Ionic Reactions in the Spiran Series. II. Effect of Variation of the Size of the Ring Bearing the Leaving Group on the Solvolytic Rates of Neopentyl-Type Tosylates of the Spiran Series

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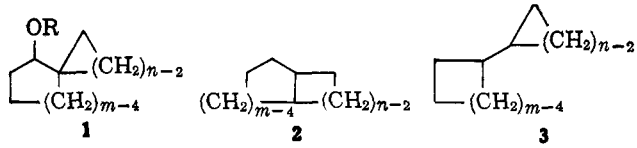
The first-order rate constants, the products, and the activation parameters for the acetolysis of 2,2-dimethylcycloalkyl tosylates (six- and seven-membered rings) and several spiran tosylates (**6**, m = 6 and 7; n = 5 and 6) have been determined. These rates and products have been found to be dependent on ring size. In all cases of an adjacent five-membered ring (**6**, m = 6 and 7; n = 5), the products result from ring expansion, with an enhancement of the acetolysis rate. In cases of an adjacent six-membered ring (**6**, m = 6 and 7; n = 6) the major products are formed from ring contraction. The results are interpreted in terms of release of ring strain by participation at the transition state. The ratios of the rates of the 2,2-dimethylcycloalkyl tosylates (size of ring: five, six, and seven) to the cycloalkyl tosylates of the same ring size at 25° are found to be 0.54, 2.9, and 2.2, respectively. The products of the zinc chloride dehydrations of the corresponding alcohols are similar to those of the acetolysis experiments (except in two cases). The implications of these results are discussed.

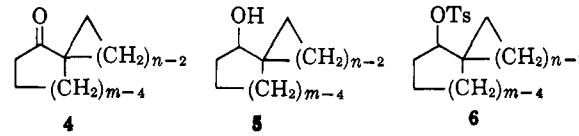
Spirans with α-substituents are of interest because a neopentyl-type system is also part of an alicyclic ring, and any rearrangement process which occurs must result in a change of ring size. The rearrangement of the carbon skeleton of **1** can lead to products of carbon skeleton of type **2** or **3**. These arise by way of a ring expansion and a ring contraction, respectively. Products of unrearranged carbon skeleton are also possible.



A study of reactions proceeding under ionic conditions has been undertaken to assess the effect of adjacent ring size and conformation on product composition and solvolysis rate. The initial paper of this sequence described a study of the acetolysis rates of system **1** (m = 5; n = 4, 5, and 6).[1] In these systems it was expected and experimentally shown that products of ring contraction (type **3**) did not result. The products and the kinetic results were rationalized in terms of the effect of ring strain on anchimeric assistance to yield ring-expanded products (type **2**). This study has now been extended to spiran tosylates of type **1** where m is varied along with n.

Synthesis.—The preparation of the spiranones followed routes previously described in the literature. Spiro[4,5]decan-6-one (**4**, m = **6**; n = 5) was prepared by the pinacol rearrangement of 1,1′-dihydroxy-1,1′-dicyclopentyl.[2] Spiro[4,6]undecan-6-one[3] (**4**, m = 7; n = 5) and spiro[5,6]dodecan-7-one[4] (**4**, m = 7; n = 6) were prepared by the reaction of 1,4-dibromobutane and 1,5-dibromopentane, respectively, with cycloheptanone in the presence of potassium t-butoxide. Spiro[5,5]undecan-1-one[3] (**4**, m = 6; n = 6) was prepared by the reaction of 1,5-dibromopentane with cyclohexanone in the presence of potassium t-butoxide. The 2,2-dimethylcyclohexanone was prepared by the alkylation procedure reported by King.[5] The 2,2-dimethylcycloheptanone was prepared by the procedure described by Meerwein from the acidic rearrangement of 1-(1′-hydroxycyclohexyl) dimethylcarbinol.[6]

The corresponding alcohols **5** were all prepared by the reduction of the spiranones with lithium aluminum hydride. The reduction of the 2,2-dimethylcycloalkanones was accomplished in the same manner. The tosylates **6** were prepared by the normal tosylation procedure.[7]



Solvolysis Results.—The specific first-order rate constants for the acetolysis of the spiran tosylates **6** and for 2,2-dimethylcyclohexyl tosylate and 2,2-dimethylcycloheptyl tosylate are summarized in Table I, along with the temperature interval studied and the calculated activation energy. In each run the reaction was usually followed to at least 70% completion and six or more values of the first-order rate constant were de-

