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The Favorskii Rearrangement of 2-Bromobicyclo[3.2.1]octan-3-one. The Question of Bishomoantiaromaticity

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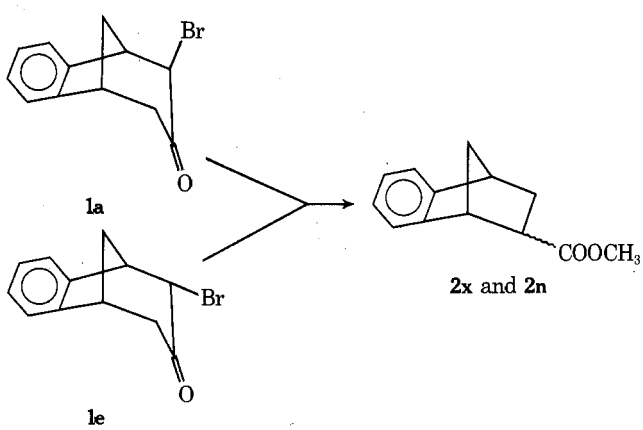
Bicyclo[3.2.1]octan-3-one (**4**) was brominated with *N*-bromosuccinimide (NBS) and benzoyl peroxide in carbon tetrachloride to give axial 2-bromobicyclo[3.2.1]octan-3-one (**3a**) but no equatorial isomer (**3e**). The Favorskii rearrangement of axial bromo ketone **3a** with sodium methoxide in methanol gives only small amounts of Favorskii ring contraction compared to its benzo analogue 2-bromobenzo[6,7]bicyclo[3.2.1]oct-6-en-3-one (**1a**). The major reaction of bromo ketone **3a** is halide displacement by methoxide ion. The facile rearrangement of **1a** is explained in two ways. Inductive withdrawal of the aromatic ring could stabilize enolate **7** and at the same time retard the solvolytic side reaction by destabilizing ion **15**. Secondly, bishomoantiaromaticity may contribute to the instability of ion **15**. Zwitterion **9** is also bishomoantiaromatic, causing a more rapid and less reversible ring closure to the cyclopropanone.

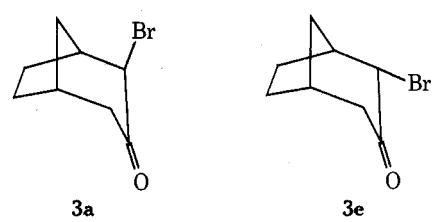
The Favorskii rearrangement has been the subject of intensive research since its discovery in 1894.[1] Monocyclic ring contraction in this base-catalyzed rearrangement of α-halo ketones is well known. However, rearrangement of bicyclic systems has been studied to a lesser extent, with some notable successful rearrangements[2] and other more negative results.[3] Until recently only bridgehead halogenated compounds have been tried. Wilt and Rasmussen[4] were the first to study a substrate having halogen at a position other than a bridgehead. Reaction of axial or equatorial 2-bromobenzo[6,7]bicyclo[3.2.1]oct-6-en-3-one (**1a** and **1e**) with sodium methoxide in either methanol or 1,2-dimethoxyethane (glyme) proceeded smoothly to a mixture of exo and endo epimers of methyl benzonorbornene-2-carboxylate (**2x** and **2n**).



An examination of the literature of this rearrangement in bicyclic rings leaves one confused and unable to predict whether new examples might be synthetically viable. Previous work has not centered on a study of the synthetic usefulness and breadth of this rearrangement. Of the examples cited above, all except one[4] had bridgehead halogens. All of the carbonyl groups except two[2n,4] were located in a one-carbon bridge. Only a few ring sizes have been studied, especially the [3.3.1] and the [2.2.1] skeletons. With the exception of two papers[2o,4] very little mechanistic work has been reported.

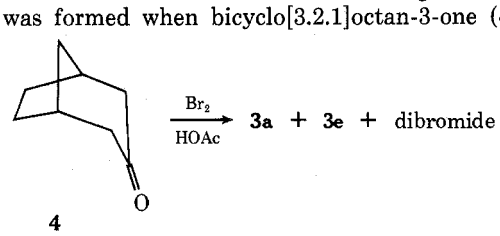
For these reasons we decided to embark on a study of this rearrangement in a number of different bicyclic bromo ketones to determine the effect of ring size, the effect of a bridgehead vs. a nonbridgehead α halogen or α' hydrogen, and the effect of unsaturation on the success of these rearrangements.

