The Synthesis and Solvolytic Rearrangement of the Spiro[2.3]hexane-4-methanol System[1]

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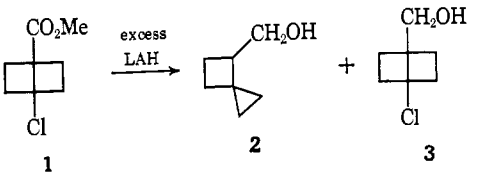
Abstract: Spiro[2.3]hexane-4-methanol (**2**) was formed upon prolonged treatment of methyl 4-chlorobicyclo-[2.2.0]hexane-1-carboxylate (**1**) with lithium aluminum hydride, and the rearrangement of the *p*-toluenesulfonate ester **4** of this alcohol was studied. The rate of this rearrangement in acetic acid buffered with sodium acetate was the same as that of cyclobutylmethyl *p*-toluenesulfonate, indicating that the cyclopropyl ring had no effect on the rate of the solvolysis. The products derived from this rearrangement were those expected from the two intermediate spiro[2.4]heptanyl cations **13** and **14**.

The preparation of bicyclo[2.2.0]hexane-1-methanol from methyl 4-chlorobicyclo[2.2.0]hexane-1-carboxylate (**1**) has recently been reported.[3] This chloro ester also has been converted to spiro[2.3]hexane-4-methanol (**2**), a compound which contains both a cyclopropylethyl system[4] and a cyclobutylmethyl system.[5]

The extent of participation of the cyclopropyl ring in cyclopropylethyl solvolyses is uncertain. High percentages of rearrangement products in some cases[4,6] and rates of the same order as neopentyl systems suggest that the ratio of the SN1 rate to the SN2 rate for this primary system has been increased sufficiently so that the SN1 process competes favorably with the SN2 rate expected for a primary system.[6] Cyclopropylethyl *p*-bromobenzenesulfonate itself undergoes extensive rearrangement during formolysis but in buffered acetic acid the SN2 reaction leading to unrearranged product takes over.[7] Participation in the cyclobutylmethyl system results in a rate enhancement of at least 1000 over that expected for ionization of a primary system such as isobutyl.[5] Spiro[2.3]hexane-4-methanol (**2**) is of interest since it should provide additional information on the reactions and interactions of cyclopropylethyl and cyclobutylmethyl systems, the nature of the cyclobutylmethyl transition state, and the interaction of this transition state with a developing cyclopropylmethyl system. Geometrical requirements for interaction are potentially accessible in a study of this rigid compound since the planes of the cyclobutyl and cyclopropyl rings are held at right angles. A study of the reaction rate and products of the acetolysis of the *p*-toluenesulfonate ester **4** should provide some insight into these areas of concern.

4-Chlorobicyclo[2.2.0]hexane-1-carboxylic acid[8] was esterified with an ethereal solution of diazomethane and the resulting ester **1** was allowed to react with a tenfold excess of lithium aluminum hydride at 36° for 11 days. The reaction gave a mixture of 97% spiro[2.3]hexane-1-methanol (**2**) and 3% 4-chloro[2.2.0]hexane-1-methanol (**3**). Spinning-band distillation further enriched the major product to greater than 99%. Structure was assigned on the basis of spectral properties. This rearrangement of **1** to **2** can be viewed as solvolysis of the aluminum chloroalkoxide complex of **3** with reduction of the rearranged carbonium ion to give the alkoxide of **2**. This type of solvolysis in solutions of both lithium aluminum hydride and sodium borohydride has been reported for 7-norbornadienyl *p*-toluenesulfonate.[9] A similar rearrangement has been observed in the reaction of **3** with aqueous silver ion.[10]



The *p*-toluenesulfonate ester **4** was prepared in the standard manner without difficulty and its solvolysis was studied in acetic acid buffered with sodium acetate. The rates were determined by monitoring the change in the ultraviolet absorption at 272 mμ.[11] The rate of cyclobutylmethyl *p*-toluenesulfonate was determined by this same method. The results are compiled in Table I.[12]

There is no significant difference in rates of these two compounds at either temperature; therefore, they share activation parameters previously reported for cyclobutylmethyl *p*-toluenesulfonate: $\Delta H^{\ddagger} = 24.9$ kcal/mol and $\Delta S^{\ddagger} = -8$ eu.[5]

The mixture of materials from the solvolysis was reduced with lithium aluminum hydride and the following product distribution was determined by vapor phase chromatography and nmr spectroscopy. The identity of six of the seven alcoholic products, **5**, **6**, **7**, **8**,

