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SOLVOLYTIC REARRANGEMENT OF THE 2-(Δ^1-CYCLOPENTENYL)ETHYL SYSTEM[1]

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Abstract—The acetolysis of 2-(Δ^1-cyclopentenyl)ethyl bromobenzenesulfonate (I) yields four rearranged acetates. The major product is 3-methylenecyclohexyl acetate, while spiro[2.4]heptan-4-yl, bicyclo[3.2.0]heptan-1-yl, and bicyclo[3.1.0]hexane-1-methyl acetate are produced in smaller amounts. Consideration of the solvolytic reactions of derivatives possessing these rearranged structures allows presentation of an overall scheme of reaction for acetolysis of I.

NEIGHBORING group participation by double bonds during solvolytic reactions of primary systems has grown rapidly into one of the more fascinating areas of organic chemistry.[3] Until recently, though, evidence for participation by homoallylic double bonds at primary centers was scant and usually limited to deamination reactions.[4] Lately, however, several workers have shown that suitably substituted homoallylic double bonds not only interact with primary centers, but often provide considerable driving force for ionization.[5] Probably the remarkable cyclization of 4,4-dicyclopropylbut-3-enyl chloride on hydrolysis[6] also proceeds with rate acceleration, but kinetic measurements are lacking. It has even been shown that the bare system, allylcarbinyl toluenesulfonate, undergoes solvolytic cyclization with rate enhancement under suitable conditions (formic acid), albeit sluggishly.[7] Recently, Hanack and Schneider have presented interesting work concerning homoallylic cyclopentenylalkyl systems.[8,9] As part of a general investigation of solvolytic cyclization reactions we have studied the solvolysis of 2-(Δ^1-cyclopentenyl)ethyl *p*-bromobenzenesulfonate and wish to outline the results from this and related reactions.

[1] [a] A preliminary account of this work appeared in *Tetrahedron Letters* 3831 (1964). [b] Supported in part by the Petroleum Research Fund, administered by the American Chemical Society (Grant No. 1272-A4).

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[3] [a] R. G. Lawton, *J. Amer. Chem. Soc.* **83**, 2399 (1961); [b] P. D. Bartlett and S. Bank, *Ibid.* **83**, 2591 (1961); [c] G. LeNy, *C.R. Acad. Sci. Paris*, **251**, 1526 (1960); [d] S. Winstein and P. Carter, *J. Amer. Chem. Soc.* **83**, 4485 (1961); [e] P. D. Bartlett, *Liebigs Ann.* **653**, 45 (1962); [f] E. L. Allred and T. J. Maricich, *Tetrahedron Letters* 949 (1963); [g] G. E. Gream and D. Wege, *Ibid.* 535 (1964); [h] W. D. Closson and G. T. Kwiatkowski, *J. Amer. Chem. Soc.* **86**, 1887 (1964); [i] M. Hanack and W. Kaiser, *Angew. Chem.* (Int. Ed.), **3**, 583 (1964); [j] W. Herz and G. Caple, *J. Amer. Chem. Soc.* **84**, 3517 (1962); [k] W. S. Johnson and J. K. Crandall, *Ibid.* **86**, 2085 (1964); W. S. Johnson *et al.*,* *Ibid.* **86**, 1959 (1964); [l] F. C. Uhle, *Tetrahedron Letters* 3099 (1964); [m] P. D. Bartlett *et al.*,* *J. Amer. Chem. Soc.* **87**, 1288, 1297, 1308, 1314 (1965).

[4] E. Renk and J. D. Roberts, *J. Amer. Chem. Soc.* **83**, 878 (1961).

[5] [a] J. B. Rogan, *J. Org. Chem.* **27**, 3910 (1962); [b] C. F. Wilcox, Jr. and D. L. Nealy, *Ibid.* **28**, 3454 (1963); [c] R. S. Bly and R. T. Swindle, *Ibid.* **30**, 10 (1965).

[6] H. Hart and J. M. Sandri, *J. Amer. Chem. Soc.* **81**, 320 (1959).

[7] K. L. Service and J. D. Roberts, *J. Amer. Chem. Soc.* **86**, 3773 (1964).

[8] M. Hanack and H. J. Schneider, *Tetrahedron* **20**, 1863 (1964).

[9] M. Hanack and H. J. Schneider, *Angew. Chem.* **76**, 783 (1964).

* The large number of co-authors precluded publication of all the names.

The rates of ethanolysis and acetolysis of 2-(Δ^1-cyclopentenyl)ethyl *p*-bromobenzenesulfonate (I) are presented in Table 1. In addition, kinetic data for 2-cyclopentylethyl (II), 2-(Δ^2-cyclopentenyl)ethyl (III), 3-cyclopentylpropyl (IV), and 3-(Δ^1-cyclopentenyl)propyl broslyate (V) are shown for comparison.