Succeeding papers will deal with the first two mentioned effects, but we wish to report an unusual result of unsaturation which appeared when we attempted a Favorskii rearrangement of the aliphatic analogue of bromo ketone **1a**, axial 2-bromobicyclo[3.2.1]octan-3-one (**3a**).



Results

Axial bromo ketone **3a** and its equatorial isomer **3e** have been prepared by Waegell and Jefford, but **3e** was said to be unstable. A mixture of these two isomers along with a dibromide was formed when bicyclo[3.2.1]octan-3-one (**4**) was



treated with bromine in acetic acid.[5] Since the benzo bromo ketone **1** gave essentially the same product composition whether the axial or equatorial isomer was used,[4] it was decided to prepare pure axial bromo ketone **3a** to simplify the study. These bicyclic bromo ketones probably equilibrate rapidly in basic solution, as evidenced by rapid deuteration of the parent ketones bicyclo[3.2.1]octan-3-one (**4**) and benzo[6,7]bicyclo[3.2.1]oct-6-en-3-one with sodium methoxide in methanol-d_4.

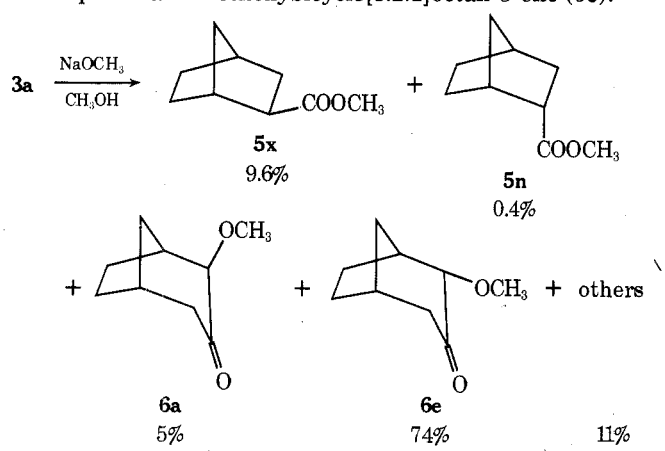
Table I. Products of Bromo Ketones 1a and 3a in $NaOCH_3/CH_3OH$

Bromo ketone	$NaOCH_3$ concn, M	% products[a] Exo ester	Endo ester	Ax CH_3O ketone	Eq CH_3O ketone
1a[b]	2.0	54	14		
3a[c]	2.0	9.6	0.4	5	74
1a[b]	0.1	44	0		
3a[c]	0.1	0	0	100	0

[a] Percentages are based on total area by gas chromatographic analysis. [b] Reference 4. Other products were not identified but included methoxy ketones. [c] This study. At 2 M base, 11% unidentified products were found.

N-Bromosuccinimide (NBS) and benzoyl peroxide in carbon tetrachloride was chosen as the brominating agent since it was found to react in the benzo analogue to form only axial bromo ketone **1a**.[4] Likewise bromination of ketone **4** under these conditions gave axial product **3a**. No evidence of equatorial isomer **3e** was found.

Bromo ketone **3a** was submitted to Favorskii conditions exactly the same as for **1a** (2 M sodium methoxide in methanol, 25 °C, 4 h). Although the benzo analogue **1a** gave a Favorskii yield of 70% (56:14 mixture of exo:endo esters **2x** and **2n**) plus other products including methoxy ketones, the aliphatic bromo ketone **3a** gave only 9.6% methyl norbornane-*exo*-2-carboxylate (the Favorskii product **5x**) and 0.4% endo isomer **5n**, while the major reaction was halide displacement to give 5% axial 2-methoxybicyclo[3.2.1]octan-3-one (**6a**) and 74% equatorial 2-methoxybicyclo[3.2.1]octan-3-one (**6e**).



