of the two remaining products were isolated by preparative gas chromatography. Infrared spectral comparison showed that the major isomer of longer retention time was identical with ester **15**. The minor isomer of shorter retention time was identical with **14**. The ratio of **15** to **14** was approximately 6:1.

***endo*-7-Methyl-*exo*-bicyclo[4.1.0]hept-2-ene-7-carboxylic Acid (23).** A 118-mg sample of chloro ketone **21**, isolated by preparative gas chromatography, was stirred with 95 mg of lithium hydroxide in 1.3 ml of water. The solution was added to dilute hydrochloric acid and extracted with ether. After drying over sodium sulfate, the solvent was removed by rotary evaporator. The yield of crude acid was 72 mg (68%): mp 82–84 °C; NMR (CCl_4) δ 5.79 (2 H, m), 2.5–1.6 (6 H, m), 1.33 (3 H, s); mass spectroscopic molecular weight, 152.0840 (calcd for $C_9H_{12}O_2$, 152.0837).

***endo*-7-Methyl-*exo*-bicyclo[4.1.0]heptane-7-carboxylic Acid (20).** A 0.291-g sample of the ester mixture obtained by addition of carboethoxymethylcarbene to cyclohexene was heated at reflux for 3 h with 0.2 g of potassium hydroxide in 3 ml of water and 3 ml of methanol. Most of the methanol was removed by distillation and the solution was extracted with a portion of ether. The aqueous phase was added to cold dilute hydrochloric acid and the precipitated acid **20** was collected and air dried. The yield of acid **20** was 0.169 g (69%): mp 89–93 °C; NMR (CCl_4) δ 2.2–1.0 (10 H, m), 1.19 (3 H, s); mass spectroscopic molecular weight, 154.0992 (calcd for $C_9H_{14}O_2$, 154.0994).

A 260-mg sample of unsaturated acid **23** was dissolved in 10 ml of

ether and 20 mg of platinum oxide was added. The mixture was hydrogenated at 36 psi for 1 h and filtered through Celite and the solvent was removed by rotary evaporator. Infrared and NMR spectra of the product were identical with those of the acid obtained by saponification of ester **17**.

***exo*-7-Acetyl-*endo*-7-methylbicyclo[4.1.0]heptane (24).** A 169-mg sample of acid **20** was dissolved in 3 ml of ether and cooled to 0 °C. A 1.5-ml portion of 1.8 M methyllithium, diluted to 4 ml with ether, was added dropwise. The mixture was refluxed for 90 min, then excess ethyl acetate was added. Water was then added, the aqueous phase was separated and dried over anhydrous sodium sulfate, and solvents were removed by distillation. The residue was distilled to give 141 mg (85%) of ketone **24**: bp 75 °C (1.2 mm); NMR (CCl_4) δ 2.03 (3 H, s), 1.75–1.1 (13 H, m) with singlet at δ 1.26.

***endo*-7-Methyl-*exo*-bicyclo[4.1.0]hept-7-yl Acetate (30).** A 203-mg sample of ketone **24** in 2 ml of methylene chloride was refluxed for 1 h with peroxytrifluoroacetic acid prepared from 116 mg of 90% hydrogen peroxide, 993 mg of trifluoroacetic anhydride, and 1 ml of methylene chloride with 2.82 g of dibasic potassium phosphate. An aqueous workup gave, upon distillation, 176 mg (78%) of acetate **30**: bp 60 °C (1 mm); NMR (CCl_4) δ 1.85 (3 H, s), 1.8–0.9 (10 H, m), 1.38 (3 H, s); mass spectroscopic molecular weight, 168.1154 (calcd for $C_{10}H_{16}O_2$, 168.1150).