TABLE 1. RATES OF SOLVOLYSIS OF CYCLOPENTENYLALKYL BROSYLATES AT 80°

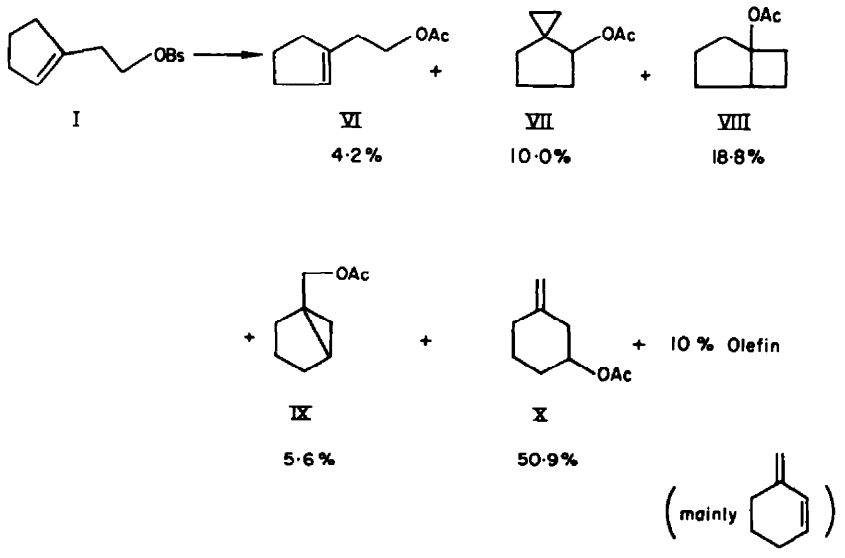
Compound	EtOH 10^5 k,sec^{-1}	AcOH[a] 10^5 k,sec^{-1}	Ref.
 CH_2CH_2OBs (I)	7·75 ± 0·05	11·0 ± 0·2	
 CH_2CH_2OBs (I)[b]	——	11·4 ± 0·1[b]	
 CH_2CH_2OBs (II)	6·78 ± 0·06	0·281 ± 0·002	
 CH_2CH_2OBs (III)	7·16 ± 0·33[c]	0·278 ± 0·010	*d*
 $CH_2CH_2CH_2OBs$ (IV)	13·4 ± 1·0[c]	0·411 ± 0·012	*d*
 $CH_2CH_2CH_2OBs$ (V)	——	0·399 ± 0·010	

[a] Containing excess (0·036 M) sodium acetate.
[b] Containing 0·0025 M lithium perchlorate.
[c] Measured conductimetrically.
[d] Ref. 3h.

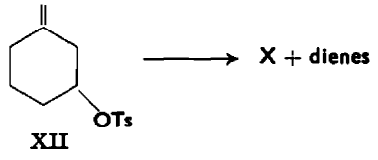
While II, III,[3a,b] and IV yield exclusively the corresponding acetates on acetolysis and V produces more than 90% of unrearranged ester, I yields only a minor amount of 2-(Δ^1-cyclopentenyl)ethyl acetate (VI). The major portion of the acetolysis product from I was a complex mixture of rearranged acetates as shown in Chart I. All of these were shown to be stable under the conditions of formation (100°, buffered acetic acid, 24 hr). The identities of the product acetates were determined by comparison with authentic samples, or in the case of bicyclo[3.2.0]heptan-1-yl acetate (VIII), by comparison of the properties of the corresponding alcohol with literature values.[9] Hanack and Schneider have recently reported that deamination of 2-(Δ^1-cyclopentenyl)ethylamine in aqueous solution produces the tertiary alcohol corresponding to VIII in 65% yield, while solvolysis of the naphthalenesulfonate ester related to I, in acetone-water yielded 21% of the tertiary alcohol, unrearranged alcohol being the major product in the latter case.[9]

To gain more information concerning the nature of the rearrangements during

Chart I

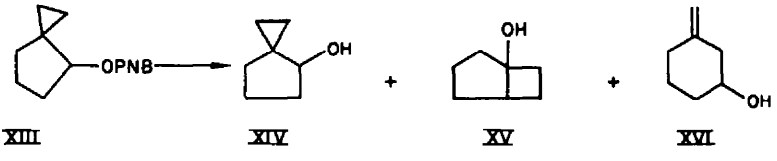


acetolysis of I, we investigated the solvolytic reactions of certain of the rearranged structures. First, the acetolysis of 3-methylenecyclohexyl tosylate (XII) was studied. The products were found to consist of 63 % X and the same two dienes formed in the acetolysis



of I; the minor component (6·6%) being 3-methylenecyclohexene. The rate of acetolysis at 80° was only $5{\cdot}07 \pm 0{\cdot}05 \times 10^{-5}$ sec^{-1} about half that of cyclohexyl tosylate ($10{\cdot}7 \times 10^{-5}$ sec^{-1}),[10] measured under the same conditions.

The second rearranged structure investigated was the spiro[2.4]heptan-4-yl system. For reasons of convenience, solvolysis of the *p*-nitrobenzoate (XIII) in buffered 60% aqueous acetone was investigated. From XIII was obtained a mixture of alcohols consisting of 61% spiro[2.4]heptan-4-ol (XIV), 25% bicyclo[3.2.0]heptan-1-ol (XV) and 14% 3-methylenecyclohexanol (XVI). No trace of bicyclo[3.1.0]hexane-1-methanol



(XVII) was found. While all of these alcohols were stable under the conditions of solvolysis (lutidine buffer), in the presence of free *p*-nitrobenzoic acid at 100° XIV was converted to a mixture of 63·5% XV and 36·5% XVI after 2·5 hr. Further heating did not change the composition of the mixture.

[10] J. D. Roberts and V. C. Chambers, *J. Amer. Chem. Soc.* **73**, 5034 (1951).

The solvolysis of bicyclo[3.1.0]hexane-1-methyl *p*-nitrobenzoate (XVIII) in buffered 60% aqueous acetone was next investigated. The major product (83%) in this case was XVI. A small amount of olefin (2·5%), probably 3-methylenecyclohexene, was also obtained. The remainder of the product consisted of 1·5% XIV, 4·3% XV, and 8·9% XVII.