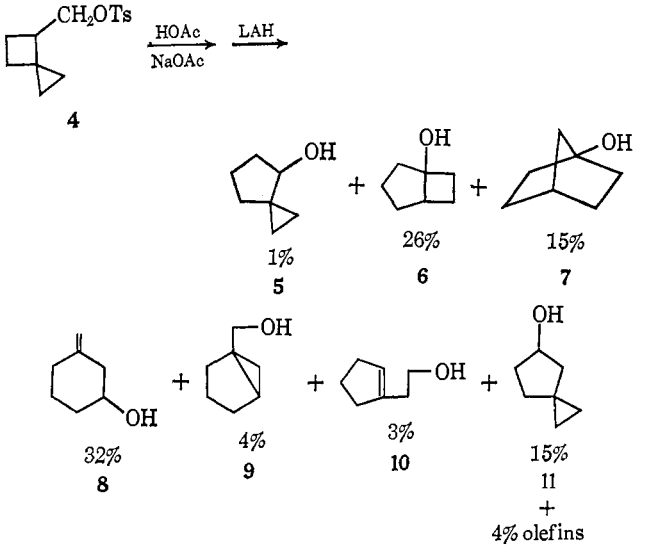
(1) This work was supported in part by Grant GP-3890, National Science Foundation.
(2) National Institutes of Health Predoctoral Fellow, 1966–1968.
(3) W. G. Dauben, J. L. Chitwood, and K. V. Scherer, *J. Amer. Chem. Soc.*, 90, 1014 (1968).
(4) For references on some recent work see R. R. Sauers, J. A. Beisler, and H. Feilich, *J. Org. Chem.*, 32, 569 (1967), and the references therein.
(5) For references on some recent work see K. B. Wiberg and B. A. Hess, Jr., *J. Amer. Chem. Soc.*, 88, 4433 (1966), and the references therein.
(6) K. B. Wiberg and G. R. Wenzinger, *J. Org. Chem.*, 30, 2278 (1965).
(7) R. R. Sauers and R. W. Ubersax, *ibid.*, 31, 495 (1966).
(8) K. V. Scherer, Jr., *Tetrahedron Lett.*, 5685 (1966).
(9) P. R. Story and M. Saunders, *J. Amer. Chem. Soc.*, 84, 4876 (1962); H. C. Brown and H. M. Bell, *ibid.*, 85, 2324 (1963).
(10) K. V. Scherer, Jr., and K. Katsumoto, *Tetrahedron Lett.*, 3079 (1967).
(11) C. G. Swain and C. R. Morgan, *J. Org. Chem.*, 29, 2097 (1964).
(12) We are indebted to Professor A. Streitwieser for providing copies of LSKIN1 computer program which was developed by Professor D. F. DeTar, Florida State University. We also wish to express our appreciation to the University of California Computer Center, Berkeley, Calif., for their services.

Table I. First-Order Rate Constants in Buffered Acetic Acid for Alkyl *p*-Toluenesulfonate

Substrate[a] (*p*-toluenesulfonate)	Temp, °C[b]	$k_1 \times 10^5$ sec^{-1} [c]
Spiro[2.3]hexane-4-methyl	44.5	0.12 ± 0.01
	74.5	3.0 ± 0.7
Cyclobutylmethyl	44.5	0.12 ± 0.01
	74.5	3.34 ± 0.05
	75.0	3.57[d]

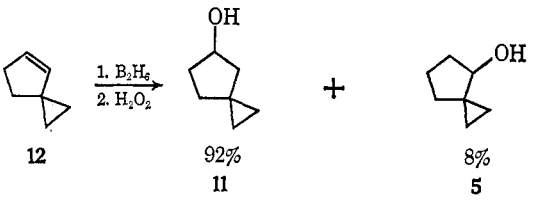
[a] Approximately 0.001 *M* in substrate. [b] ±0.1°. [c] These recorded standard deviations of the rates were the lowest of several determinations at each of the given temperatures. In a few of these determinations some difficulty was encountered with small amounts of impurities whose absorption changed during solvolysis. [d] See ref 5.

