Ionic Reactions in the Spiran Series. III. Solvolysis of Medium-Sized-Ring Spiro Compounds

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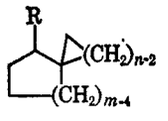
The first-order rate constants, the products, and the activation parameters for the acetolysis of 2,2-dimethylcyclooctyl β-naphthalenesulfonate and several medium-sized-ring spiran esters have been determined. The spiro compounds studied were **1** with $m = 8$ and $n = 5$, 6, and 7; **1** with $m = 6$ and $n = 7$; and **1** with $m = 9$ and $n = 8$. The 2,2-dimethylcyclooctyl β-naphthalenesulfonate yielded products arising exclusively from ring contraction. For the spiran arylsulfonates with the leaving group on the eight-membered ring (**1**, $m = 8$ and $n = 5$, 6, and 7) the rates were 8.1, 8.4, and 11.7 $\times 10^{-4}$ sec^{-1}, respectively, at 25°. The major products in these cases were also ring-contracted materials. The spiran arylsulfonate with the leaving group on the nine-membered ring (**1**, $m = 9$ and $n = 8$) underwent almost total ring contraction. The rate was one-half that of cyclononyl tosylate. The implications of these results are discussed.

The α-substituted spiro systems **1** are well suited for assessment of ring strain *vs.* anchimeric assistance as a driving force in rearrangements of the Wagner–Meerwein type. Because of the presence of a neopentyl system, any rearrangement process which occurs must result in a change of ring size (**2** or **3**); products of unrearranged carbon skeleton are also possible.



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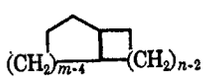

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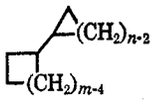

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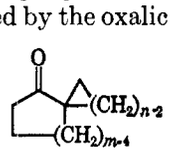
The present study concerns itself with the solvolytic rates and products of spiran arylsulfonates containing the leaving group on an eight-membered ring (**1**, $m = 8$ with $n = 5$, 6, or 7). The model system for this series of spirans was 2,2-dimethylcyclooctyl β-naphthalenesulfonate. Also studied were spiro[5.6]dodecan-1-yl tosylate (**1**, $m = 6$, $n = 7$) and spiro[7.8]hexadecan-9-yl β-naphthalenesulfonate (**1**, $m = 9$, $n = 8$).

Synthesis.—The 2,2-dimethylcyclooctanone was prepared by methylation of 2-methylcyclooctanone and was separated from the other methylated isomers by preparative vapor phase chromatography.[2] Spiro[4.7]dodecan-6-one (**4**, $m = 8$, $n = 5$) and spiro[5.7]tridecan-7-one (**4**, $m = 8$, $n = 6$) were prepared by a procedure similar to that employed by Mousseron for the preparation of spiro ketones.[3] The 2-carbethoxycyclooctanone was alkylated with 1,*n*-dibromoalkane ($n = 4$ and 5, respectively) followed by decarboxylation[4] and cyclization to yield the desired ketones. Spiro[6.7]tetradecan-8-one (**4**, $m = 8$, $n = 7$) was obtained by the oxalic acid rearrangement of 1,1′-dicycloheptyldiol.[5] Spiro[5.6]dodecan-1-one (**4**, $m = 6$, $n = 7$) was prepared by the pinacol rearrangement of 1,1′-cyclopentylcycloheptanediol.[6] The ketone was purified by acid hydrolysis of the oxime. Spiro[7.8]hexadecan-9-one (**4**, $m = 9$, $n = 8$) was prepared by the oxalic acid rearrangement of 1,1′-dicyclooctyldiol. The ketone was separated from the diene by elution chromatography and could be isolated in about a 15% yield.[7]



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The corresponding alcohols were obtained by lithium aluminum hydride reduction of the ketones. Tosylates were prepared[8] from spiro[6.7]tetradecan-8-ol and spiro[5.6]dodecan-1-ol. The tosylates of the other spiro alcohols in this study were too unstable to work with at room temperature. It was found that the β-naphthalenesulfonates could be handled for periods of time sufficiently long at room temperature before decomposition occurred.

Solvolysis Results.—The specific first-order rate constants and the activation energies for 2,2-dimethylcyclooctyl β-naphthalenesulfonate and the spiran arylsulfonates are listed in Table I. In each kinetic run, the reaction was followed to at least 70% completion and six or more values of the first-order rate constant were determined from appropriately spaced titrations. The reactions were carried out in volumetric flasks immersed in a constant-temperature bath and the rate constants were determined by the infinity titer technique. The acetolysis procedures and conditions chosen were similar to those utilized by Winstein, *et al.*[9] The activation parameters were calculated according to the usual procedure[10] and are tabulated in Table II.