XVIII

The rates of solvolysis of XIII,[11] XVIII, and related *p*-nitrobenzoate esters are shown in Table 2.

TABLE 2. RATES OF SOLVOLYSIS OF *p*-NITROBENZOATE ESTERS IN 60% AQUEOUS ACETONE

Ester	T, °C	10^5 k, sec^{-1}	Ref.
spiro[2.4]heptan-4-yl	100	53·6	*a*
spiro[2.4]heptan-4-yl	75	4·95	*a*
bicyclo[3.1.0]hexane-1-methyl	100	2·17 ± 0·02	
cyclopropylmethylcarbinyl	75	0·58	*b*
cyclopropylcarbinyl	100	ca. 0·003	*c*

[a] Ref. 11.

[b] R. A. Sneen and A. L. Baron, *J. Amer. Chem. Soc.* **83**, 614 (1961).

[c] Estimated from 2% reaction after 200 hr.

From the data of Table 1 it can be seen that the ethanolysis rate of Δ^1-cyclopentenylethyl brosylate (I) is essentially identical with that of the other 2-substituted ethyl brosylates (II and III). On changing to acetic acid, a less nucleophilic but somewhat more polar solvent, the reactivity of I actually increases slightly while II and III exhibit a normal sharp decrease in reaction rate. The rate of I relative to II or III thus changes from *ca.* one in ethanol to about forty in acetic acid. This insensitivity of I to change in nucleophilicity of solvent is fairly typical of systems that solvolyze with participation of double bonds.[3b,d,7] These kinetic considerations combined with the formation of almost completely rearranged product clearly indicate participation of the double bond in the ionization step during acetolysis of I.

It is of interest to estimate the extent of anchimeric assistance in this reaction. Ideally one should know the rate of non-assisted acetolysis of I, but this, of course, is impossible to assess. Model compounds which do not solvolyze with neighboring group participation provide perhaps the best recourse if one keeps in mind all the differences between the model and the compound in question. The most obvious choices for I are the saturated analog II, and the double bond isomer III. It seems reasonable that there are no anchimeric effects on the rates of these compounds.[12] Sterically, the differences

[11] We would like to thank Professor A. P. Krapcho of the Chemistry Department, University of Vermont, for furnishing us with the solvolysis constant of spiro[2.4]heptan-4-yl *p*-nitrobenzoate.

[12] One could argue that the double bond in III does participate in the solvolysis step without resulting in formation of rearranged product, and that the solvolysis rate of III is accelerated to the extent of cancelling an adverse inductive effect of the double bond, resulting in identical rates for II and III. This argument is made very unlikely by the fact that II and III solvolyze at identical rates in *both* EtOH and acetic acid.

between I, II, and III are small, and if anything, probably on the side of somewhat less hindrance near the reaction center for I. This should make unassisted acetolysis of I very slightly faster than for II and III since moving the branched portion of the chain one carbon further from the reaction site as in 3-cyclopentylpropyl (IV), and 3-(Δ^1-cyclopentenyl)propyl brosylate (V) results in only a 40 to 50% increase in rate. (Neither IV nor V undergoes extensive rearrangement on acetolysis, IV yielding only unrearranged acetate[3a] and V producing more than 90% unrearranged substitution product.) The inductive effect of the double bond in I on the hypothetical unassisted rate is more difficult to judge. In III, where the double bond is one position further from the reaction center, there appears to be no effect; III and II undergoing both ethanolysis and acetolysis at identical rates.[13] This is contrary to the results of many other investigators[3e,m,14] but in conformationally mobile systems such as these, unknown factors such as differences in ground state solvation[15] and preferred spatial orientation would combine to render any simple explanation unreliable. The lack of any significant difference in acetolysis rate between the homolog of I (V) and IV supports the conclusion that inductive effects in these flexible and relatively unhindered systems are minor, and that anchimeric acceleration in the acetolysis of I is only about forty-fold.

Comparison with other primary homoallylic systems indicates that the 2-(Δ^1-cyclopentenyl)ethyl system is only moderately reactive. Thus, among acyclic systems, acceleration in acetolysis varies from about nil for 3-butenyl[16] to a factor of 10^7 for the 2,2,3-trimethyl-3-pentenyl system.[5b] Probably the most similar system previously studied is that of Δ^2-cyclopentenylcarbinyl naphthalenesulfonate.[8] This was observed to undergo acetolysis about ten times faster than its saturated analog. The saturated system, cyclopentylcarbinyl, is known to solvolyze in acetic acid with concurrent ring expansion which results in a moderate (five to six-fold) rate enhancement.[17,3m] Thus, a better value for anchimeric acceleration in the Δ^2-cyclopentenylcarbinyl system is fifty to sixty-fold.

Clearly, the enhanced rate and the production of rearranged products (Chart I) on acetolysis of I indicate participation of the double bond. However, direct ionization to an intermediate cation capable of yielding all of the rearranged acetates seems unlikely. The first-formed intermediate should account for the rate enhancement, and some of the products, if possible. The bicyclobutonium ion XIX would account for rate enhancement and would also explain the formation of spiro[2.4]heptan-4-yl acetate (VII) and bicyclo[3.2.0]heptan-1-yl acetate (VIII).[18] The unrearranged acetate VI could also be derived from XIX but probably comes from a competing solvolytic

[13] Professor R. S. Bly, of the Department of Chemistry, University of South Carolina, has informed us of similar experiments by him and J. Schwartz which show that the first-order rates of acetolysis of II and III at 100° differ by only a few per cent. We would like to thank Professor Bly for informing us of this.