TABLE I

SOLVOLYTIC RATE DATA FOR THE TOSYLATES

System	m	n	Temp., °C.[a]	k_1, sec.$^{-1}$[b]	E_a, kcal.
6	6	5	30.0	$4.15 \pm 0.11 \times 10^{-5}$	23.4
			40.0	$1.43 \pm 0.01 \times 10^{-4}$	
6	6	6	45.3	$1.10 \pm 0.01 \times 10^{-5}$	28.5
			60.1	$8.13 \pm 0.03 \times 10^{-5}$	
6	7	5	19.7	$1.69 \pm 0.40 \times 10^{-4}$	22.2
			30.0	$6.07 \pm 0.09 \times 10^{-4}$	
6	7	6	30.4	$6.16 \pm 0.01 \times 10^{-5}$	25.0
			45.3	$4.28 \pm 0.10 \times 10^{-4}$	
2,2-Dimethylcyclohexyl tosylate			60.1	$2.02 \pm 0.06 \times 10^{-5}$	27.7
			70.0	$6.87 \pm 0.20 \times 10^{-5}$	
2,2-Dimethylcycloheptyl tosylate			40.0	$5.06 \pm 0.10 \times 10^{-5}$	26.1
			55.0	$3.43 \pm 0.15 \times 10^{-4}$	

[a] Temperature deviation of ±0.06°. [b] The rate constants are average values and deviations from the average of two independent kinetic runs.

(1) A. P. Krapcho and M. Benson, *J. Am. Chem. Soc.*, **84**, 1036 (1962).
(2) P. A. Naro and J. A. Dixon, *ibid.*, **81**, 1681 (1959).
(3) M. Mousseron, R. Jacquier, and H. Christol, *Bull. soc. chim. France*, 346 (1957).
(4) P. A. Naro and J. A. Dixon, *J. Org. Chem.*, **26**, 1021 (1961).
(5) F. E. King, T. J. King, and J. P. Topliss, *J. Chem. Soc.*, 919 (1957).
(6) H. Meerwein and J. Schafer, *J. prakt. Chem.*, **104**, 289 (1922).
(7) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1941).

termined from appropriately spaced titrations. No trends in these values were detectable and the rate constants were reproducible. The rate constants were determined by the infinity titer technique and all infinity titers checked to within at least 4% of the calculated values. All procedures were similar to those previously described.[1]

The activation parameters were calculated according to the usual procedure[8] and are tabulated in Table II.

TABLE II

ACTIVATION PARAMETERS CALCULATED FROM THE SOLVOLYSIS DATA

System	m	n	ΔH^{*a}	ΔS^{*b}
6	6	5	22.8	−3.3
6	6	6	27.9	+6.2
6	7	5	21.6	−2.0
6	7	6	24.4	+2.6
2,2-Dimethylcyclohexyl tosylate			27.1	+1.2
2,2-Dimethylcycloheptyl tosylate			25.5	+3.0

[a] Probable error of ±1 kcal. [b] Probable error of ±2 e.u.

Acetolysis Products.—The product studies were performed in solutions which were about 0.3 *M* in tosylate and 0.35 *M* in sodium acetate. The products of the acetolysis (isolated in yields of greater than 70%) were predominantly olefins with small amounts of acetate (a maximum of 15% in one case). The acetates were not characterized because of the limited amounts which were formed. In most cases the direct analysis of the olefinic mixture was not attempted, but the mixture was catalytically hydrogenated, and the analysis of the saturated hydrocarbon mixture thus obtained was performed by vapor phase chromatography. In this manner the products from ring expansion (type **2**), ring contraction (type **3**), and unrearranged carbon skeleton could most readily be established. The results of the product analyses from the solvolytic runs are listed in Table III.