9, and **10**, was established by comparison of vapor phase chromatographic retention time and a comparison of infrared spectra with those of authentic samples previously reported.[13] The remaining alcohol

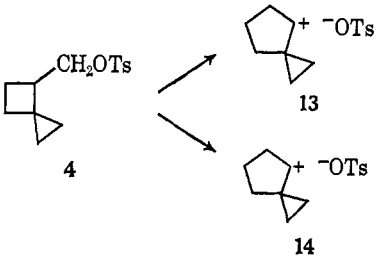


11 had the same retention time on 10% Carbowax (10% KOH) columns as alcohols **6** and **7**, but they could be separated on 10% TCEP columns. A chemical method was desirable for separating these compounds; therefore, a sample of the three alcohols was subjected to Jones oxidation conditions and the resulting ketone derived from alcohol **11** was easily separated by vapor phase chromatography from the tertiary alcohols **6** and **7**.

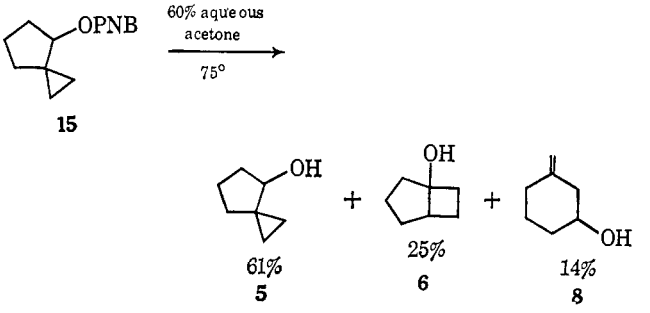
The spectral features of alcohol **11** and its related ketone were in accord with the assigned structure and this structure was established by the synthesis of **11**. It has recently been reported that hydroboration of spiro[2.5]oct-4-ene gave 78% of the 5-ol due to directive electronic properties of the cyclopropane ring.[14] Thus, application of this process to spiro[2.4]hept-4-ene should give predominately the desired alcohol **11**. The xanthate ester of spiro[2.4]heptan-4-ol (**5**) upon pyrolysis yielded spiro[2.4]hept-4-ene (**12**). The olefin was hydroborated and 92% of the desired alcohol **11** was obtained. The alcohol **5** accounted for the remaining 8% of alcohols formed. Oxidation of the synthetic spiro alcohol **11** yielded a ketone which was identical with the material obtained from the oxidation of the solvolysis alcohol.



Cyclobutylmethyl *p*-toluenesulfonate gives cyclopentyl acetate on solvolysis with the cyclopentyl cation as the first intermediate.[5] Analogous bond participation during the solvolysis of the spiro derivative **4** should give two cyclopentyl intermediates, **13** and **14**, as shown below.

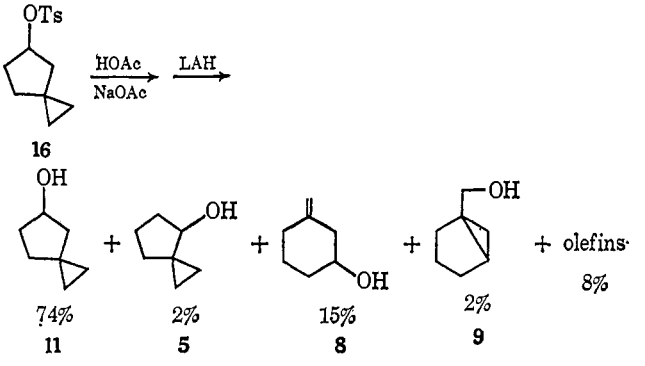


It was of interest to obtain some indication of the products expected from each of these intermediates. Related to the ion **13**, Closson has studied the solvolysis of the *p*-nitrobenzoate ester **15** of spiro[2.4]heptan-4-ol in buffered 60% aqueous acetone with the following results.[13a]



Compounds **9** and **10** were not reported to have been observed but the aqueous solvent system used probably reduced the extent of rearrangement.[13a]

The *p*-toluenesulfonate ester **16** of spiro[2.4]heptan-5-ol was prepared and subjected to reaction in buffered acetic acid at 75° for 35 hr. The products were reduced



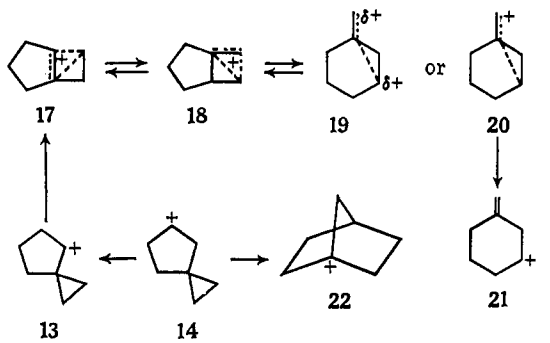
(13) (a) W. D. Closson and G. T. Kwiatkowski, *Tetrahedron*, **21**, 2779 (1965). (b) We wish to thank Professors K. B. Wiberg and D. B. Denney for a sample and spectral data of 1-norbornanol and Professor W. D. Closson for samples and infrared spectra of the remaining alcohols.