The Favorskii esters **5x** and **5n** were compared with authentic samples. The two methoxy ketones were assigned configurations on the basis of their NMR spectra which are discussed in the next section.

The reaction of bromo ketone **3a** was also studied in 0.1 M sodium methoxide/methanol. A summary of the products of aromatic bromo ketone **1a** and aliphatic bromo ketone **3a** at both base concentrations is given in Table I.

Note that at each base concentration there is *more* Favorskii rearrangement occurring for aromatic bromo ketone **1a** compared to aliphatic bromo ketone **3a** and that the percentage of Favorskii rearrangement is *increased* with more concentrated base.

Synthetically, a much better Favorskii rearrangement occurs when sodium methoxide in glyme is used. Both bromo ketones give increased amounts of rearrangement with this aprotic solvent. Bromo ketone **3a** gave exo and endo esters **5x** and **5n** *exclusively* in a ratio of 76:24 with glyme.

Discussion

The assignment of axial and equatorial configurations to methoxy ketones **6a** and **6e** was aided by the excellent NMR analysis of a series of substituted cyclohexanones studied by Jefford and Waegell.[5,6] Although it is true that in simple cyclohexane derivatives axial protons often absorb upfield from equatorial protons,[7] cyclohexanones have α axial protons which are downfield compared to α equatorial protons.[8] Jefford and Waegell found that the equatorial bromo ketone **3e** has an α axial proton at δ 4.68 (CCl_4)[6b] and therefore follows this general rule for cyclohexanones, since this is downfield compared to the α equatorial proton of axial bromo ketone **3a** appearing at δ 3.96 (CCl_4).[6b,9] Wilt and Rasmussen found that the benzo bromo ketones **1a** and **1e** follow this generality. The α axial proton of equatorial bromo ketone **1e** appears at δ 4.93 ($CDCl_3$), downfield from the α equatorial proton of axial bromo ketone **1a** located at δ 4.23 ($CDCl_3$).[4] So there is good precedent for assigning α axial and equatorial configurations by chemical shift not only on cyclohexanones but more particularly bicyclo[3.2.1]octan-3-ones.

Table II. Partial NMR Analysis of Methoxy Ketones 6a and 6e in δ (CCl_4)

Methoxy ketone	$CHOCH_3$	OCH_3
6a	3.0–3.2 (eq)	3.21 (ax)
6e	3.4–3.6 (ax)	3.42 (eq)

By this analysis one product was found to be equatorial methoxy ketone **6e**, since its α axial proton is further downfield at δ 3.4–3.6 than the α equatorial proton of axial methoxy ketone **6a**, which appears at δ 3.0–3.2 (see Table II). Examination of the methoxy protons of compounds **6a** and **6e**, however, show that they are outside the dominating magnetic influence of the carbonyl, being farther removed, and the equatorial methoxy protons are farther downfield than the axial methoxy protons (δ 3.42 vs. 3.21).