TABLE III

ACETOLYSIS PRODUCTS[a]

System	m	n	Catalytic hydrogenation products (%)
6	6	5	$\Delta^{9,10}$-Octalin (75), $\Delta^{1,9}$-octalin (25)[b]
6	6	6	Spiro[5,5]undecane (11), cyclohexylcyclopentane (64), *cis*-bicyclo[5,4,0]undecane (25)
6	7	5	*trans*-Bicyclo[5,4,0]undecane (23), *cis*-bicyclo[5.4.0]undecane (71), unidentified (6)
6	7	6	Cyclohexylcyclohexane (80), spiro[5,6]dodecane (15), unidentified (5)
2,2-Dimethylcyclohexyl tosylate			1,1-Dimethylcyclohexane (4), isopropylcyclopentane (68), *cis*-1,2-dimethylcyclohexane (27)
2,2-Dimethylcycloheptyl tosylate			Isopropylcyclohexane (75), 1,2-dimethylcycloheptane (*cis* or *trans*) (20), unidentified (5)

[a] See the Experimental section for the detailed characterization procedures. All per cents are based on uncalibrated v.p.c. area calculations. [b] The olefinic material was analyzed and the catalytic hydrogenation was not performed.

(8) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd Ed. John Wiley and Sons, Inc., New York, N. Y., 1961.

Zinc Chloride Dehydration Studies.—Concurrently with the product analyses from the acetolysis experiments, the zinc chloride dehydrations of several of the spiranols and the 2,2-dimethylcycloalkanols were also performed. The olefinic mixtures obtained in these reactions were catalytically hydrogenated and the saturated hydrocarbons were analyzed by vapor phase chromatography. The results of these dehydrations are tabulated in Table IV.

TABLE IV

PRODUCTS FROM THE ZINC CHLORIDE DEHYDRATIONS OF THE ALCOHOLS

System	m	n	Catalytic hydrogenation products (%)
5	6	6	Spiro[5,5]undecane (11), cyclohexylcyclopentane (62), *trans*-bicyclo[5,4,0]-undecane (27)
5	7	5	Cyclohexylcyclopentane (81), *cis*-bicyclo-[5,4,0]undecane (15), unidentified (4)
5	7	6	Cyclohexylcyclohexane (89), spiro[5,6]-dodecane (11)
2,2-Dimethylcyclo-hexanol			1,1-Dimethylcyclohexane (2), *trans*-1,2-dimethylcyclohexane (10), *cis*-1,2-dimethylcyclohexane (50), isopropylcyclopentane (30)
2,2-Dimethylcyclo-heptanol			Isopropylcyclohexane (93), 1,2-dimethylcycloheptane (*cis* or *trans*) (7)

Discussion.—To facilitate the comparison of the ring size effects from the rate data presented here with the data previously reported, the rates of various tosylates have been calculated at 25° and are tabulated in Table V.

TABLE V

RATE DATA CALCULATED AT 25° FROM OTHER TEMPERATURES

System	m	n	Calcd. $k \times 10^6$ sec.$^{-1}$
6	5	5	151[a]
6	5	6	2.36[a]
6	6	5	21.7
6	6	6	0.51
6	7	5	320
6	7	6	28.9
Cyclopentyl tosylate			1.62[b]
Cyclohexyl tosylate			0.05[b]
Cycloheptyl tosylate			2.82[b,c]
2,2-Dimethylcyclopentyl tosylate			0.88[a]
2,2-Dimethylcyclohexyl tosylate			0.15
2,2-Dimethylcycloheptyl tosylate			6.16

[a] Ref. 1. [b] H. C. Brown and G. Ham, *J. Am. Chem. Soc.*, **78**, 2736 (1956); S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *ibid.*, **74**, 1113 (1952). [c] R. Heck and V. Prelog, *Helv. Chim. Acta*, **38**, 1541 (1955).

Previous studies have shown that the ease with which solvolyses occur in cycloalkyl tosylates is markedly dependent on the size of the ring.[9] The relative acetolysis rates of cyclopentyl, cyclohexyl, and cycloheptyl tosylates at 25° are 31.6, 1.0, and 55.6, respectively (data from Table V). The I-strain concept, introduced by H. C. Brown,[10] has been applied to the interpretation

(9) (a) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, and references cited therein; (b) see J. Sicher in "Progress in Stereochemistry," Vol. 3, P. B. D. de la Mare and W. Klyne, Ed., Butterworth, Inc., Washington, D. C., 1962, p. 202.