Acetolysis Products.—The product studies were performed in acetic acid which was about 0.3 *M* in tosylate ester and 0.35 *M* in sodium acetate, or 0.1 *M* in β-naphthalenesulfonate and 0.12 *M* in sodium acetate (if more concentrated solutions of the β-naphthalenesulfonate were employed, the solubility of sodium β-naphthalenesulfonate was exceeded and the salt precipitated). The products of the acetolysis were predominantly rearranged olefins with about 10–20%

(1) Abstracted from a thesis presented to the Graduate College of the University of Vermont, Aug 1966, in partial fulfillment of the requirements for the Ph.D. degree. Presented at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, Abstract 41S.

(2) A. C. Cope, E. Ciganek, and J. Lazar, *J. Am. Chem. Soc.*, **84**, 2591 (1962).

(3) H. Christol, M. Mousseron, and F. Plenat, *Bull. Soc. Chim. France*, 543 (1959).

(4) R. Mayer, G. Wenshuh, and W. Topelmann, *Chem. Ber.*, **91**, 1616 (1958).

(5) M. Godchot and G. Cauquil, *Compt. Rend.*, **186**, 767 (1928).

(6) R. D. Sands, *Tetrahedron*, **21**, 887 (1965).

(7) D. S. Greidinger and D. Ginsberg, *J. Org. Chem.*, **22**, 1406 (1957).

(8) R. S. Tipson, *ibid.*, **9**, 235 (1944).

(9) S. Winstein, H M. Walborsky, and K. Schreiber, *J. Am. Chem. Soc.*, **72**, 5795 (1950).

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

TABLE I

SOLVOLYTIC RATE DATA FOR THE SPIRO ARYLSULFONATES

System	m	n	Temp,[a] °C	k_1,[b] sec^{-1}	E_a,[c] kcal
1-O-β-Ns	8	5	20.0	$4.23 \pm 0.11 \times 10^{-4}$	22.6
			30.0	$1.52 \pm 0.10 \times 10^{-3}$	
1-O-β-Ns	8	6	20.0	$4.29 \pm 0.27 \times 10^{-4}$	23.4
			30.0	$1.48 \pm 0.15 \times 10^{-3}$	
1-OTs	8	7	20.0	$4.61 \pm 0.08 \times 10^{-4}$	21.0
			30.0	$1.51 \pm 0.07 \times 10^{-3}$	
1-OTs	6	7	45.0	$4.82 \pm 0.06 \times 10^{-5}$	27.2
			55.0	$1.80 \pm 0.06 \times 10^{-4}$	
1-O-β-Ns	9	8	40.0	$1.44 \pm 0.05 \times 10^{-4}$	26.0
			50.0	$5.24 \pm 0.16 \times 10^{-4}$	
2,2-Dimethylcyclooctyl β-naphthalenesulfonate			20.0	$8.32 \pm 0.12 \times 10^{-5}$	23.0
			30.0	$3.07 \pm 0.08 \times 10^{-4}$	

[a] Temperature deviation of ±0.10°. [b] The rate constants are average values and deviations from the average of two or more independent kinetic runs. The calculations of the first-order rate constants were performed on an IBM 1620 computer. [c] Error of ±1 kcal.

TABLE II

ACTIVATION PARAMETERS CALCULATED FROM THE SOLVOLYSIS DATA

System	m	n	$\Delta H^{\ddagger}$,[a] kcal	$\Delta S^{\ddagger}$,[b] eu
1-O-β-Ns	8	5	22.0	1.1
1-O-β-Ns	8	6	22.8	4.0
1-OTs	8	7	20.3	−4.4
1-OTs	6	7	26.6	5.2
1-O-β-Ns	9	8	25.4	4.5
2,2-Dimethylcyclooctyl β-naphthalenesulfonate			22.4	−0.1

[a] Error of ± 1.3 kcal. [b] Error of ±3.6 eu.

of acetate, except for the 2,2-dimethylcyclooctyl system which yielded about 50% acetate. In all cases except the 2,2-dimethylcyclooctyl β-naphthalenesulfonate, the acetates were not characterized. The olefins were catalytically hydrogenated and the hydrogenated mixture was analyzed by vapor phase chromatography and infrared spectroscopy. Using retention times and spectral comparisons to authentic samples, the carbon skeleton could be determined. In this manner the products from ring expansion, ring contraction, and unrearranged olefin could most readily be established. Table III lists the composition of the hydrogenated acetolysis products.