***endo*-7-Methyl-*exo*-bicyclo[4.1.0]hept-7-yl Triflate (3).** A solution of 200 mg of acetate **30** in 3 ml of ether was cooled to 0 °C and 1.75 ml of 1.8 M methyllithium was added dropwise. The mixture was then cooled to −78 °C and water was added. After warming to about 10 °C, the organic phase was separated, washed with saturated sodium chloride, and dried over anhydrous sodium sulfate. Solvent was removed by rotary evaporator. The residue was dissolved in a small amount of ether and added to a solution of 0.6 g of trifluoromethanesulfonic anhydride in 3 ml of pyridine at −5 °C. After 3 h, the mixture was worked up in the usual manner as rapidly as possible using cold aqueous washes. After the organic extract was dried over anhydrous sodium sulfate, the solvent was removed by distillation through a Vigreux column. The temperature was not allowed to rise above about 40 °C. The residue was distilled to give 0.197 g (64%) of triflate **3**: bp 46–48 °C (0.4 mm); NMR (CCl_4) δ 1.70 (3 H, s), 1.95–1.05 (10 H, m). Triflate **3** was stored at −5 °C and used as soon as possible after preparation.

Solvolysis of *endo*-6-Methyl-*exo*-bicyclo[3.1.0]hex-6-yl Triflate (2) in Acetic Acid. A solution of 0.266 g of triflate **2** in 10 ml of acetic acid containing 0.1 g of acetic anhydride and 0.124 g of sodium acetate was held at room temperature for 9 h and then heated at 50 °C for 2 h. The mixture was then poured into water and extracted with two portions of ether. The combined extracts were washed with water and dilute potassium carbonate and dried over anhydrous sodium sulfate. Solvents were removed by distillation through a Vigreux column and the residue was distilled to give 0.149 g (89%) of acetate **30**: bp 83 °C (15 mm); NMR (CCl_4) δ 5.62 (1 H, m), 5.15 (1 H, m), 1.99 (3 H, s), 2.2–1.5 (9 H, m); mass spectroscopic molecular weight, 154 (calcd for $C_9H_{14}O_2$, 154).

Solvolysis of *endo*-6-Methyl-*exo*-bicyclo[3.1.0]hex-6-yl Triflate (2) in Aqueous Diglyme Containing Sodium Borohydride. A solution was prepared from 8 ml of water, 25 ml of diglyme, 0.4 g of sodium hydroxide, and 2 g of sodium borohydride. Triflate **2** (0.53 g) was added to 16 ml of this mixture and the solution was stirred at 40 °C for 5 h. The mixture was poured into water and extracted with pentane. The organic extract was washed with water and dried over anhydrous sodium sulfate. The pentane was removed by distillation through a Vigreux column. The residue was distilled at atmospheric pressure. The infrared spectrum of the distillate (CCl_4) was identical with that of an authentic sample of 1-methylcyclohexene (Satler spectrum no. 3387). The NMR spectrum showed no trace of 6-methylbicyclo[3.1.0]hexane.

Solvolysis of *endo*-7-Methyl-*exo*-bicyclo[4.1.0]hept-7-yl Triflate (3) in Acetic Acid. A 95-mg sample of triflate **3** was dissolved in 5 ml of acetic acid containing 0.1 M sodium acetate and 1% acetic anhydride. After 25 h, the mixture was poured into water and extracted with ether. Acetic acid was removed by washing with dilute potassium carbonate and the ether was dried over anhydrous sodium sulfate. Solvent was removed by distillation through a Vigreux column. The residue was distilled through a short-path condenser to give 49 mg (80%) of an acetate, homogeneous by gas chromatography, and identical spectrally with acetate **30**, prepared by the Baeyer–Villiger oxidation of ketone **24**.

Solvolysis of 1-Methylcyclopropyl Triflate (1) in Aqueous Diglyme Containing Sodium Borohydride. Triflate **1** (1.0 g) was added to a solution of 2 g of sodium borohydride and 0.3 g of sodium hydroxide in 6 ml of water and 21 ml of diglyme. A distillation head was attached along with a receiver cooled to −78 °C. The solution was heated to approximately 60 °C. A portion of the distillate was transferred to a cooled (−78 °C) NMR tube by allowing the flask containing the crude distillate to warm. The NMR spectrum showed only isobutylene with no trace of 1-methylcyclopropane.

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