(10) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 265, and references cited therein.

of rates in simple cyclic series of this type. Recently a quantitative approach to the calculation of solvolysis rates has geen proposed in which the rates of acetolysis of cyclopentyl, cyclohexyl, and cycloheptyl tosylates are effectively correlated with bond-angle strain and torsional strain parameters.[11]

This study has been particularly concerned with determining whether rates would be more dependent on the size of the ring bearing the leaving group or on the participation effects exhibited by the adjacent rings, relative to their size. In the spiran tosylates and the 2,2-dimethylcycloalkyl tosylates a rate enhancement could result from a skeletal rearrangement (ring expansion or ring contraction) *via* a bridged-ion transition state. This would produce a tertiary carbonium ion as the first intermediate, and the normal secondary carbonium ion would play no role in the reaction. In these systems an evaluation of the steric requirements for bridged-ion transition states could be made from the participation effects observed. However, in a comparison of this rate data to that of the unsubstituted cycloalkyl tosylates, some small increase in rate might be expected in the 2,2-dimethylcycloalkyl and spiran tosylates from the inductive effects of the methyl groups and the adjacent ring. Streitwieser has previously correlated acetolysis reactions which involve the formation of secondary carbonium ions with Taft's σ^*-values.[12] Wilcox has studied driving forces in the solvolysis of dimethylcyclobutylcarbinyl *p*-nitrobenzoates using a $\rho^*\sigma^*$ treatment, and he has concluded that relief of ring strain, not polar stabilization, is the dominant factor in the driving force for the solvolysis.[13] The σ^*-values for the cyclopentyl and the cyclohexyl systems are reported to be -0.20 and -0.15, respectively.[14] In the absence of complicating effects of a conformational nature, a small rate enhancement would be expected from the inductive contribution when the adjacent ring is changed from a six-membered ring to a five-membered ring (m held constant).

From the relative rate data tabulated in Table V, a comparison of pairs of spirans where m is held constant and n is varied from 5 to 6 (five- and six-membered adjacent ring) illustrates that a spiran with an adjacent five-membered ring undergoes acetolysis considerably faster than the corresponding system with an adjacent six-membered ring.

The predominant products in all cases in which the adjacent ring is five-membered ($n = 5$) are formed by expansion of this to a six-membered ring (Table III). The products formed in the cases with an adjacent six-membered ring ($n = 6$) depend on the size of the ring bearing the leaving group. Thus in spiro[4,5]decan-1-yl tosylate (**6**, $m = 5$; $n = 6$) the major product is the ring-expanded product.[1] In spiro[5,5]undecan-1-yl tosylate (**6**, $m = 6$; $n = 6$) the major product results from a ring contraction as can be seen from the data in Table III. In this case some ring-expanded product and unrearranged solvolysis products were also formed. In the case of spiro[5,6]dodecan-7-yl tosylate (**6**, $m = 7$; $n = 6$) about 80% of the ring-contracted product was obtained (contraction of the seven-membered ring to a six-membered ring).

Within the spiran systems studied an adjacent cyclopentane ring gives rise to ring-expanded products with a pronounced rate acceleration in comparison to the rates for the unsubstituted cycloalkyl tosylates or the corresponding 2,2-dimethylcycloalkyl tosylates. The rate ratios for the tosylates with an adjacent five-membered ring in which m increases from 5 to 6 to 7 compared to cyclopentyl, cyclohexyl, and cycloheptyl tosylate are 93, 423, and 113. When comparison is made to the 2,2-dimethylcycloalkyl tosylates, the results are 172, 144, and 52. The products arising from the 2,2-dimethylcyclopentyl tosylate were not investigated, but, in a study performed in 80% aqueous acetone, Wilcox reports mainly products from methyl migration.[13] The 2,2-dimethylcyclohexyl tosylate yields 68% ring contraction and 27% methyl migration. The 2,2-dimethylcycloheptyl tosylate yields 75% ring contraction and 20% methyl migration.

The rate ratios for the tosylates with an adjacent six-membered ring ($n = 6$) in which m increases from 5 to 6 to 7 compared to cyclopentyl, cyclohexyl, and cycloheptyl tosylates are 1.4, 10.0, and 10.1. When comparison is made to the corresponding 2,2-dimethylcycloalkyl tosylates, rate ratios of 3.5, 2.7, and 4.7 are obtained. It can be seen from the latter comparison that there is only a small rate increase for an adjacent six-membered ring when compared to the 2,2-dimethylcycloalkyl system of the same ring size.