TABLE III

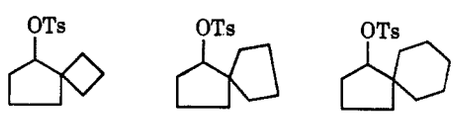
ACETOLYSIS PRODUCTS

System	m	n	Hydrogenated products	%
1-O-β-Ns	8	5	Cyclopentylcycloheptane	63
			Bicyclo[6.4.0]dodecane	27[a]
			Unidentified	10
1-O-β-Ns	8	6	Cyclohexylcycloheptane	86
			Unidentified	14
1-OTs	8	7	Bicycloheptyl	90
			Unidentified	10
1-OTs	6	7	Cyclopentylcycloheptane	50
			Bicyclo[6.4.0]dodecane	38[a]
			Spiro[5.6]dodecane	12
1-O-β-Ns	9	8	Bicyclooctyl	96
			Unidentified	4
2,2-Dimethylcyclooctyl β-naphthalenesulfonate			Isopropylcycloheptane	48
			Dimethylcycloheptylcarbinyl acetate	52

[a] Not rigorously identified; see Experimental Section.

Discussion

Rate enhancements in the solvolysis of spiran esters have been previously reported. In 1962, Krapcho and Benson[11] found a significant rate acceleration in the acetolysis of **5** as compared to the model 2,2-dimethylcyclopentyl tosylate, the rate ratio being 4440:1.0 at 25°, respectively. They also found relative accelerations at 25° of 172 and 2.7 for **6** and **7**, respectively, as compared to the model 2,2-dimethylcyclopentyl tosylate. The accelerations of **5** and **6** were attributed primarily to relief of ring strain by anchimeric assistance since the major product in these spiran systems was the ring-expanded carbon skeleton.



5 **6** **7**

Krapcho[12] has also reported rate accelerations in the acetolysis of **8** and **9** as compared to cyclohexyl tosylate, the relative rates at 25° being 434:10.2:1.0, respectively. The only product in the case of **8** was ring-expanded material, while **9** gave products of both ring expansion and ring contraction.

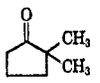
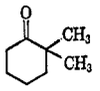
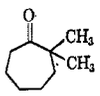
8 **9**

Since quantitative approaches have been reasonably successful in the correlation of acetolysis rates with the infrared stretching frequencies of the corresponding ketones,[13] it was of interest to make such a comparison with some of the spiro ketones whose acetolysis rates had been reported previously.[11,12] The carbonyl stretching frequencies should provide information on the effect of the angle at the site of the leaving group

(11) A. P. Krapcho and M. Benson, *J. Am. Chem. Soc.*, **84**, 1036 (1962).
(12) A. P. Krapcho, J. E. McCullough, and K. V. Nahabedian, *J. Org. Chem.*, **30**, 139 (1965).
(13) (a) C. S. Foote, *J. Am. Chem. Soc.*, **86**, 1853 (1964); (b) P. von R. Schleyer, *ibid.*, **86**, 1854, 1856 (1964).

TABLE IV

INFRARED DATA AND ACETOLYSIS RATES FOR SPIRO KETONES[a]

				
ν, cm^{-1}	1748[b]	1742	1737	1738
Relative rates, 25°	1	0.5	93	1.4
				
ν, cm^{-1}	1716[b]	1710[c]	1709	1708
Relative rates, 25°	1	3.0	424	10
				
ν, cm^{-1}	1705[b]	1706	1700	1702
Relative rates, 25°	1.0	2.2	112	10.1

[a] Except where noted, all infrared measurements were kindly performed by Professor C. S. Foote, Department of Chemistry, U.C.L.A. They were run in dilute carbon tetrachloride solutions on a Perkin-Elmer 421 grating instrument. Expanded scale, reduced slit width, and nitrogen sweep were used; frequencies are accurate to ±1 cm^{-1}. [b] Reference 13a. [c] M. Fetizon, J. Gore, P. Laszlo, and B. Waegell, *J. Org. Chem.*, **31**, 4047 (1966).

as reflected in the acetolysis rates. The data for the spiro ketones are tabulated in Table IV.

The application of the first term of the Schleyer equation[13b] for the effect of the carbonyl stretching frequency on the acetolysis rate (relative to cyclohexyl tosylate in acetic acid at 25°) shows a rate enhancement of 10 for a decrease in carbonyl frequency of 8 cm^{-1} (1715 cm^{-1} as the comparison frequency). Application of this term to the series of ketones containing the carbonyl group in the six-membered ring does not reveal any simple direct correlation of the rates with the carbonyl frequencies. The 2,2-dimethylcyclohexyl tosylate solvolyzed about three times faster than cyclohexyl tosylate (calculated value is 4 times faster). The spiranones in this series have essentially the same carbonyl stretching frequencies and the acetolysis rates for the corresponding tosylates differ by about 42 for the systems with the adjacent five- and six-membered rings, respectively.

It can be seen from the data of Table IV that all the spiranones with an adjacent five- or six-membered ring do not differ in carbonyl frequency (within the limits of the experimental accuracy). The acetolysis rates for the tosylates with the adjacent five-membered ring are faster than the comparable system with the adjacent six-membered ring. This data would tend to add some support to participation at the transition state by partial relief of ring strain in systems **6** and **8**. The other terms of the Schleyer equation are quite difficult to estimate owing to the difficulty in interpretation of the effects of adjacent substitution.[14] To facilitate comparisons, the rate constants (calculated or experimentally determined at 25°) for the spiro arylsulfonates and other model systems utilized in this study are tabulated in Table V.