[14] [a] P. D. Bartlett and M. R. Rice, *J. Org. Chem.* **28**, 3351 (1961); [b] C. F. Wilcox and S. S. Chibber, *Ibid.* **27**, 2332 (1962); [c] S. Winstein, M. Battiste, and R. Pande, *6th Report on Research under the sponsorship of the Petroleum Research Fund* p. 178 (1961).

[15] E. M. Arnett, P. D. Duggleby and J. J. Burke, *J. Amer. Chem. Soc.* **85**, 1350 (1963).

[16] Estimated from the small difference in reactivity between 3-butenyl and n-butyl tosylate in formic acid.[7]

[17] H. Felkin and G. LeNy, *Bull. soc. chim. Fr.* 1169 (1957).

[18] The stereochemistry of VIII and the related alcohol have not been rigorously proved, but if they are derived from XIX they should be *cis*. Their stability to fairly acidic media also argues that they are the more stable (i.e., *cis*) isomers.

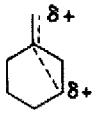
displacement at the primary carbon of I. The relatively large amounts of bicyclo-[3.2.0]heptan-1-ol formed in reactions of the Δ^1-cyclopentenylethyl system in aqueous solvents[9] also supports initial formation of XIX since it would be expected that the first-formed cation would be rapidly trapped under these conditions. (In the case of

XIX

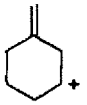
deamination of Δ^1-cyclopentenylethylamine[9] the first carbonium ion may be the "hot" primary ion, but intramolecular displacement of nitrogen, yielding XIX, is at least equally plausible.)

Spiro[2.4]heptan-1-yl *p*-nitrobenzoate (XIII) should also yield ion XIX initially, and in aqueous acetone 86% of the observed products (XIV and XV) can be rationalized as derived from it. The reactivity of XIII, as indicated by its rate of solvolysis,[11] is high but only typical of secondary cyclopropylcarbinyl systems. (Table 2.) Kosower has found that the spatial arrangement of the cyclopropane ring in spiro[2.4]heptan-4-one gives rise to an unusually low $\pi \rightarrow \pi^*$ transition energy.[19] However, this factor does not appear to be manifested in the solvolytic reactivity of XIII.

The other two rearranged acetates cannot be obtained from XIX. While a "stripped cholesteryl" ion, XX, could be considered to be the precursor of 3-methylenecyclohexyl (X) and bicyclo[3.1.0]hexane-1-methyl acetate (IX), its intermediacy is not consistent with all the data. If XX were of particular stability, one should expect to obtain



XX



XXI

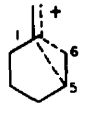
it on acetolysis of 3-methylenecyclohexyl tosylate (XII). The fact that XII undergoes acetolysis at a rate slower than cyclohexyl tosylate, and produces no bicyclic substitution product seems to call for no more than the simple 3-methylenecyclohexyl cation (XXI) as an intermediate. The observed small rate decrease relative to cyclohexyl (50%) is in the range of inductive effects of double bonds in similar cyclic systems.[3e,m,14] The only other noteworthy effect of the double bond is the production of a relatively large amount of substitution product. Cyclohexyl arenesulfonates yield only a meager amount (ca. 15%) of cyclohexyl acetate on acetolysis,[3e,m,10] and generally give poor yields in S_N2 reactions.[20] This change in the substitution-elimination ratio may be due to a simple conformational effect or to some minor electronic interaction with the double bond after the transition state is passed.

On the other hand, solvolysis of bicyclo[3.1.0]hexane-1-methyl *p*-nitrobenzoate (XVIII) appears to be greatly accelerated. It is about 600 times as reactive as cyclopropylcarbinyl *p*-nitrobenzoate. (Table 2.) Normally, substitution on the ring positions of the cyclopropylcarbinyl system has only a small to moderate effect on solvolytic

[19] E. M. Kosower and M. Ito, *Proc. Chem. Soc.* 25 (1962).

[20] A. Streitwieser, Jr. and C. E. Coverdale, *J. Amer. Chem. Soc.* 81, 4275 (1959); A. C. Cope, M. Brown and Hiok-Huang Lee, *Ibid.* 80, 2855 (1958).

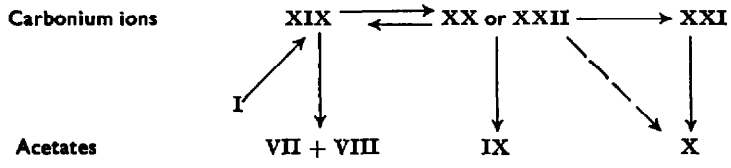
reactivity.[21] The high reactivity of XVIII could be due either to the immediate production of a particularly stable cation, or to relief of strain in the ground state.[22] Considering that the major portion (83%) of the solvolysis product of XVIII is relatively strainless 3-methylenecyclohexanol (XVI), the latter hypothesis is most attractive. The conversion of XVIII to XVI would result in almost complete loss of both cyclopentane and cyclopropane ring strain, an amount that is probably close to the value of 30 kcal/mole estimated for bicyclo[3.1.0]hexane.[23] This energy will be available to the extent that the transition state for ionization of XVIII resembles ion XXI. Immediate production of XXI appears ruled out since about 6% of spiro alcohol (XIV) and bicyclo[3.2.0]heptanol (XV) as well as 8·8% of unrearranged alcohol (XVII) are formed from XVIII.[24] What we feel is most reasonable is ionization of XVIII to either the bridged homoallylic ion XX, or a bridged cation of structure XXII where 1,6-bonding is stronger than 1,5-bonding. Strain relief would be appreciable in either case at this



XXII

stage and conversion to ion XXI would involve only minor changes in bond lengths and conformation. Ion XXII or XX could give rise to XVII by reaction at the primary carbon. Conversion of a small fraction back to ion XIX would account for the other bicyclic alcohols.