Also of interest is the trend shown by the ratios of the rates of the 2,2-dimethylcycloalkyl tosylates to those of the cycloalkyl tosylates of the same ring size which are 0.54, 2.9, and 2.2 for the five-, six-, and seven-membered rings, respectively. When the 2,2-dimethylcyclopentyl tosylate is compared to the unsubstituted system a rate decrease is noted. On the basis of I-strain, a rate enhancement would be expected in this case because of the release of more severe nonbonded repulsions by the adjacent methyl groups and the carbon to which the leaving group is attached. In addition, a rate enhancement due to inductive stabilization should also be found. The rate enhancement in the comparison of 2,2-dimethylcyclohexyl tosylate to cyclohexyl tosylate and 2,2-dimethylcycloheptyl tosylate to cycloheptyl tosylate is consistent with an inductive contribution. It is to be noted that the major products from these dimethylcycloalkyl tosylates are ring-contracted products. The exact nature of the rate-decelerating factor in the case of 2,2-dimethylcyclopentyl tosylate is being investigated further at this time.

Another trend in the data can be seen in a comparison of the rates of the spirans in which n is held constant and m is varied from 5 to 6 to 7. When $n = 5$ (adjacent five-membered ring) the relative rates are 7.0, 1.0, and 14.7, respectively. In a similar comparison when $n = 6$ (adjacent six-membered ring), the relative rates are 4.6, 1.0, and 58.5. These can be compared to the relative rates of cyclopentyl, cyclohexyl, and cycloheptyl tosylates and qualitatively illustrate the same order, the difference being one of magnitude.

In the spiran sequences studied, where ring-expanded products are formed (as in all cases where the adjacent ring is five-membered) the rate acceleration and prod-

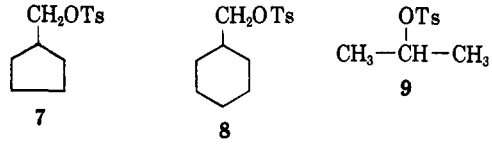
(11) (a) C. S. Foote, *J. Am. Chem. Soc.*, **86**, 1853 (1964); (b) P. R. Schleyer, *ibid.*, **86**, 1854, 1856 (1964).

(12) A. Streitwieser, Jr., *ibid.*, **78**, 4935 (1956).

(13) C. F. Wilcox, Jr., and M. E. Mesirov, *ibid.*, **84**, 2757 (1962).

(14) (a) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Prentice-Hall Co., Inc., New York, N. Y., 1956, p. 619; and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, p. 222.

ucts formed can most readily be interpreted as involving a transition state utilizing participation of the five-membered ring with partial release of the adjacent ring strain. The free energy of the transition state is effectively lowered by this participation and an accelerated rate is observed. While the conformational considerations of the leaving group are important, the energy difference between the conformers is probably low (skew interactions of about 1.6 kcal. for the axial tosylate if one assumes no interaction of the adjacent ring with the tosylate group in the equatorial conformation) and may not be effective in determining the course of the reaction. The strain in the five-membered ring is in the order of 6[15] to 10[16] kcal. and the magnitude of partial release of this strain at the transition state would probably outweigh any ground-state conformational preference of the tosylate group. Neighboring group participation of the five-membered ring has been observed before. The acetolysis of **7** has been reported to proceed about five times faster than the acetolysis of **8** or **9**.[17]



7 **8** **9**

In the comparison of the rates for the five-membered adjacent ring to those for the six-membered adjacent ring, in which m varies from 5 to 6 to 7, the ratios are 64, 42, and 11, respectively. The extreme variation of about 6 between the cases where $m = 5$ (five-membered ring) and $m = 7$ (seven-membered ring) can be interpreted as reflecting an increased solvolytic rate for the spiro[5,6]dodecan-7-yl tosylate (**6**, $m = 7$; $n = 6$) compared to that of spiro[4,5]decan-1-yl tosylate (**6**, $m = 5$; $n = 6$). Examination of models reveals that, when the tosylate group in the former compound is placed in the equatorial conformation, it can encounter skew interactions with the adjacent cyclohexane ring.[4] However, effective participation of the seven-membered ring with the equatorially oriented tosylate should be energetically quite favorable and a bridged-ion transition state leading to the major ring-contracted product should result. The free energy of the transition state should be lowered by the strain released in the transition from a seven- to a six-membered ring (maximum release of strain from heat of combustion measurements of about 5 kcal.).[15b]