In the solvolysis of spiro[5.6]dodecan-1-yl tosylate (**1**, $m = 6$, $n = 7$), both ring-contraction and ring-expansion routes are unfavorable: contraction involves

(14) A. P. Krapcho and D. E. Horn, *Tetrahedron Letters*, 6107 (1966).

TABLE V

RATE CONSTANTS FOR THE ARYLSULFONATES AT 25°

System	m	n	k_1,[a] sec^{-1} × 10^6
Cyclohexyl tosylate	...	...	0.05[b]
1-OTs	6	7	2.7
Cyclononyl tosylate	...	...	24.3[b]
1-O-β-Ns	9	8	13.2
1-O-β-Ns	8	5	607
1-O-β-Ns	8	6	632
1-OTs	8	7	842
Cyclooctyl tosylate	...	...	28.2[b]
2,2-Dimethylcyclooctyl β-naphthalenesulfonate	...	...	121

[a] The solvolytic rates of the β-naphthalenesulfonates are corrected by a factor of 0.75 for direct comparison to the tosylates (experimentally determined ratio). See also H. G. Richey and N. C. Buckley, *J. Am. Chem. Soc.*, **85**, 3057 (1963). [b] H. C. Brown and G. Ham, *ibid.*, **78**, 2735 (1956).

a six- to a five-membered ring change and expansion leads to an eight-membered ring from a seven-membered ring.[15] In this case it might be expected that a substantial amount of normal elimination product (spiro[5.6]dodecane upon hydrogenation) would occur. However, 88% of the hydrocarbon product characterized arises from carbon skeletal changes and the relative rate is 55 compared to cyclohexyl tosylate.

Molecular models give an indication of the conformation of the molecule on approaching a potential bridged transition state and the probable factors controlling the product distribution. A transition state for ring contraction requires that the leaving group be situated in an equatorial position on the six-membered ring. The tosylate group in this position suffers from skew interactions with the cycloheptyl ring. When the leaving group is positioned in an axial manner, there are no skew interactions with the cycloheptyl ring, rather axial interactions with the cyclohexane ring. In this case, the molecular geometry is favorable for a bridged transition state leading to ring expansion. The interaction of the tosylate group in the equatorial position with the adjacent ring causes this position to be favored only slightly over the axial position. Hence, it is perhaps reasonable to find products of both ring expansion and ring contraction. The rate enhancement could perhaps have its origin in a steric acceleration with some driving force exerted by the formation of a tertiary carbonium ion (in spite of the increased strain energy afforded in the bridged transition states leading to ring expansion or ring contraction).

Of course, it is possible to interpret the results by the formation of a secondary carbonium ion as the first intermediate (rate enhancement by a steric acceleration) and subsequent partitioning of this ion *via* the three transition states leading to unrearranged, ring-expanded, and ring-contracted carbon skeletons. From the standpoint of the products, the tertiary ion from the ring-contraction process might be expected to be of greater stability than the ion formed from the ring expansion. In the latter ion, greater ring distortions in the bicyclic system would tend to introduce non-

(15) (a) J. Coops, H. van Kamp, W. A. Lambgrets, B. J. Visser, and H. Dekker, *Rec. Trav. Chim.*, **79**, 1226 (1960). (b) The data in ref a are summarized in J. D. Roberts and M. C. Casserio, "Basic Principles of Organic Chemistry," W. A. Benjamin, Inc., New York, N. Y., 1964, p 112. The strain energies for cycloalkanes are compared to cyclohexane set at 0.0 kcal/mole. The value for cyclononane in the total strain column should be 12.6 kcal/mole.

bonded interactions. This might rationalize the greater percentage of ring-contracted product observed (50% cyclopentylcyclohexane).

Some support for this latter sequence (nonparticipating acetolysis) is perhaps shown by the fact that the carbonyl stretching frequency of ketone **4** ($m = 6$, $n = 7$) is 1705 cm^{-1}. On this basis, the tosylate might be expected to undergo acetolysis slightly faster than the tosylate from system **4** ($m = 6$, $n = 6$) (carbonyl frequency in Table IV, 1708 cm^{-1}). The trend here is at least in the right direction.

The ring-contraction process observed in the solvolysis of spiro[7.8]hexadecan-9-yl β-naphthalenesulfonate **1** ($m = 9$, $n = 8$) might be rationalized with an assisted solvolysis. The strain in the nine-membered ring (strain energy difference between cyclononane and cyclooctane of 3 kcal/mole[15]) is relieved by contraction to an eight-membered ring. If an expansion were to occur, there would result an ion with two fused nine-membered rings (increase in strain); the energy for this expansion is probably too high. Hence, the product is almost exclusively ring contracted (96%) and is suggestive of a bridged transition state in which the free energy of activation is lowered by partial ring strain release with formation of the tertiary carbonium ion. Subsequent proton loss leads to olefinic products of a ring-contracted carbon skeleton.