(14) S. Nishida, I. Moritani, K. Ito, and K. Sakai, *J. Org. Chem.*, **32**, 939 (1967).

with lithium aluminum hydride to give the above product composition as determined by vapor phase chromatography and infrared spectroscopy.

Compounds **6** and **7** were present in amounts no greater than 2%. The finding of the acetates of **5**, **8**, and **9** in the solvolysis mixture indicates that a hydride shift can convert the intermediate **14** into the cyclopropylmethyl intermediate **13**. No attempt was made to determine the extent of direct displacement giving the acetate of **11**.

From the results obtained with the esters **15** and **16**, it is evident that all solvolysis products of spiro[2.3]-hexane-4-methanol except the acetates of **7** and **11** are expected to arise from intermediate **13**.[13a] It is not surprising that the solvolyses of **15** and **16** do not give the same product percentages as the solvolysis of **4** since the geometry of the precursors is different and since the cations **13** and **14** coming from **15** and **16** are lower vibrational isomers of the cations **13** and **14** coming from **4**.[15] Cation **13** could give the acetate of **5** and cation **17** could lead directly to the acetates of **5**, **6**, and **10**. Cation **18** could give the acetates of **6** and **9**. The acetates of **8** and **9** could come from cations **19** or **20** and the acetate of **8** could also come from cation **21**. The formation of 1-norbornyl acetate probably comes *via* intermediate **14** since cyclopropylethyl *p*-bromobenzenesulfonate undergoes a similar rearrangement during pyridine-buffered formolysis, giving 60% of cyclopentyl formate.[7] The acetate of **11** could come directly from **14**. It is difficult to determine quan-



titatively the relative amounts of intermediates **13** and **14** from the solvolysis of **4** by separately forming these intermediates since it has been shown that product ratios can be dependent upon the structure of the precursor used to generate the intermediate.[15] However, it is evident from the product percentages that more than 30% of the reaction proceeds *via* intermediate **14**, and the lack of any apparent influence of the cyclopropyl ring on the rate of reaction suggests equal ease in forming intermediates **13** and **14**.

Since the degree of participation of the cyclopropyl ring in the cyclopropylethyl system is highly variable, if present at all, it is not surprising that the cyclopropyl ring had no effect initially as a cyclopropylethyl system in the rate-determining step of the acetolysis of **4**. It is also reasonable that the cyclopropyl ring does not interact as a cyclopropylmethyl system with the transition state leading to intermediate **13**. If the bonding of the three carbons associated with the migrating bond in the transition state of a cyclobutylmethyl solvolysis is viewed as electronically resembling a cyclopropyl ring, then, in the case of **4** (transition state **23**), the plane of this cyclopropyl-like three-center bonding and the plane of the cyclopropyl ring are approximately orthogonal and little overlap would be expected. It may well be that the transition state has

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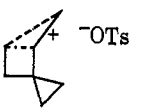
not developed to the extent depicted as **23** but is more like **24** or some intermediate species. In this event, the carbon adjacent to the cyclopropyl ring would bear



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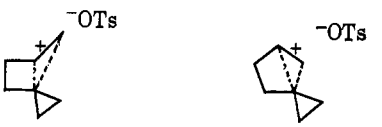
little p character which could be delocalized by a cyclopropylmethyl system. However, after the transition state a free p orbital with the preferred orientation for maximum overlap is found on this cyclopropylmethyl carbon. This then accounts for the rearrangements expected from the cyclopropylmethyl system formed after the initial, rate-controlling cyclobutyl bond migrations.

Migration of the cyclobutane bond leading to intermediate **14** would give a transition state resembling **25**, **26**, or some intermediate species. This transition state must also be similar in energy to that of an unsubstituted cyclobutylmethyl system. Since the migrating group carries little of the positive charge,[16] one would not expect the cyclopropyl ring to have a large effect on this migratory pathway. One would also



25 **26**

expect that the extent of the inductive effects of the cyclopropyl ring would be small.

In conclusion, it would appear from the rate of this solvolysis that the cyclopropyl ring has a minor effect on the ease of bond migration leaving the rate basically that of the cyclobutylmethyl system. The major effects of the cyclopropyl ring, which are manifest in the additional rearrangements, are subsequent to the formation of the two intermediates, **13** and **14**.