The comparison of spiro[5,5]undecan-1-yl tosylate (**6**, $m = 6$; $n = 6$) to cyclohexyl tosylate shows a rate increase of 10, and a factor of 3.5 when it is compared to 2,2-dimethylcyclohexyl tosylate. In this tosylate a bridged-ion transition state would involve participation with the equatorial tosylate group leading to a more strained five-membered like, higher energy transition state. In this case it would be expected that the participation effect would be small and this is possibly reflected in the rate ratios of the five-adjacent to six-adjacent ring pattern (not much difference in the cases of $m = 5$ or 6). However, some participation may possibly occur because of the rather high per cent of ring-contracted product formed.

The products from the zinc chloride dehydration studies[18] can be compared to the products from the acetolysis experiments (Tables III and IV). In all the spiranols studied, coupled with the results of Dixon[2] for spiro[4,5]decan-6-ol, which he has reported to yield $\Delta^{9,10}$-octalin and $\Delta^{1,9}$-octalin in about the same proportions as found in the acetolysis products, the products from both reactions are quite similar. As has been previously suggested by Dixon,[4] in the zinc chloride dehydration of spiro[5,6]dodecan-7-ol participation is possibly occurring at the transition state, with the transition-state free energy lowered by participation of the seven-membered ring.

For 2,2-dimethylcyclohexanol, different results were obtained. In the acetolysis the major product was obtained from ring contraction (68%), while in the zinc chloride dehydration the product was mainly obtained from methyl migration (60%). With spiro[4,6]undecan-6-ol the zinc chloride dehydration yielded 81% ring-contraction products and the acetolysis primarily ring-contracted products. It appears that the coordination of the zinc chloride with the equatorial hydroxyl group is favored, resulting in a ring-contracted product (seven- to six-ring contraction), possibly through a bridged transition state.

It is also of interest to note that when expansion of a five-membered adjacent ring occurs the ΔS^* values are all negative with values of -3.9, -3.3, and -2.0 e.u. for the cases where $m = 5$, 6, and 7, respectively. This is to be compared to the six-membered adjacent ring sequence where $m = 5$, 6, and 7, where the ΔS^* values are -0.6, $+6.2$, and $+2.6$ e.u., respectively. The latter two compounds give predominantly ring-contracted products. The ΔS^* values for the 2,2-dimethylcyclohexyl and the 2,2-dimethylcycloheptyl tosylates are + 1.2 and +3.0 e.u., respectively. Both yield predominantly products of ring contraction.

Experimental

All melting points are corrected. The vapor phase chromatographic analyses were performed on the Aerograph A-90-P All percentage data from the v.p.c. analyses are based on areas calculated by the peak-height, half-width procedure.

Materials.—The spiranones and the 2,2-dimethylcycloalkanones were all known compounds and were synthesized by methods described in the literature (see Synthesis). The ketones were reduced by lithium aluminum hydride in ethyl ether to the corresponding alcohols in nearly quantitative yields. The physical properties and analytical data for unreported spiranols are listed in Table VI.

TABLE VI
PHYSICAL PROPERTIES AND ANALYTICAL DATA FOR THE NEW SPIRANOLS

Compd.	B.p. (mm.) or m.p., °C.	Calcd., % C	Calcd., % H	Found, % C	Found, % H
Spiro[5,5]undecan-1-ol (**5**, $m = 6$; $n = 6$)	36–37	78.51	11.98	78.52	11.82
Spiro[4,6]undecan-6-ol (**5**, $m = 7$; $n = 5$)	83 (0.9)	78.51	11.98	78 67	12.04

The tosylates were prepared according to the procedure of Tipson.[7] All were crystallized from pentane at low tempera-

(15) (a) S. Kaarsemaker and J. Coops, *Rec. trav. chim.*, **71**, 261 (1952). (b) C. T. Mortimer, "Reaction Heats and Bond Strength," Pergamon Press, Addison-Wesley Publishing Co., Inc., Reading, Mass., 1962, p. 26.

(16) K. S. Pitzer and W. E. Donath, *J. Am. Chem. Soc.*, **81**, 3213 (1959).