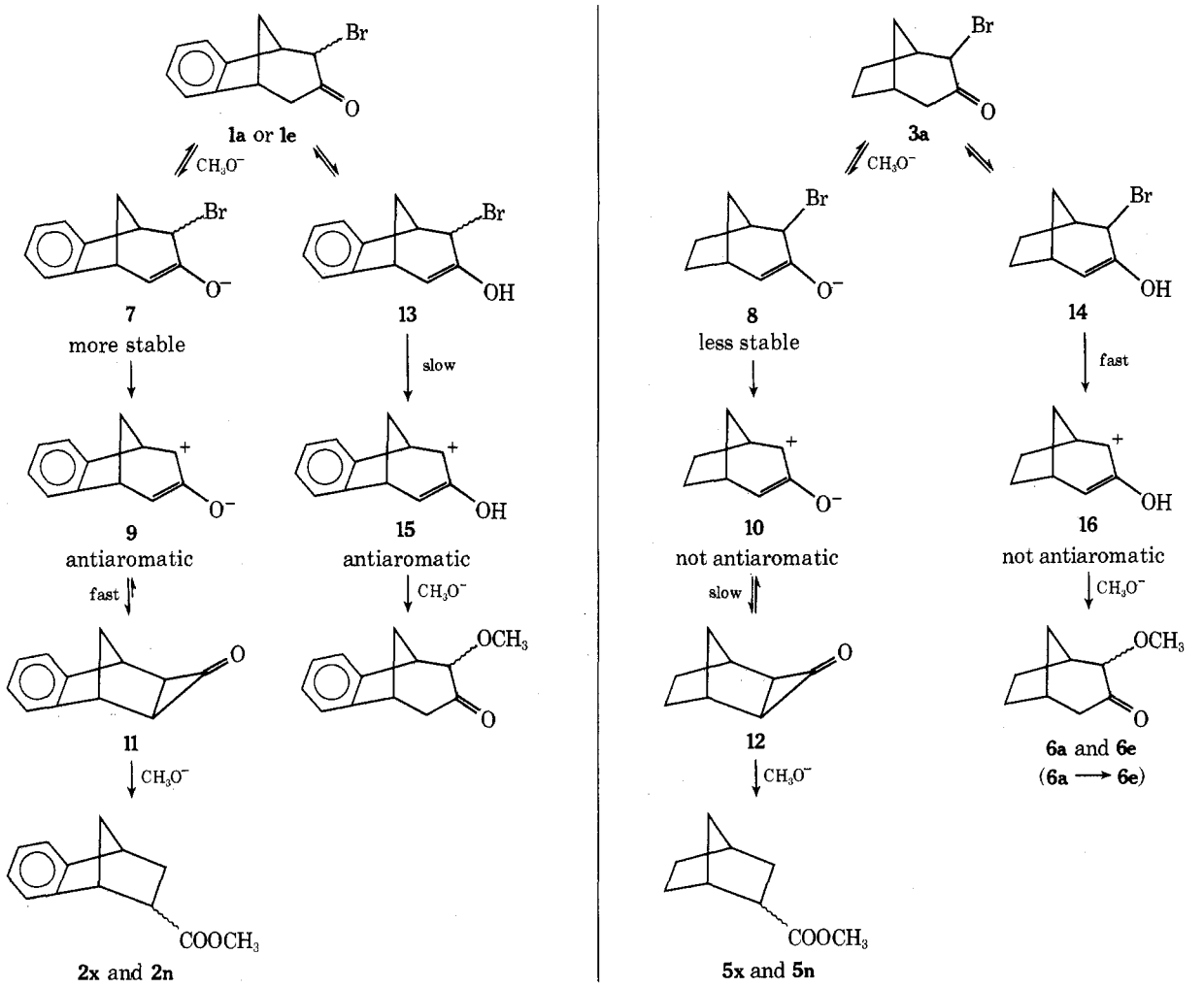
The results of the reaction of bromo ketones **1a** and **3a** are outlined in the most recent mechanism for the Favorskii rearrangement (Chart I). This incorporates current work by Bordwell,[10] House,[11] and Smissman.[12] The important intermediates in the present concept of the Favorskii rearrangement are enolates such as **7** and **8**, zwitterions like **9** and **10**, and cyclopropanones exemplified by **11** and **12**. The competing solvolysis is usually thought of as taking place through enol allylic halides such as **13** and **14** and allylic ions like **15** and **16**. Higher base concentrations or use of unsolvated bases (in glyme) help formation of enolates rather than enol allylic halides. Larger percentages of Favorskii products result. Low base concentrations favor the alternative formation of methoxy ketones at the expense of the rearrangement. Our results substantiate this mechanism.

But if bromo ketones **1a** and **3a** are compared, it is noted that aliphatic bromo ketone **3a** does *not* as readily undergo the Favorskii rearrangement with sodium methoxide/methanol as the aromatic bromo ketone **1a**. This can be explained most logically in one of two ways.

One possibility for the larger percentages of Favorskii product in the benzo analogue is an inductive withdrawal of electron density by the aromatic ring. This may substantially increase the acidity of the α' hydrogen by stabilizing enolate **7** compared to **8**. The inductive withdrawing effect of aromatic rings is well documented for a variety of reaction types and substrates,[13] including benzonorbornenes[14] and benzonorbornadienes.[15] Aromatic electron withdrawal would also retard ionization of the bromide and make ion **15** less stable than **16**. Favorskii product formation would be more favored in the aromatic bromo ketone.