Experimental Section

The nmr spectra were obtained on a Varian A-60 nmr spectrometer with TMS as internal standard. Infrared spectra were recorded with Perkin-Elmer 137 and 237 spectrophotometers. A Varian M66 mass spectrometer provided the mass spectra. Vapor phase chromatography was performed on Aerograph Model A-90-P (thermal conductivity detector) and Hi Fi Model 600-D (hydrogen flame detector) gas chromatographs. Analyses were performed by the Microanalytical Laboratory, College of Chemistry, University of California, Berkeley, Calif.

The pyridine used was reagent grade material distilled from potassium hydroxide and then from *p*-toluenesulfonyl chloride;

(15) J. Berson and J. Gajewski, *J. Amer. Chem. Soc.*, **86**, 5020 (1964); W. G. Dauben and D. L. Whalen, *ibid.*, **88**, 4739 (1966); P. D. Bartlett, W. D. Closson, and T. J. Cogdell, *ibid.*, **87**, 1308 (1965).

(16) A. Streitwieser, Jr., "Molecular Orbital Theory," John Wiley and Sons, Inc., New York, N. Y., 1961, p 380.

it was dried and stored over barium oxide. Dry ether was commercial grade diethyl ether distilled from phosphorus pentoxide and stored over sodium wire.

Methyl Ester of 4-Chlorobicyclo[2.2.0]hexane-1-carboxylic Acid (1). An ethereal solution of diazomethane was added dropwise to 5.4 g of 4-chlorobicyclo[2.2.0]hexane-1-carboxylic acid in 50 ml of diethyl ether until the yellow color remained. The solution was stirred at room temperature for 3.5 hr and the ether distilled through a 12-in. Vigreux column at atmospheric pressure giving 8.2 g of crude ester. The ester could be vpc collected from an SE-30 column, mp 20–25°; $\nu_{max}^{CCl_4}$ 2998, 2992, 1735, 1430, 1250, 1200, 1170, and 1130 cm^{-1}; nmr (δ, CCl_4): 3.5 (3 H, singlet), 3.1–2.4 (4 H, complex), and 2.3–1.7 (4 H, complex).

Anal. Calcd for $C_8H_{11}O_2Cl$: C, 55.00; H, 6.35; Cl, 20.31. Found: C, 55.14; H, 6.39; Cl, 20.58.

Spiro[2.3]hexane-4-methanol (2). A stirred solution of 6 g of crude ester in 300 ml of dry diethyl ether was cooled in an ice bath and 10 g (approximately tenfold excess) of lithium aluminum hydride was added. The mixture was stirred for 47 hr at room temperature and 29 hr at 36°. Methanol and then saturated ammonium chloride solution were added until salts precipitated. The ether layer was decanted, and the salts were washed with ether. The combined ethereal solutions were washed with water, saturated sodium bicarbonate solution, and water and dried over anhydrous sodium sulfate. The ether solution was filtered and the ether removed by rotary evaporation. The alcohol mixture obtained was 65% spiro[2.3]hexane-4-methanol (**2**) and 35% 4-chlorobicyclo-[2.2.0]hexane-1-methanol (**3**). The alcohol mixture was resubmitted to reducing conditions (7 g of LAH in 300 ml of dry ether), this time for 10 days at reflux. The mixture was worked up as before. Vpc analysis of the crude mixture showed the rearrangement to be essentially complete. The reaction mixture was distilled through an 18-in. spinning-band column, bp approximately 75° (19 mm), giving a total of 1.019 g of alcohol (97.2% of the total was spiro[2.3]hexane-4-methanol by vpc analysis; the first of four fractions was 470 mg and 99.7% spiro[2.3]hexane-4-methanol). There was approximately 1.5 g of residue remaining which contained no detectable amount of spiro[2.3]hexane-4-methanol by infrared or vpc. The recovered yield was about 30% of the theoretical; $\nu_{max}^{CCl_4}$ 3400, 3080, 2930, 2850, and 1005 cm^{-1}; nmr (δ, CCl_4): 3.5 (2 H, doublet, J = 7 cps), 2.8 (1 H, broad singlet, hydroxyl), 2.6–1.4 (5 H, complex), and 0.47–0.08 (4 H, complex); mass spectrum (*m/e*): base peak, 79; molecular ion, 112.

Anal. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 74.78; H, 10.57.