Considering, now, the acetolysis of Δ¹-cyclopentenyl brosylate (I), a scheme can be written as shown:



Other cations, such as the bicyclobutonium ion XXIII, could also be present and may be intermediate stages between the ions in the scheme proposed. The proposed scheme,

[21] [a] E. F. Cox, M. Caserio, M. S. Silver and J. D. Roberts, *J. Amer. Chem. Soc.*, **83**, 2719 (1961); R. A. Sneen, K. Lewandowski, I. Taha and B. Smith, *Ibid.* **83**, 4843 (1961); J. W. Wilt and D. D. Roberts, *J. Org. Chem.* **27**, 3430 (1962); [b] D. D. Roberts, *Ibid.* **29**, 294 (1964); **30**, 23 (1965).

[22] S. Winstein and E. M. Kosower, *J. Amer. Chem. Soc.* **81**, 4399 (1959).

[23] C. T. Mortimer, *Reaction Heats and Bond Strengths* p. 45. Pergamon Press, New York, N.Y. (1962).

[24] Admittedly, there is a minor weakness in this argument. The solvolytic reaction of the 3-methylenecyclohexyl and bicyclo[3.1.0]hexanemethyl systems have not been examined under identical conditions and the possibility exists that the former *might* yield bicyclic products under the conditions used for solvolysis of the latter system. Unfortunately, 3-methylenecyclohexyl *p*-nitrobenzoate would undoubtedly be too unreactive to study and the toluenesulfonate of bicyclo[3.1.0]hexanemethanol is probably too reactive to prepare. (Crude comparison with cyclopropyl carbinyl tosylate[21b] indicates a half-life for the bicyclic tosylate of about 10 seconds in acetic acid at 15°.)

however, is sufficient to account for the products and provide reasonable explanation of the reactivities of the related systems.

XXIII

In acetolysis of I and solvolysis of the bicyclic *p*-nitrobenzoates there appears a strong drift toward the 3-methylenecyclohexyl system. Thermodynamically, the latter structure is certainly more stable than the various bicyclic structures but it is probably only a few kcal/mole more stable than the starting cyclopentenylethyl structure.[25] The lack of formation of any large amount of cyclopentenylethyl derivatives in these solvolytic reactions must be due either to the low quasi-equilibrium concentration of any ion that can yield the ethyl compound or to the low relative rate for the reaction of the important cations (probably XIX, XXII, and XX) with solvent in a suitable manner. The observation of Applequist and Landgrebe that treatment of spiro[2.4]heptan-4-ol with thionyl chloride leads to a mixture of 2-(Δ^1-cyclopentenyl)ethyl chloride and a methylenecyclohexyl chloride[28] indicates that under equilibrating conditions production of the cyclopentenylethyl system does compete with formation of methylenecyclohexyl derivatives.

This general reaction class may have synthetic utility. Hanack has already pointed out its potential use as a route to bicyclic systems possessing a fused cyclobutane ring.[9] Application of the complete rearrangement to produce 3-methylenecyclohexyl derivatives also appears promising. (Amusingly, the two carbons of the ethyl chain in I should no longer be bonded to each other in the final product.) Finally, it should be pointed out that the 2-(β-indolyl)ethyl structure, so common in biological systems, is analogous in many ways to the 2-(Δ^1-cyclopentenyl)ethyl structure and possibly may undergo some of the same transformations. This is currently under investigation.

EXPERIMENTAL

2-(Δ^1-Cyclopentenyl)ethanol. Δ^1-Cyclopentenylacetic acid (Aldrich Chemical Co.), (25 g, 0·20 mole) was dissolved in tetrahydrofuran and reduced with LAH in the usual manner. Isolation and distillation of the alcohol yielded 20 g (90%) material, b.p. 65–66°/3 mm, n_D^{25} 1·4781 (lit.[29] b.p. 76·5–76·8°/8·5 mm, n_D^{25} 1·4765).

2-Cyclopentylethanol. This was prepared from cyclopentylacetic acid in a manner similar to that described above. The yield of alcohol was similar, b.p. 77–78°/3 mm (lit.[30] b.p. 96·5–97°/24 mm.).

3-(Δ^1-Cyclopentenyl)propanol. 2-(Δ^1-Cyclopentenyl)ethanol was converted to 2-(Δ^1-cyclopentenyl)ethyl bromide by the method of Toldy *et al.*[31] From 17 g (0·15 mole) of Δ^1-cyclopentenylethanol was obtained 10 g (38%) of Δ^1-cyclopentenylethyl bromide, b.p. 43–44°/0·5 mm (lit.[34] b.p.