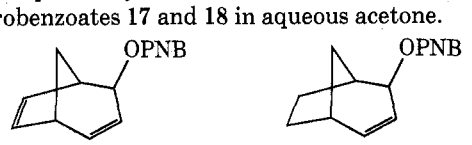
A second explanation differs in degree from the first. Ion **15** is bishomoantiaromatic but **16** is not. This would destabilize **15** dramatically and would favor the Favorskii product. The antiaromatic character of zwitterion **9** also may be a factor

Chart I



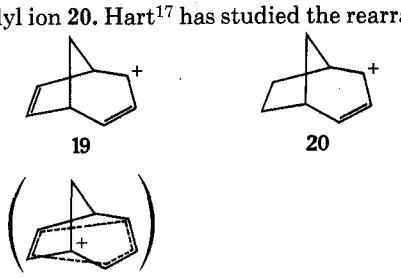
in the product distribution. Although **9** may be more slowly formed relative to **10**, it would have a very short lifetime and would rapidly and less reversibly ring close to cyclopropanone **11**. The ring closure of **10** to **12** would be slower and more reversible. This would explain the greater percentages of Favorskii products in the benzo analogue.

Precedence for bishomoantiaromatic character in this ring system is reported by Winstein,[16] who studied the solvolysis of *p*-nitrobenzoates **17** and **18** in aqueous acetone.



17 **18**

The presence of the additional double bond in **17** is markedly rate retarding, with *exo*-**17** solvolyzing 235 times slower than *exo*-**18**. Winstein suggested that "the rate retardation is probably even larger than can be ascribed to the rate-retarding inductive effect of the second olefinic group." He suggested that **17** solvolyzes very slowly because it forms the unstable ion **19** which is bishomoantiaromatic, whereas **18** yields the allyl ion **20**. Hart[17] has studied the rearrangement



19 **20**

of the nonamethyl derivative of ion **19** by NMR and has drawn attention to "the importance of bishomoantiaromaticity as a factor in these rearrangements." Bishomoantiaromatic ion **19** is analogous to **9** and **15** and ion **20** is similar to **10** and **16**.

Stereochemical results with bromo ketone **3a** are strongly analogous to Winstein's work with *exo*-*p*-nitrobenzoate **18**. In dilute base the axial product is formed preferentially by stepwise loss of the axial bromine, formation of ion **16**, and attack by methoxide on the axial side stereospecifically. Likewise, solvolysis of *p*-nitrobenzoate **18** proceeded stereospecifically and with retention.[16] Only in the more concentrated base does **6e** predominate and this could be formed by epimerization of **6a**. Epimerization studies in 2 M sodium methoxide showed that the axial and equatorial methoxy ketones **6a** and **6e** readily equilibrate.

Experimental Section

Melting and boiling points are uncorrected. The melting points were taken in capillaries in a Thomas-Hoover apparatus. The following instruments were used: Varian T-60 NMR spectrometer, Perkin-Elmer 727 infrared spectrophotometer, and a Varian Aerograph Model 700 Autoprep gas chromatograph. NMR data are given in parts per million (δ) relative to internal Me_4Si, with the usual splitting abbreviations followed by number of protons and interpretation. Only significant ir absorptions are listed in cm^{-1}. Gas chromatography was performed on an SE-30 or QF-1 column with helium carrier gas. Microanalyses were performed by Micro-Tech Laboratories, Skokie, Ill.

Bicyclo[3.2.1]octan-3-one (4). This ketone was prepared from norbornene by the method of Jefford et al.[18]