Spiro[2.3]hexane-4-methyl *p*-Toluenesulfonate (4). A 67.7-mg portion (0.61 mmol) of spiro[2.3]hexane-4-methanol in 8.5 ml of dry pyridine was cooled with stirring in an ice–methanol bath. To this solution was added 195 mg (40% excess) of tosyl chloride. The mixture was stirred 2 hr, poured into ice water, and extracted with four portions of diethyl ether. The ether solution was dried over anhydrous magnesium sulfate. Filtration and evaporation gave an oil which was distilled at 80° (10 μ) to give 118.6 mg (74%) of a white semisolid; $\nu_{max}^{CCl_4}$ 3085, 3025, 3000, 2980, 2870, 1600, 1350, 1170, 1095, 1010, 950, and 835 cm^{-1}; nmr (δ, CCl_4): 7.5 (4 H, doublet of doublets, J = 27, 8 cps), 4.0 (2 H, doublet, J = 7 cps), 2.9–1.5 (8 H, complex), 0.6–0.0 (4 H, complex).

Anal. Calcd for $C_{14}H_{18}O_3S$: C, 63.15; H, 6.81; S, 12.04. Found: C, 63.43; H, 6.65; S, 12.03.

Cyclobutylmethyl *p*-Toluenesulfonate. This *p*-toluenesulfonate ester was made from cyclobutylmethanol in the same manner as spiro[2.3]hexane-4-methyl *p*-toluenesulfonate was made from its corresponding alcohol, **2**.[17] Cyclobutanol was obtained from the commercially available cyclobutanecarboxylic acid (Aldrich Chemical Co.) by esterification of the acid with an ethereal solution of diazomethane and then reduction of the ester with lithium aluminum hydride.

Xanthate Ester of Spiro[2.4]heptan-4-ol. To 1.55 g (13.8 mmol) of spiro[2.4]heptan-4-ol (**5**) in 9 ml of dry diethyl ether was added 0.4 g of chopped sodium metal. After the mixture had been stirred under nitrogen for 30 hr, the excess sodium was mechanically removed, 1.3 ml of carbon disulfide was slowly added, and the solution was stirred for 1 hr. A 2.0-ml portion of methyl iodide was added, and the solution was stirred overnight. An additional 0.7 ml of methyl iodide was added and stirring continued for 1 hr. The reaction mixture was then filtered, and the salts were washed with diethyl ether. Evaporation of the ether gave 2.3 g (82%) of a yellow liquid; $\nu_{max}^{CCl_4}$ 3050, 2930, 1220, 1145, 1080, 1055, 1020, and 955 cm^{-1}; nmr (δ, CCl_4): 5.4 (1 H, complex), 2.5 (3 H, singlet), 2.2–1.6 (6 H, complex), and 0.9–0.5 (4 H, complex).

Anal. Calcd for $C_9H_{14}OS_2$: C, 53.46; H, 6.98; S, 31.65. Found: C, 53.58; H, 7.12; S, 31.58.

Spiro[2.4]heptan-5-ol (11). A 1.3-g portion of the xanthate ester of spiro[2.4]heptan-4-ol was placed in a 25-ml, pear-shaped flask fitted with a condenser. The ester was stirred with a magnetic stirrer and heated to effect cracking. The temperature was maintained at 120–130° for 1 hr and 45 min; $\nu_{max}^{CCl_4}$ 3060, 2990, 2930, 2850, 1610, 1045, 1015, 955, 932, 888, and 868 cm^{-1}; nmr (δ, CCl_4): 5.75–5.45 (1 H, complex), 5.25–5.05 (1 H, complex), 2.75–2.25 (2 H, complex), 2.15–1.65 (2 H, complex), and 0.60 (4 H, singlet).

A 100-mg portion (1.06 mmol) of spiro[2.4]hept-4-ene (**12**) in 150 μl of reagent grade tetrahydrofuran was cooled in an ice bath with stirring. To this solution was added 1 ml of 1 *M* diborane and stirring was continued at room temperature for 30 min. Water was then added until bubbling stopped. The solution was heated to 50–60° and 240 μl of 3 *N* sodium hydroxide solution was added. This was followed by the dropwise addition of 480 μl of 30% hydrogen peroxide. The heating bath was then removed and the solution allowed to cool to room temperature. About 50 ml of diethyl ether was added, and the mixture was washed with saturated solutions of sodium chloride, sodium sulfite, and sodium chloride. The ethereal solution was then dried over anhydrous magnesium sulfate, filtered, and concentrated on a rotary evaporator. The resulting alcohols, **5** and **11**, were separated by preparative vapor phase chromatography on a 10-ft 10% Carbowax (10% KOH) column. The ratio of alcohols was 91.5% **11** and 8.5% **5**. The total weight of **11** collected was 54 mg (50% yield of alcohols). The actual yield of alcohols was, of course, greater than the amount which could be collected from the column; $\nu_{max}^{CCl_4}$ 3335, 3080, 3000, 2995, 2880, 1420, 1340, 1070, 1045, 1010, 980, 955 cm^{-1}; nmr (δ, CCl_4): 4.5–4.1 (1 H, complex), 4.0 (1 H, broad singlet, hydroxyl), 2.1–1.3 (6 H, complex), 0.6–0.3 (4 H, complex).