The fact that the observed rate is one-half that of cyclononyl tosylate might well reflect an inhibition of solvation effect. The infrared carbonyl stretching frequency for cyclononanone is 1704 cm^{-1} while that for **4** ($m = 9$, $n = 8$) is 1701 cm^{-1}. One would thus expect a slight acceleration for the acetolysis rate comparisons on the "angle" effect. In this large, bulky molecule, the approach of the solvent might be energetically difficult and the internal energy released on contraction to a bridged transition state may be compensating for the retardation effect of inhibition of solvation.

The evidence for assistance is certainly not very compelling in this case since the rate is actually slower than that of the model system used for comparison. The fact that the major product results from ring contraction is certainly not demanding that the reaction proceed through a bridged transition state. It is again possible that the normal secondary carbonium ion might be involved in the rate-controlling step.[16]

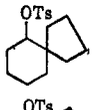
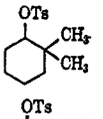
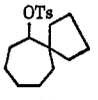
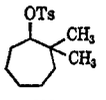
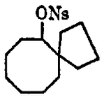
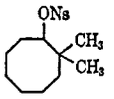
Cope[17] has solvolyzed cyclooctyl brosylate-1,2,2,8,8-d_5 in various media. The products were deuterated cyclooctyl acetate (53%) and cyclooctene (47%). Extensive transannular 1,5-hydride shifts had occurred as evidenced by mass spectrographic analysis. The absence of appreciable 1,3-hydride migration during solvolysis suggests that the 3 position is less favored as a site of migration initiation than the 5 position. Other solvolytic data suggest that there are preferred conformations of the cyclooctyl ring under solvolytic conditions.[18]

The 2,2-dimethylcyclooctyl β-naphthalenesulfonate solvolyzes at a rate somewhat more rapid than the unsubstituted cyclooctyl system (a relative rate increase of 4.3). The slight increase in rate is in line with an inductive stabilization of the transition state leading to the normal secondary carbonium ion. However, since the products arise predominantly from ring contraction, it seems likely, but not compelling, that the release of the ring strain in the eight-membered ring at the transition state would be of importance also. Models seem to reveal that the *trans* coplanar conformer required for ring contraction places the methyl groups out of steric interaction with the ring protons. However, the *trans* coplanar state required for methyl migration places the methyl groups in interaction with the protons of the carbon in the 4 position (relative to the *gem*-dimethyl group carbon). This fact, in addition to release of ring strain at the transition state in the event of ring contraction, probably limits the energetics of the solvolysis sufficiently that the sole pathway is ring contraction.

With respect to the spiro series with the leaving group on the eight-membered ring, the present series differs from those previously studied.[11,12] There is not a marked dependency of rate on the adjacent ring size (Table V). In this series, it is instructive to look at the products. In each case, the major products are of ring-contracted skeletons. This might be suggestive that the solvolytic route is being controlled by the strain of the eight-membered ring. Release of this strain at the transition state is great enough so that ring contraction predominates to give the less-strained cycloheptyl ring.[15] A trend pertinent to the present discussion is illustrated in Table VI, which shows

TABLE VI

COMPARISON OF SPIRO TOSYLATES CONTAINING FIVE-MEMBERED ADJACENT RINGS WITH THE RESPECTIVE 2,2-DIMETHYLCYCLOALKYL TOSYLATES

Suiro tosylate	2,2-Dimethylcycloalkyl tosylate	Relative rate, 25°
		144
		52
		5

that there is a decreasing kinetic dependence upon the adjacent five-membered ring as the size of the ring bearing the leaving group is increased.

Molecular models indicate that with an adjacent five-membered ring the nonbonded repulsions encountered by the geminal dimethyl grouping are somewhat lessened and the *trans* coplanar conformer required for ring expansion can be somewhat more easily attained. This five- to six-membered ring expansion would also provide a driving force by release of ring strain. The adjacent six- and seven-membered rings encounter repulsions similar to the geminal dimethyl group and these repulsions appear to prohibit the geometry necessary for expansion. Ring

(16) For a discussion of the neopentyl tosylate problem, see J. E. Nordlander, S. P. Jindal, P. von R. Schleyer, R. C. Fort, Jr., J. J. Harper, and R. D. Nicholas, *J. Am. Chem. Soc.*, **88**, 4475 (1966); R. L. Heidke and W. H. Saunders, Jr., *ibid.*, **88**, 5816 (1966).

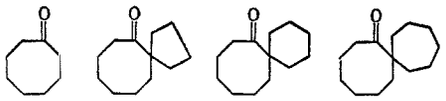
(17) A. C. Cope and D. M. Gale, *ibid.*, **85**, 3747 (1963).