[25] One can estimate that the Δ^1-cyclopentenylethyl structure is only 1–2 kcal/mole less stable than the methylenecyclohexane system by considering heats of hydrogenation of methylenecyclohexane and 1-methylcyclopentene,[26] and the difference in strain energy between cyclopentane and cyclohexane.[27]

[26] R. B. Turner, *Theoretical Organic Chemistry* pp. 67–83. Butterworth, London (1959).

[27] E. L. Eliel, *Stereochemistry of Carbon Compounds* p. 189. McGraw-Hill, New York, N.Y. (1962).

[28] D. E. Applequist and J. E. Landgrebe, *J. Amer. Chem. Soc.* **86**, 1543 (1964).

[29] R. T. Arnold, R. W. Amidon and R. M. Dodson, *J. Amer. Chem. Soc.* **72**, 2871 (1950).

[30] G. R. Yohe and R. Adams, *J. Amer. Chem. Soc.* **50**, 1503 (1928).

[31] L. Toldy, T. Nogradi, L. Vargha and G. Ivanovics, *Acta Chim. Acad. Sci. Hung.* **4**, 303 (1954).

[33] M. Julia and F. LeGoffic, *C.R. Acad. Sci., Paris*, **255**, 714 (1962).

[33] C. J. Albisetti, N. G. Fisher, M. J. Hogsed and R. M. Joyce, *J. Amer. Chem. Soc.* **78**, 2637 (1956).

[34] A. S. Dreiding and J. S. Hartman, *J. Amer. Chem. Soc.* **75**, 939 (1953).

65–70°/2 mm). The bromide (10 g, 57 mmoles) was mixed with 4·55 g (70 mmoles) KCN in 25 ml ethylene glycol and heated at 100° for 2·5 hr. The solution was cooled, poured into sat. NaCl aq and extracted with ether. The combined ether extracts were washed with sat. salt solution and concentrated. The crude residue was hydrolyzed without further purification by mixing it with 200 ml 20% KOH aq and heating at 95° for 20 hr. The solution was then cooled, washed with ether, and acidified with HCl aq. The acidic solution was then extracted with ether, the ether extract washed with water, dried, and concentrated under vacuum to yield 2·5 g 3-(Δ^1-cyclopentenyl)propionic acid, m.p. 58–61° (lit.[33] m.p. 64–65°). This was reduced with LAH in tetrahydrofuran and isolated in the usual manner, yielding 1·9 g (84%), b.p. 66–67°/3 mm (lit.[33] b.p. 97°/15 mm).

3-*Methylenecyclohexanol* (XVI) was prepared by the method of Albisetti *et al.*,[33] b.p. 97·5–98°/43 mm (lit.[33] b.p. 172–174°); NMR(CCl_4) contained peaks at 5·05 τ (singlet, OH), 5·32 τ (singlet, >C=CH_2), 6·42 τ (multiplet, >CH—O—) and multiplets at 7·5 τ, 8·0 τ, 8·2 τ, and 8·5 τ; $\nu_{max}^{CS_2}$ (cm^{-1}) 3680 (m) (OH stretch), 2995 (s), 1660 (w) (C=C stretch), 1055 (s) (C—O stretch), and 897 (s) (>C=CH_2 deformation).

Spiro[2.4]*heptan*-4-*ol* (XIV). 2-Methylenecyclopentanol, prepared by the method of Dreiding and Hartman,[34] was converted to XIV as follows: To 2·0 g Zn–Cu couple (prepared by the method of LeGoff[35]) in 30 ml dry ether was added 1·14 g (11·6 mmole) 2-methylenecyclopentanol in 7 g CH_2I_2. The mixture was stirred overnight, 5 ml sat. NH_4Cl aq added, and the organic layer separated. The aqueous layer and solid were washed further with ether, and the ether added to the organic layer. The ether solution was washed 4 times with Na_2CO_3 aq and twice with sat. salt solution, then dried and concentrated under vacuum. The residual oil was added to 10 ml sat. solution of MeONa under a N_2 atm. and the resulting solution allowed to stand overnight. The solution was then poured into sat. salt solution and extracted with ether. The ether extracts were washed with sat. salt solution until the aqueous layer was neutral, dried, and concentrated under vacuum. Distillation of the residue afforded 1·0 g (8·9 mmoles, 77% yield) XIV, b.p. 75–78°/27 mm (lit.[36] b.p. 100°/68 mm). The material was contaminated with a small amount of CH_2I_2, but the NMR spectrum was in agreement with that reported by Applequist.[38]

Bicyclo[3.1.0]*hexane*-1-*methanol* (XVII) was prepared from Δ^1-cyclopentenylmethanol[37] in the same manner described for the preparation of XIV. From 3·6 g (37 mmoles) of cyclopentenylmethanol was obtained 1·8 g (16 mmoles, 43%) XVII, b.p. 96–98°/40 mm; NMR(CCl_4) contained peaks at 5·6 τ (singlet, OH), 6·4 τ (singlet, —CH_2—O—), 9·6–9·68 (doublet, cyclopropane methylene), and multiplets centered at 8·3 τ and 8·8 τ; $\nu_{max}^{CS_2}$ (cm^{-1}) 3590 (m) (O—H stretch), 3060 (w) and 3020 (w) (cyclopropane C—H); 2995 (s), 1120 (s) (probable C—O stretch), and 1050 (s) and 1030 (s) (probable cyclopropane ring deformation). The *p*-nitrobenzoate (XVIII) melted at 44–45°. (Found: C, 64·41; H, 5·86. Calc. for $C_{14}H_{15}NO_4$: C, 64·35; H, 5·79%.)