Anal. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 75.03; H, 11.05.

Spiro[2.4]heptan-5-one. To 8 mg of spiro[2.4]heptan-5-ol (**11**) in 1 ml of reagent grade acetone was added with stirring 30 μl of Jones reagent (26.7 g of chromium trioxide and 23 ml of concentrated sulfuric acid diluted to 100 ml with distilled water). 2-Propanol was immediately added to destroy excess Jones reagent. The resulting mixture was then poured into a saturated solution of sodium bicarbonate. This solution was extracted with three portions of diethyl ether. The ether extracts were dried over anhydrous magnesium sulfate, filtered, and concentrated on a rotary evaporator. The ketone was isolated by vpc on a 10-ft 10% Carbowax (10% KOH) column; $\nu_{max}^{CCl_4}$ 3080, 2970, 1745, 1405, 1150, 1130, 1015, and 960 cm^{-1}.

Spiro[2.4]hept-5-yl *p*-Toluenesulfonate (16). This *p*-toluenesulfonate (**16**) was made in the same manner as the preceding two *p*-toluenesulfonates.[17]

Determination of Solvolyses Products. A 49.2-mg portion of spiro[2.3]hexane-4-methyl *p*-toluenesulfonate (**4**) and 16.3 mg of sodium acetate (10% excess) were placed in an nmr tube and dissolved in 300 μl of glacial acetic acid (reagent grade from Allied Chemical, distilled from 3% acetic anhydride before use). The tube was then cooled in a Dry Ice–acetone bath, evacuated to 2 mm, and sealed. An nmr spectrum was recorded and the tube was placed in a 76.5° bath. The sample was withdrawn at 3-hr intervals and cooled to room temperature and its nmr spectrum recorded. In this manner a crude rate was determined by monitoring the disappearance of the methylene protons' absorption at δ 4.0 relative to the aromatic protons' absorption at δ 7.5 as determined by nmr integrations. The sample was maintained at 76.5° a total of 41 hr (a little more than ten half-lives). The solution was then cooled, poured into 1 ml of water, and extracted with six portions of pentane. The pentane extracts were washed with a saturated solution of sodium bicarbonate until bubbling ceased, then with water. The solution was dried over a mixture of anhydrous magnesium and sodium sulfates and filtered and the solution concentrated by distilling the pentane through an 18-in. Vigreux column. About 100 ml of dry diethyl ether was added, the stirred solution was cooled in an ice bath, and 200 mg of lithium aluminum hydride was added. The mixture was stirred for 1 hr at 0°. A saturated ammonium chloride solution was then added dropwise until salts precipitated. The ether layer was decanted, and the salts were dried over anhydrous magnesium sulfate. The solution was filtered and the product ratios were determined by vpc on 10-ft 10% Carbowax (10% KOH) and 5-ft 10% TCEP columns. The solution was then con-

(17) R. S. Tipson, *J. Org. Chem.*, 9, 235 (1944).

centrated by rotary evaporation and the products were determined by a comparison of infrared spectra of the collected peaks and vpc retention time with those of authentic samples. The amount of alcohols **9** and **10** was not sufficient to give infrared spectra of the desired intensity; the resulting spectra were very similar to, but not necessarily identical with, the spectra provided by Professor Closson.[13b] The identity of alcohol **11** was determined by oxidation with Jones reagent to the corresponding ketone and comparing the infrared spectra with that of spiro[2.4]heptan-5-one. The resolution of alcohols **6**, **7**, and **11** was poor by vpc until alcohol **11** was removed by oxidation. In order to determine the amount of alcohol **11** initially present in the solvolysis mixture, a comparison of the nmr integrals of the cyclopropyl protons and the exocyclic methylene protons of the complete solvolysis mixture was made. Since the amount of alcohol **8** and the amount of the alcohols, other than **11**, containing cyclopropyl rings were known the amount of alcohol **11** could be estimated. Repetitions of this study with ester concentrations of 0.02 *M* gave similar results.