(18) A. C. Cope, M. M. Martin, and M. A. McKervey, *Quart. Rev.*, **20**, 119 (1966).

expansions in the latter two cases also represent increases in internal ring strain.

The carbonyl stretching frequencies and acetolysis rates for the eight-membered ring spiranones are tabulated in Table VII. The most interesting facet in

TABLE VII
INFRARED AND ACETOLYSIS RATES FOR THE EIGHT-MEMBERED SPIRANONES



ν,[a] cm^{-1}	1704	1698	1698	1698
Relative rates,[b] 25°	1.0	20.8	22.4	29.8
Registry No.	502-49-8	3002-04-8	4728-92-1	13169-19-2

[a] Measured on a Perkin-Elmer Model 21 infrared spectrophotometer calibrated against the polystyrene standard. Estimated reliability ± 1 cm^{-1}. [b] Data from Table V.

Table VII is the constancy of the carbonyl stretching frequency for the eight-membered spiranones, a fact consistent with the near identity in the acetolysis rates.[13]

In the series of compounds studied with an eight-membered ring bearing the leaving group, factors such as ring strain release, product stabilities, and conformational preferences seem to favor the contraction of the eight-membered ring. The absence of high yields of normal elimination products would seem to indicate that these solvolyses might be assisted and that the secondary carbonium ion plays no major role in the reaction. However, the data presented in Table VII are at least qualitatively consistent with the expected trend for an unassisted solvolysis based only on the "angle" effect. Certainly the actual situation is more complex in these cases and this agreement may be fortuitous. Further studies of medium-ring systems are currently under investigation to probe more deeply into the factors controlling the rates.

Experimental Section

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

Ketone Synthesis.—The spiro ketones utilized in the preparation of the spiro esters have been described in the literature (see Synthesis) except for spiro[5.7]tridecan-7-one (**4**, $m = 8$, $n = 6$) and spiro[4.7]dodecan-6-one (**4**, $m = 8$, $n = 5$).

Spiro[5.7]tridecan-7-one (**4**, $m = 8$, $n = 6$).—Sodium hydride (5.3 g after removal of the oil, 0.22 mole) was dispersed in dry benzene and to the stirred slurry was added 2-carbethoxycyclooctanone (50.0 g, 0.25 mole) over period of 3 hr. The reaction was then stirred at room temperature until the evolution of hydrogen ceased. In one portion, 1,5-dibromopentane (115.0 g, 0.50 mole) was added and the reaction was then refluxed overnight. The mixture was cooled and filtered, and the salts were washed with benzene. After removal of the benzene, 2-carbethoxy-2-(ω-bromopentyl)cyclooctanone distilled at 115–119° (0.08 mm) and the yield was 31.2 g (70%).

Anal. Calcd for $C_{16}H_{27}BrO_3$: Br, 23.01. Found: Br, 22.99.

The 2,2-disubstituted cyclooctanone was decarboxylated over pulverized clay plate following the procedure of Mayer, *et al.*[4] The decarboxylated compound, 2-(ω-bromopentyl)cyclooctanone, distilled at 145–149° (1.0 mm). The yield was 21.0 g (85%).

Anal. Calcd for $C_{13}H_{23}BrO$: Br, 29.04. Found: Br, 28.67.

A refluxing slurry of sodium hydride (0.91 g after freeing from oil, 0.038 mole) in 50 ml of 1,2-dimethoxyethane was prepared and 2-(ω-bromopentyl)cyclooctanone (10.0 g, 0.036 mole) was added. After the reaction had refluxed for 6 hr, the solvent was distilled at atmospheric pressure and water was added to the cooled residue. The organic material was extracted with ether and the ether layer was dried over magnesium sulfate, filtered, and concentrated. The product, spiro[5.7]tridecan-7-one, distilled at 72–75° (0.1 mm) and the yield was 8.7 g (87%).

Anal. Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.14. Found: C, 80.20; H, 11.30.

Spiro[4.7]dodecan-6-one (**4**, $m = 8$, $n = 5$).—The same procedure as above was followed, except that the 2-carbethoxycyclooctanone was alkylated with 1,4-dibromobutane. The 2-carbethoxy-2-(γ-bromobutyl)cyclooctanone distilled at 135–140° (0.05 mm) and was obtained in a 77% yield.

Anal. Calcd for $C_{15}H_{25}BrO_3$: Br, 23.99. Found: Br, 23.98.

The decarboxylated substance, 2-(γ-bromobutyl)cyclooctanone, distilled at 115–119° (0.2 mm) and was obtained in an 82% yield.

Anal. Calcd for $C_{12}H_{21}BrO$: Br, 30.61. Found: Br, 30.38.