Axial 2-Bromobicyclo[3.2.1]octan-3-one (3a). Ketone **4** (8.68 g, 0.0700 mol), *N*-bromosuccinimide (freshly recrystallized from

water, 12.40 g, 0.0700 mol), benzoyl peroxide (0.96 g), and carbon tetrachloride (60 ml) were refluxed for 22 h. White succinimide began precipitating after 1 h, and a dark mixture was obtained after the full heating period. The mixture was cooled in an ice bath and the succinimide was suction filtered (6.48 g, 0.0654 mol, 94%, mp 123–126 °C, lit.[19] mp 125–126 °C). The precipitate was washed with chilled carbon tetrachloride (2 × 50 ml). The combined filtrate was washed twice with 10% sodium bicarbonate and once with water, dried with magnesium sulfate, and rotary evaporated. Gas chromatographic analysis (SE-30, 192 °C, 56 ml/min) showed unreacted ketone **4** and brominated product in a 31:69 ratio. Addition of more NBS (4.96 g) and further reflux and workup still left some ketone **4** in a 21:79 ratio. Short-path distillation gave a small forerun of **4** which was scraped from the condenser followed by bromo ketone **3a** as a white solid which crystallized in the receiving flask (7.66 g, 0.0378 mol, 54%), bp 80–95 °C (0.25 mm). Further purification gave bp 65–71 °C (0.19–0.25 mm), mp 50–51 °C (lit.[5] mp 49–50 °C). No evidence was obtained for any equatorial isomer **3e** being formed.

Reaction of Bromo Ketone 3a with 2 M Sodium Methoxide in Methanol. A solution of sodium methoxide in methanol (2 M, 150 ml) was stirred with bromo ketone **3a** (1.56 g, 0.00768 mol, 96.3% pure by VPC) at 25 °C for 4 h. A pale yellow color was apparent at the end of this time. The solution was chilled to 0 °C and neutralized with glacial acetic acid. Ether (750 ml) was added and the mixture was cooled in a freezer overnight. The sodium acetate was suction filtered and washed with ether (150 ml). The ether was rotary evaporated. High vacuum caused the residue to solidify because of a small amount of sodium acetate still present. Ether (10 ml) was added and the solid was gravity filtered and washed with ice-cold ether (20 ml). Evaporation of the solvent from the filtrate gave a yellow oil (0.87 g, 0.00565 mol, 74% isolated yield based on $C_9H_{14}O_2$).

Preparative gas chromatography (QF-1, 192 °C, 60 ml/min) was used to separate the products of the reaction. The products and percentages are given in order of increasing retention times: 10% methyl norbornane-2-carboxylate (**5x** and **5n**), 5% axial 2-methoxybicyclo[3.2.1]octan-3-one (**6a**), and 74% equatorial 2-methoxybicyclo[3.2.1]octan-3-one (**6e**). Two other peaks were not identified: 8%, overlapping partially with methoxy ketone **6e**, and 3%, of longer retention time. The same column at 115 °C separated **5x** and **5n** in a 96:4 ratio.

The exo ester **5x** was compared to an authentic sample prepared below and was found to agree in retention time and spectral properties. The peak assigned as the endo ester **5n** had a retention time identical with that of the authentic compound, but spectral properties were not taken owing to the small amount of this product.

The axial methoxy ketone **6a** was a colorless liquid: ir (neat) 3000, 2950, 2900 (C–H), 1715 (C=O), 1450, 1405, 1330, 1170, and 1065 cm^{-1} (C–O); NMR (CCl_4) δ 3.21 (s, 3, CH_3O), 3.0–3.2 (m, 1, $CHOCH_3$), 1.2–2.8 (m, 10).

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.53; H, 9.27.

A light orange 2,4-dinitrophenylhydrazone was recrystallized three times from ethanol, mp 189–191 °C.

Anal. Calcd for $C_{15}H_{18}N_4O_5$: N, 16.76. Found: N, 16.69.

The equatorial methoxy ketone **6e** was a colorless liquid: ir (neat) 3050, 2970, 2920 (C–H), 1740 (C=O), 1460, 1200, 1120, 1100 (C–O), 1060, 1020, and 910 cm^{-1}; NMR (CCl_4) δ 3.4–3.6 (m, 1, $CHOCH_3$), 3.42 (s, 3, CH_3O), 2.1–2.6 (m, 4, $CH_2C{=}O$ and two bridgehead H), 1.4–1.8 (m, 6).

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.90; H, 9.22.

A light orange 2,4-dinitrophenylhydrazone was recrystallized from ethanol six times, mp 147–149 °C.

Anal. Calcd for $C_{15}H_{18}N_4O_5$: N, 16.76. Found: N, 17.04.