A 33-mg portion of the *p*-toluenesulfonate ester **16** of spiro[2.4]-heptan-5-ol and 20 mg (100% excess) of sodium acetate were dissolved in 50 ml of acetic acid (prepared as above). The solution was kept under nitrogen and maintained at 75° for 35 hr. The solution was cooled, poured into 50 ml of water, and extracted with six portions of pentane. The pentane extracts were washed with a saturated solution of sodium bicarbonate and dried over anhydrous magnesium sulfate. The filtered solution was then concentrated by distilling the pentane through an 18-in. Vigreux column. About 100 ml of dry diethyl ether was added and the stirred solution was cooled in an ice bath. A 40-mg portion (10 equiv) of lithium aluminum hydride was added and the mixture was stirred for 2 hr at room temperature. The work-up was the same as for the solvolysis mixture above. The identities of the products were determined by vpc retention time. The identities of the two major products were confirmed by a comparison of the infrared spectra of the collected vpc peaks with those of authentic samples.

Procedure for Kinetic Runs. For each run the *p*-toluenesulfonate ester was about 0.001 *M* in acetic acid (reagent grade glacial acetic acid from Allied Chemical, distilled from 3% acetic anhydride, bp 117.0–117.8°). There was an 85–100% molar excess of anhydrous sodium acetate present for each run. The reaction was followed by the decrease in absorption at 272 mμ with time as recorded on a Beckman DU spectrometer. For the runs at 75°, aliquots were removed at timed intervals and stored until the completion of the run. The ultraviolet spectra were then recorded. For the runs at 45°, the solutions were placed directly in a spectrometer with a constant-temperature cell compartment maintained at 45°.

The Synthesis of Fluorammonium Salts[1]

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Abstract: The reaction of alkyl N-fluorocarbamates with sulfuric acid gave fluorammonium bisulfate, which was identified by nmr spectra and by reactions with cyclohexanone and *n*-butyraldehyde to give ε-caprolactam and *n*-butyronitrile, respectively. Fluorammonium perchlorate and fluorammonium methanesulfonate were isolated as pure salts from reactions of N-fluorocarbamates with perchloric acid and methanesulfonic acid, respectively. Ethyl N-fluoro-N-methylcarbamate and sulfuric acid gave methylfluorammonium bisulfate, which reacted with cyclohexanone to give N-methylcaprolactam. Nmr spectra of fluorammonium perchlorate indicated rapid hydrogen exchange in acetonitrile and ethyl acetate, but not in sulfuric acid.

Of the four possible fluorine-substituted ammonium ions, only the tetrafluoro derivative has been reported as a stable salt.[2,3] Difluoramine and trifluoramine have been reported to form reversible complexes with Lewis acids at low temperatures.[4] Fluoramine was claimed to be a by-product of the electrolysis of ammonium bifluoride[5,6] but the results have been shown to be in error.[7] Dimethylfluoramine was synthesized by the fluorination of unsymmetrical dimethylsulfamide and the compound was sufficiently basic to form a stable hydrochloride.[8] Fluorimmonium salts prepared by the rearrangement of alkyldifluoramines[9] can also be considered as alkylidene derivatives of substituted fluoramines.

Simple salts of fluoramine have now been prepared by the reaction of alkyl N-fluorocarbamates with strong acids. The starting materials are synthesized readily by the fluorination of alkyl carbamates.[10]

Fluorammonium Bisulfate. Fluorimmonium salts have been prepared and characterized in sulfuric acid. Under these conditions, the hydrolysis of N-fluorocarbamates in sulfuric acid would be expected to give the fluorammonium ion, which also should be stable.

When a solution of ethyl N-fluorocarbamate in concentrated sulfuric acid was heated at 85 to 90°, carbon dioxide and ethylene were evolved. The ^{19}F nmr spectrum of the sulfuric acid solution consisted of a quartet at 36.8 ppm relative to external trifluoroacetic acid, with a coupling constant of 38 cps. Thus, the fluorine was coupled to three equivalent hydrogens, and it is noteworthy that the hydrogens did not exchange rapidly with the solvent. By contrast, the ^{19}F spectrum of an unheated solution of ethyl N-fluorocarbamate in sulfuric acid consisted of a single broadened signal at 27.5 ppm; the NH protons of the starting material thus exchanged with the solvent rapidly by the nmr time scale.

Additional evidence for the fluorammonium ion structure was obtained from reactions with carbonyl compounds. The reaction of cyclohexanone with a sulfuric

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