The cyclization reaction to form spiro[4.7]dodecan-6-one occurred in 72% yield. The compound did not form a 2,4-dinitrophenylhydazone derivative or an oxime under normal procedures.

Anal. Calcd for $C_{12}H_{20}O$: C, 79.74; H, 11.18. Found: C, 79.77; H, 11.34.

The ketones were reduced by lithium aluminum hydride in ethyl ether to the corresponding alcohols in nearly quantitative yields. The physical properties and the analytical data for unreported alcohols are listed in Table VIII.

The tosylates and β-naphthalenesulfonates were prepared according to the procedure of Tipson.[8] All were crystallized at low temperatures from pentane and they all were somewhat unstable at room temperature. Owing to the instability of a few of the arylsulfonates, it was difficult to obtain precise analytical values. The pertinent data for the tosylates and β-naphthalenesulfonates are listed in Table IX.

Kinetic Procedures.—The acetolysis procedures and conditions were the same as those described in a previous publication in this series.[12] 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, or about 0.035 M in β-naphthalenesulfonate (if there was a higher concentration of β-naphthalenesulfonate, sodium β-naphthalenesulfonate would precipitate).

Acetolysis Products. Typical Procedure. A. Acetolysis of Spiro[5.6]dodecan-1-yl Tosylate (**1**, $m = 6$, $n = 7$).—The tosylate (2.35 g, 7.0 mmoles) and sodium acetate (0.62 g, 7.8 mmoles) were heated at 90° for 3 hr in 25 ml of solvent acetic acid. The mixture was cooled and poured into ice water. The material was extracted into pentane and the 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 by evaporation and 1.0 g of a colorless oil remained (90% yield if it was all olefinic). The infrared analysis of the liquid showed the presence of an acetate band at 1735 cm^{-1} (estimated to be about 15–20% of the total product).

In order to facilitate the product identification, the crude acetolysis product was catalytically hydrogenated using platinum in acetic acid. The product absorbed 78% 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 was performed on a 10% Apiezon L column (225°) and the results are listed in Table III.

Each component was identified by comparing its retention time with that of an authentic sample. The spiro[5.6]dodecane was prepared by Wolff–Kishner reduction of the corresponding ketone. Cyclopentylcycloheptane was prepared by a procedure described by Kohler.[19] The third substance to elute from the column was assigned the ring-expanded carbon skeleton, bicyclo[6.4.0]dodecane. This structure was not proven unequivocably, but since two of the three possible hydrocarbon skeletons were identified, the bicyclo structure was assigned by elimination.

B. Acetolysis of Spiro[7.8]hexadecan-9-yl β-Naphthalenesulfonate (**1**, $m = 9$, $n = 8$).—This was performed as in A and yielded 70% of a colorless liquid. The infrared spectrum of the crude product indicated about 10–15% acetate. The sample was

(19) E. P. Kohler and J. Kable, *J. Am. Chem. Soc.*, **57**, 917 (1935).

TABLE VIII

PHYSICAL PROPERTIES AND ANALYTICAL DATA FOR THE NEW ALCOHOLS

Compound	Bp (mm) or mp, °C	Calcd, %		Found, %	
		C	H	C	H
2,2-Dimethylcyclooctanol	66–69 (1.5)	76.86	12.90	77.10	12.89
Spiro[4.7]dodecan-6-ol (1, $m = 8$, $n = 5$)	70–72 (1.0)	79.06	12.16	78.89	12.30
Spiro[5.7]tridecan-7-ol (1, $m = 8$, $n = 6$)	64–66	79.53	12.32	79.38	12.40
Spiro[5.6]dodecan-1-ol (1, $m = 6$, $n = 7$)	84–85 (0.9)	78.51	11.98	78.67	12.04
Spiro[7.8]hexadecan-9-ol (1, $m = 9$, $n = 8$)	60–62	80.60	12.68	79.95	12.34
Spiro[6.7]tetradecan-8-ol (1, $m = 8$, $m = 7$)	61–62	79.93	12.46	79.77	12.43

TABLE IX

MELTING POINTS AND ANALYTICAL DATA FOR THE ARYLSULFONATES

Compound	Mp, °C	Calcd, %		Found, %	
		C	H	C	H
Spiro[5.6]dodecan-1-yl tosylate (1, $m = 6$, $n = 7$)	54–55	67.83	8.39	68.03	8.53
Spiro[7.8]hexadecan-9-yl β-naphthalenesulfonate (1, $m = 9$, $n = 8$)	80–81	72.86	8.47	72.28	8.35
Spiro[4.7]dodecan-6-yl β-naphthalenesulfonate (1, $m = 8$, $n = 5$)	40 dec	70.94	7.58	70.03	7.67
Spiro[5.7]tridecan-7-yl β-naphthalenesulfonate (1, $m = 8$, $n = 6$)	64–66	71.48	7.82	71.25	7.79
Spiro[6.7]tetradecan-8-yl tosylate (1, $m = 8$, $n = 7$)	33–34	69.20	8.85	68.69	8.72
2,2-Dimethylcyclooctyl β-naphthalenesulfonate	60–61 dec	69.34	7.57	Unstable	

hydrogenated and absorbed 86% of the calculated amount of hydrogen for one double bond. The vapor phase chromatographic analysis (10% Apiezon column at 250°) indicated that the product was bicyclooctyl (retention time was the same as an authentic sample). The infrared spectrum of the hydrogenated product was superimposable upon that of authentic bicyclooctyl (except for the small acetate band at 1735 cm^{-1} in the former).