Reaction of Bromo Ketone 3a with 0.1 M Sodium Methoxide in Methanol. A solution of sodium methoxide in methanol (0.1 M, 20 ml) was stirred with bromo ketone **3a** (0.20 g, 0.00100 mol) at 25 °C for 4 h. The solution was not basic at the end of this time. Acetic acid (3 drops) and ether (80 ml) were added but no precipitate was obtained. The residue was rotary evaporated and analyzed by VPC (QF-1, 191 °C 60 ml/min) and NMR. Only axial methoxy ketone **6a** was present.

Reaction of Bromo Ketone 3a with Sodium Methoxide in Glyme. A suspension of sodium methoxide (0.28 g, 0.00522 mol) and bromo ketone **3a**, (0.20 g, 0.00100 mol) in glyme (8 ml) was stirred magnetically for 1 h at 25 °C. A brown color was formed after 5 min. The mixture was cooled in an ice bath and acetic acid (17 drops) was added to neutralize the base. Addition of ether (80 ml) precipitated the salt, which was suction filtered and washed with ether (50 ml). Rotary evaporation left a residue which was analyzed by VPC (QF-1, 115 °C, 60 ml/min). Only esters **5x** and **5n** were obtained in a ratio of 76:24.

Epimerization of Methoxy Ketones 6a and 6e. A small sample of **6a** was stirred with sodium methoxide in methanol (2 M, 20 ml) and processed as before. VPC analysis (QF-1, 189 °C, 60 ml/min) showed three peaks, identified as **6a** (13%), **63** (82%), and a third compound (5%) having a retention time identical with that of the extra, unidentified peak observed in the Favorskii studies.

Epimerization of equatorial methoxy ketone **6e** was studied in similar fashion to give **6a** (7%), **6e** (86%), and the same unidentified trace product (7%).

Methyl Norbornane-2-carboxylate (5x and 5n). The exo and endo esters **5x** and **5n** were prepared as 69:31 mixture starting with norbornane-2-carbonitrile (Aldrich Chemical Co.) by the normal methods of hydrolysis to the acids[20] and esterification via diazomethane,[21] bp 42–44 °C (0.62–0.71 mm), lit.[22] bp 77 °C (10 mm) for **5x** and 76–77 °C (11 mm) for **5n**. They are easily distinguished by VPC retention times and by the NMR chemical shift of the methyl protons (δ 3.58 for **5x** and δ 3.60 for **5n** in CCl_4).[22]

Deuteration Studies of Bicyclo[3.2.1]octan-3-one (4) and Benzo[6,7]bicyclo[3.2.1]oct-6-en-3-one. The ketone (~0.1 g) was dissolved in CD_3OD (0.5 ml) and 1 drop of 2 M $NaOCH_3$ in CD_3OD was added. Both ketones behaved similarly by exchanging two of the four α hydrogens within the first 2 min, the time required to place the sample in the NMR probe and integrate the spectrum. The other two α protons exchanged gradually over about 6 h.

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Registry No.—**1a**, 54164-79-3; **3a**, 28052-02-0; **4**, 14252-05-2; **5x**, 23057-38-7; **5n**, 16646-41-6; **6a**, 59891-85-9; **6a** 2,4-DNPH, 60031-42-7; **6e**, 59891-86-0; **6e** 2,4-DNPH, 60031-43-8; *N*-bromosuccinimide 128-08-5; sodium methoxide, 124-41-4.

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

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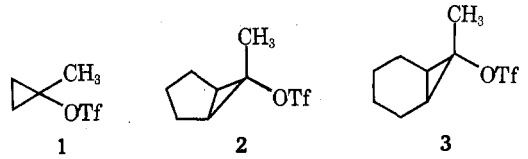
Synthetic schemes have been developed which allow the preparation of *endo*-6-methyl-*exo*-bicyclo[3.1.0]hex-6-yl triflate (**2**) and *endo*-7-methyl-*exo*-bicyclo[4.1.0]hept-7-yl triflate (**3**). Synthesis of the latter involved a copper-catalyzed addition of ethyl diazopropionate to cyclohexene which 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-



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