(17) (a) H. Felkin and G. LeNy, *Bull. soc. chim. France*, 1169 (1957); (b) G. LeNy, *Compt. rend.*, **250**, 368 (1960).

(18) See H. Christol, R. Jacquier, and M. Mousseron, *Bull. soc. chim. France*, 1027 (1957), for some zinc chloride dehydrations.

TABLE VII

MELTING POINTS AND ANALYTICAL DATA FOR THE TOSYLATES

Compd.	M.p., °C.	—Calcd., %— C	H	—Found, %— C	H
Spiro[4,5]decan-6-yl tosylate (6, $m = 6$; $n = 5$)[a]	46–47				
Spiro[5,5]undecan-1-yl tosylate (6, $m = 6$; $n = 6$)	49–50	67.06	8.13	66.97	8.10
2,2-Dimethylcyclohexyl tosylate	58–59	63.81	7.85	63.72	7.71
Spiro[4,6]undecan-6-yl tosylate (6, $m = 7$; $n = 5$)	65–66	67.06	8.13	67.32	8.13
Spiro[5,6]dodecan-7-yl tosylate (6, $m = 7$; $n = 6$)	47–48	67.83	8.39	67.85	8.46
2,2-Dimethylcycloheptyl tosylate	59–60	64.84	8.16	64.64	8.20

[a] Very unstable; not analyzed.

tures and were generally somewhat unstable. The samples were stored in a desiccator over phosphorous pentoxide in a freezer. The acetolysis equivalents determined in the kinetic runs were in good agreement with the calculated values (a maximum deviation of 4% in only one case). The pertinent data for the tosylates are listed in Table VII.

Kinetic Procedures.—The acetolysis procedures and conditions were the same as those described in a previous publication in this series.[1] All reactions were run in 10-ml. volumetric flasks and solutions were made to be about 0.09 *M* in tosylate and about 0.10 *M* in sodium acetate (except for spiro[5,6]dodecan-7-yl tosylate where a 0.07 *M* tosylate solution was utilized). In all the runs the infinity titers checked to within 4%.

Acetolysis Products. Typical Procedure. A. Acetolysis of Spiro[5,5]undecan-1-yl Tosylate (6, $m = 6$; $n = 6$).—The tosylate ester (2.3 g., 7.0 mmoles) and sodium acetate (0.63 g., 7.8 mmoles) were heated at 90° for 3 hr. in 22 ml. of solvent acetic acid. The mixture was cooled and poured into ice–water. The material was extracted into pentane and the pentane extract was washed with water, a dilute sodium bicarbonate solution, and again with water. The extract was dried over anhydrous potassium carbonate. The pentane was removed with a Rinco evaporator and 0.8 g. of a colorless oil remained (80% yield if all olefinic). The infrared analysis of this liquid showed the presence of an acetate band at 1740 cm.$^{-1}$ (estimated 10 to 15% from the band intensity). The vapor phase chromatographic analysis was performed on a 10-ft. column of 15% Bentone 34 and 5% SE-52 on 60–80-mesh Chromsorb W. Three peaks in the per cents, 22, 26, and 52 (in order of increasing retention time), were detected along with trace amounts of additional components.

In order to facilitate the product identification, the crude acetolysis product was catalytically hydrogenated using platinum in acetic acid. The products absorbed 82% of the calculated amount of hydrogen for one double bond. The products were isolated by pouring the mixture into ice–water and separating the top hydrocarbon layer. This layer was washed with a dilute sodium bicarbonate solution and then once with water. After drying over potassium carbonate, the liquid was analyzed by vapor phase chromatography. The analysis on the above Bentone column is listed in Table III.

Each component was identified by comparing its retention time to that of an authentic sample. The spiro[5,5]undecane was prepared by the Wolffe–Kishner reduction of the corresponding spiranone. The cyclohexylcyclopentane was prepared by the catalytic hydrogenation of cyclohexylidenecyclopentadiene, which was prepared by the procedure described by Kohler.[19] The mixture of *cis*- and *trans*-bicyclo[5,4,0]undecane was kindly supplied by W. G. Dauben.[20]

B. Acetolysis of Spiro[4,5]decan-6-yl Tosylate (6, $m = 6$; $n = 5$).—This was performed as in A and yielded 80% of a colorless liquid. The infrared spectrum of this crude product was recorded in the liquid phase and the major component could readily be identified as $\Delta^{9,10}$-octalin by a comparison of the spectrum with that of the product from the zinc chloride dehydration of the corresponding spiranol. This dehydration has been reported to yield this olefin as the major product.[2] The spectrum also exhibited an absorption band at 1740 cm.$^{-1}$, indicative of about 5 to 10% of an acetate (per cent estimated from the band intensity).