Cyclopropylcarbinyl p-*nitrobenzoate* was prepared from cyclopropylcarbinol and *p*-nitrobenzoyl chloride by reaction in pyridine solution, m.p. 56–57°. (Found: C, 59·82; H, 5·16. Calc. for $C_{11}H_{11}NO_4$: C, 59·73; H, 5·01%.)

Spiro[2.4]*heptan*-4-*yl* p-*nitrobenzoate* (XIII) was a gift of Professor D. E. Applequist, of the Chemistry Department, University of Illinois, Urbana, Illinois.[38]

Sulfonate esters. The *p*-bromobenzenesulfonate esters and XII were prepared from the corresponding alcohols and the appropriate sulfonyl chloride by the method of Tipson.[39] The yields and other data are presented in Table 3.

Products of acetolysis of 2-(Δ^1-*cyclopentenyl*)*ethyl* p-*bromobenzenesulfonate* (I). A solution of 11·0 g (33·2 mmoles) I and 3·3 g (40 mmoles) sodium acetate in 500 ml dry acetic acid was heated at 100° for 2 hr. The solution was then added to 1 l. water and extracted with pentane in a continuous extractor. The pentane extracts were washed with Na_2CO_3 aq until the aqueous layer remained basic, dried, and concentrated to a volume of 250 ml by slow distillation of the pentane through a vigreux column. Gas chromatographic analysis of the solution (8 ft. column of tris-1,2,3-(2-cyanoethoxy)propane at 125°) indicated that 10% of the product was two olefins in the ratio of about 4:1. Enough of the major olefin was collected to obtain an UV absorption spectrum, λ_{max}^{EtOH} 232 mμ

[35] E. LeGoff, *J. Org. Chem.* **29**, 2048 (1964).

[36] W. G. Dauben and G. H. Berezin, *J. Amer. Chem. Soc.* **85**, 468 (1963).

[37] A. H. Cook and R. P. Linstead, *J. Chem. Soc.* 956 (1934).

[38] The authors would like to express their thanks to Professor Applequist for his generous gift.

[39] R. S. Tipson, *J. Org. Chem.* **9**, 238 (1944).

(the intensity was not determined due to the very small amount of material), and it was tentatively identified as 3-methylenecyclohexene ($\lambda_{max}^{cyclohexane}$ 231 mμ, $\varepsilon = 21{,}000$).[40] The retention times of these two olefins were identical with those of the two olefins obtained on acetolysis of 3-methylenecyclohexyl toluenesulfonate.

The remaining pentane was removed under vacuum to yield 4·46 g (87·4% yield) of a mixture of acetates. This mixture was reduced with LAH in ether, and the resulting mixture of alcohols analyzed gas-chromatographically (tris-cyanoethoxypropane column). Five components were

TABLE 3. PREPARATION OF SULFONATE ESTERS

Ester	Yield (%)	Physical State	Purity (%)[a]
2-(Δ¹-Cyclopentenyl)ethyl bromobenzenesulfonate (I)	63	oil	98
2-Cyclopentylethyl bromobenzenesulfonate (II)	62	oil	96
3-(Δ¹-Cyclopentenyl)propyl bromobenzenesulfonate (V)	79	solid, m.p. 40–41·5°	93[b]
3-Methylenecyclohexyl toluenesulfonate (XII)	75	oil	90

[a] Percent of theoretical amount of sulfonic acid liberated on acetolysis. On solution in acetic acid at room temperature, all of the sulfonates were neutral to bromphenol blue. The principal contaminant in each case is probably unreacted alcohol.

[b] (Found: C, 49·21; H, 4·97. Calc. for $C_{14}H_{17}BrO_3S$: C, 48·69; H, 4·97%.)

present and each peak was collected and its NMR and IR spectra determined. Through comparison with the spectra (and retention times) of authentic samples (except in the case of bicyclo[3.2.0]-heptan-1-ol) the following compounds were shown to be present in the amounts[41] indicated: XIV (11·2%), XV (21·0%), XVI (56·9%), XVII (6·2%), and 2-(Δ¹-cyclopentenyl)ethanol (4·7%).

The tertiary alcohol, XV, was identified through consideration of its m.p. 42–43° (lit.[9] m.p. 47–48°), and spectral data; NMR(CCl_4), 5·25 τ (singlet, —OH) and complex multiplets centered near 7·5 τ, 7·95 τ, 8·3 τ, and 8·9 τ; $\nu_{max}^{CCl_4}$ (cm⁻¹) 3610 (m) (O—H stretch), 2950 (s), and 1440 (m), 1320 (m), 1305 (m), 1052 (s), and 1022 (m) (probable C—O stretch and O—H deformation). The major peak in the mass spectrum (84) appeared due to loss of ethylene, a typical fragmentation route of substituted cyclobutanols.

In a separate experiment it was shown that a mixture of the acetates of these alcohols did not change its composition under the conditions of the acetolysis reaction.

Products of acetolysis of 3-methylenecyclohexyl toluenesulfonate (XII.) A solution of 1·10 g (4·14 mmoles) XII and 11 ml 0·45 M sodium acetate in acetic acid in 100 ml dry acetic acid was heated at 100° for 3 hr. The reaction mixture was analyzed as described above. Two olefins, in a ratio of 4:1 made up about 33% of the product. An UV absorption spectrum of the mixture of products indicated that the minor component was probably 3-methylenecyclohexene. The acetate fraction, isolated in 45% crude yield, yielded only XVI on reduction. Assuming XII to be 90% pure and assuming the major impurity to be XVI gives an adjusted yield of about 37% olefins and 63% X.