C. Acetolysis of 2,2-Dimethylcyclooctyl β-Naphthalenesulfonate.—The sulfonate ester was treated as in A to yield a colorless oil in an 80% yield. The infrared spectrum indicated considerable acetate. The crude material absorbed only 42% of the calculated amount of hydrogen for one double bond. The hydrogenated product was reduced with lithium aluminum hydride and the reduced material was chromatographed on neutral alumina to yield two fractions, an alcohol and a hydrocarbon. The infrared spectrum of the alcohol was superimposable upon that of dimethylcycloheptylcarbinol, which was prepared by treating methyl cycloheptylcarboxylate with methyl magnesium iodide. The retention time and infrared spectrum of the hydrocarbon portion of the product were identical with isopropylcycloheptane, prepared by dehydration of dimethylcycloheptylcarbinol followed by hydrogenation. From the weights of the two fractions isolated by column chromatography, the yields could be calculated.

D. Acetolysis of Spiro[4.7]dodecan-6-yl β-Naphthalenesulfonate (1, $m = 8$, $n = 5$).—The acetolysis products were isolated in a 91% yield following the procedure in A. The infrared spectrum of this crude product indicated the presence of some acetate from the band at 1735 cm^{-1} (estimated at 10–15%). The crude product absorbed 72% of the calculated amount of hydrogen for one double bond. The vapor phase analysis on an Apiezon L column (190°) showed four peaks at 4, 63, 27, and 6%, in order of increasing retention times. The major peak corresponded to cyclopentylcycloheptane. The material in 27% was identified as bicyclo[6.4.0]dodecane by retention time.

E. Acetolysis of Spiro[5.7]tridecan-7-yl β-Naphthalenesulfonate (1, $m = 8$, $n = 6$).—The acetolysis was performed as in A and yielded 65% of a colorless oil. The infrared spectrum indicated about 10–15% acetate. The sample was hydrogenated and absorbed 74% of the calculated amount of hydrogen. Vapor phase analysis (10% Apiezon L) showed the presence of three components at 8, 86, and 6%, in order of increasing retention time. The major peak corresponded to cyclohexylcycloheptane by retention time and enrichment technique. The infrared spectrum of the hydrogenation product was superimposable upon that of cyclohexylcycloheptane. The other two products were not identified.

F. Acetolysis of Spiro[6.7]tetradecan-8-yl Tosylate (1, $m = 8$, $n = 7$).—The tosylate was treated as in A to yield an oily product in a 71% yield. The infrared analysis indicated very little acetate (about 5–10%). Upon hydrogenation, the material absorbed 86% of the calculated amount of hydrogen for one double bond. Vapor phase analysis (Ucon Polar 175°) indicated the presence of two products in the ratio of 90:10, in order of increasing retention time. The major peak corresponded to bicycloheptyl by enrichment and retention time. The infrared spectrum of the hydrogenated acetolysis product was nearly identical with that of authentic bicycloheptyl. The minor product was not identified.

Registry No.—1 ($m = 6$, $n = 7$), 13133-78-3; 1-OTs ($m = 6$, $n = 7$), 13133-79-4; 1 ($m = 8$, $n = 5$), 13133-80-7; 1-O-β-Ns ($m = 8$, $n = 5$), 13133-81-8; 1 ($m = 8$, $n = 6$), 13133-82-9; 1-O-β-Ns ($m = 8$, $n = 6$), 13127-25-8; 1 ($m = 8$, $n = 7$), 13133-83-0; 1-OTs ($m = 8$, $n = 7$), 13133-84-1; 1 ($m = 9$, $n = 8$), 13133-85-2; 1-O-β-Ns ($m = 9$, $n = 8$), 13127-26-9; 2,2-dimethylcyclooctyl β-naphthalenesulfonate, 13133-88-5; 2-carbethoxy-2-(ω-bromopentyl)cyclooctanone, 13133-89-6; 2-(ω-bromopentyl)cyclooctanone, 13133-90-9; 2-carboethoxy-2-(γ-bromobutyl)cyclooctanone, 13133-91-0; 2-(γ-bromobutyl)cyclooctanone, 13133-92-1; 2,2-dimethylcyclooctanol, 13133-93-2.

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