The vapor phase chromatographic analysis using a Ucon polar column indicated two olefinic components to the extent of 25 and 75%. These two products corresponded in retention time and percentage composition to the products obtained by the reduction of tetralin according to the procedure described by Dauben,[21] which yielded $\Delta^{1,9}$-octalin and $\Delta^{9,10}$-octalin.

C. Acetolysis of 2,2-Dimethylcyclohexyl Tosylate.—The acetolysis was performed as in A and yielded 66% of a colorless liquid. The infrared analysis indicated about 5 to 10% of an acetate component. The sample was hydrogenated and absorbed 94% of the calculated amount of hydrogen for one double bond. The v.p.c. analysis of the hydrogenated product was performed on a 22-ft. Ucon polar column and the results are tabulated in Table III. These products were identified by a comparison of the retention times to those of authentic samples. The 1,1-dimethylcyclohexane was prepared by the Wolffe–Kishner reduction of 2,2-dimethylcyclohexanone. The isopropylcyclopentane[22] was prepared by the catalytic hydrogenation of dimethylfulvene which was prepared according to the procedure described by Thiele.[23] *cis*- and *trans*-1,2-dimethylcyclohexane were commercially available.

D. Acetolysis of Spiro[4,6]undecan-6-yl Tosylate (6, $m = 7$; $n = 5$).—The acetolysis products were isolated in a 90% yield following the procedure in A. The infrared spectrum of this crude product indicated the presence of some acetate from the band at 1745 cm.$^{-1}$ (estimated about 5 to 10%).

The crude sample absorbed 81% of the calculated amount of hydrogen for one double bond. The vapor phase analysis on the Bentone column is listed in Table III.

E. Acetolysis of Spiro[5,6]dodecan-7-yl Tosylate (6, $m = 7$; $n = 6$).—The acetolysis products were isolated in a 70% yield following the procedure in A. The infrared spectrum of the crude product showed a weak acetate band at 1745 cm.$^{-1}$ (less than 5% from the band intensity) and was identical in most respects with the spectrum of cyclohexylcyclohexene prepared by the dehydration of cyclohexylcyclohexanol.[24] The vapor phase chromatogram of the cyclohexylcyclohexene obtained in this manner indicated about 10% of another isomeric product (Ucon polar column).

The acetolysis product was hydrogenated and absorbed 96% of the calculated amount of hydrogen for one double bond. The infrared spectrum of this product was almost identical with that of a commercial sample of cyclohexylcyclohexane. The vapor phase chromatographic analysis is listed in Table III.

F. Acetolysis of 2,2-Dimethylcycloheptyl Tosylate.—Following procedure A a 90% yield of products was obtained. The crude product contained about 15 to 20% acetate and absorbed 85% of the calculated amount of hydrogen for one double bond. The vapor phase chromatographic analysis was performed on the Ucon polar column and the results are tabulated in Table III.

Zinc Chloride Dehydrations. Typical Procedure. A. Spiro[5,5]undecan-1-ol (5, $m = 6$; $n = 6$).—The zinc chloride dehydration was performed by heating equal weights of the spiranol and anhydrous zinc chloride for 2 hr. at 130–140°. The crude material was removed from the salts by vacuum distillation. The analysis of the olefinic material showed the presence of overlapping peaks on the Bentone column roughly calculated to be 11, 64, and 25%. This mixture was catalytically hydrogenated and absorbed 99% of the calculated amount of hydrogen. The vapor phase chromatographic analysis on the Ucon polar column is tabulated in Table IV.

B.—The zinc chloride dehydrations of the spiranols and the 2,2-methylcycloalkanols listed in Table IV were all performed as in the typical procedure. The products were quantitatively hydrogenated in all cases and the results of the vapor phase chromatographic analyses are tabulated in Table IV.

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