Products of solvolysis of spiro[2.4]heptan-4-yl p-nitrobenzoate (XIII). A solution of 60 mg (0·23 mmole) XIII, and 43 mg (0·40 mmole) 2,6-lutidine in 25 ml 60% aqueous acetone was heated in a glass ampule at 100° for 4 hr. Most of the acetone was then removed by careful distillation through a vigreux column, and the aqueous solution extracted with ether. The ether extracts were

[40] W. J. Bailey and J. C. Goosen, *J. Amer. Chem. Soc.* 78, 2804 (1956).

[41] Peak areas on the gas chromatograms were determined through use of a planimeter; it was assumed that the molar response factors of the individual alcohols were identical. Olefins were assigned a molar response factor of 1·3 relative to alcohols on the basis of related experiments and their peak areas divided by this factor to give the percentages quoted here.

washed with cold dil. HCl aq, with Na_2CO_3 aq, dried, and concentrated carefully to a volume of *ca.* 4 ml. By comparison of gas chromatographic retention times, the following alcohols were shown to be present: XIV (60·6%), XV (25·4%) and XVI (14·0%). Further concentration of the ether yielded an oil whose IR spectrum contained bands present in the spectrum of each of the three alcohols.

In a separate experiment it was shown that XIV is stable when heated at 100° for 24 hr in 60% aqueous acetone containing 0·01 M *p*-nitrobenzoic acid and 0·02 M lutidine. It was also shown that lutidine does not catalyze the hydrolysis of ethyl *p*-nitrobenzoate to a measurable extent under these same conditions.

Rearrangement of spiro[2.4]*heptan-4-ol* (XIV) *with* p-*nitrobenzoic acid.* A solution of 0·50 g (4·5 mmoles) XIV and 0·17 g (1·0 mmole) *p*-nitrobenzoic acid in 100 ml 60% aqueous acetone was heated in a glass bomb at 100° for 2·5 hr. Work up and analysis of the reaction mixture as described above, showed two alcohols were present: XV (63·5%) and XVI (36·5%). Samples of the two alcohols were isolated by preparative-scale gas chromatography and their identities further substantiated through their IR spectra. In a separate experiment it was shown that a mixture of XV and XVI did not change its composition on heating with *p*-nitrobenzoic acid in 60% aqueous acetone at 100° for 24 hr. Prolonged treatment under these conditions destroyed both alcohols, yielding unidentified olefinic material.

Products of solvolysis of bicyclo[3.1.0]*hexane-1-methyl* p-*nitrobenzoate* (XVIII). A solution of 1·40 g (5·37 mmoles) XVIII and 0·936 g (8·72 mmoles) 2,6-lutidine in 100 ml 60% aqueous acetone was heated at 100° for 60 hr. The products were isolated and analyzed as described above. Gas chromatographic analysis indicated 2·5% olefin (probably 3-methylenecyclohexene), XIV (1·5%), XV (4·3%), XVI (82·8%), and XVII (8·9%). Removal of the remaining ether gave 0·571 g (95%) of a mixture of crude alcohols.

Kinetic experiments. Anhydrous acetic acid was prepared by refluxing reagent grade acetic acid with the calculated amount of acetic anhydride and a trace of sodium acetate, followed by distillation. Reagent grade absolute EtOH was used without further treatment. Aqueous acetone, 60%, was prepared by mixing 3 volumes of dry acetone (prepared by distillation from $CaCl_2$) with 2 volumes of de-ionized water at 25°. Anhydrous lithium perchlorate was obtained from the G. F. Smith Chemical Co. and dried for 12 hr under vacuum at 78° prior to use.

A. *Acetolysis.* Acetolyses were carried out by means of the ampule technique. All kinetic solutions were 0·036 M in sodium acetate and about 0·030 M in sulfonate ester. The aliquots were acidified with a measured amount of standard perchloric acid in acetic acid and then back titrated with 0·020 N sodium acetate in acetic acid, using bromphenol blue indicator. In general, reactions were followed to within 80% of completion. The values of the first-order acetolysis constants quoted in Table 1 are the averages of 2 or more independent kinetic experiments. The instantaneous first-order rate constants of most of the brosylates (II, III, IV, and V) drifted downward with time, indicating contribution from bimolecular reaction with acetate. The greatest change over 80% reaction was never more than 7 to 8%, and the true first-order rate constants for these unreactive primary brosylates are probably around 70 to 90% of the quoted values.[3m]

B. *Ethanolysis.* The ethanolysis rates were carried out by means of the ampule technique, using solutions about 0·01 M in sulfonate ester and titrating the aliquots with 0·015 M sodium methoxide in MeOH, using bromthymol blue indicator. As in the acetolysis experiments, the quoted rate constants are averages of 2 or more independent kinetic experiments.

C. *Solvolyses in* 60% *aqueous acetone.* The rates of solvolysis of the *p*-nitrobenzoate esters were determined by means of the ampule technique, also, using solutions about 0·01 M in *p*-nitrobenzoate ester and titrating the aliquots with 0·019 M NaOH to the bromthymol blue end point. Duplicate kinetic experiments were run in the case of bicyclo[3.1.0]hexane-1-methyl *p*-nitrobenzoate, but cyclopropylcarbinyl *p*-nitrobenzoate was so unreactive that its rate constant was estimated from 2% reaction after 200 hr at 100°.