added over a 10-min. period with stirring to lithium aluminum hydride (0.8 g., 20 mmoles) in dry ether (50 ml.). The reaction mixture was refluxed for 12 hr. and the inorganic salts then precipitated by the successive addition of water (2 ml.), sodium hydroxide (6 *N*, 6 ml.), and more water (40 ml.). Separation and thorough ether extraction (5 × 10 ml.) of the inorganic salts gave an ether extract which was combined with the reaction ether phase, washed with water, and freed of solvent by distillation. The oil remaining, **1-phenyl-cyclobutanol** (V), was then held at 80° and 2 mm. for 2 hr., whereupon it solidified on cooling. The alcohol was recrystallized from petroleum ether (30–60°) (1.55 g., 95%, m.p. 40–41°, the mixture m.p. with authentic material (see later) was undepressed).

Hydrolysis of 1-Phenylcyclopropylcarbinyl *p*-Toluenesulfonate (IIc).—The ester IIc (3.5 g., 15 mmoles) was stirred with aqueous sodium hydroxide (10%, 70 ml.) for 8 hr. at 25°. Evaporation of the water–oil mixture to reduce the volume and slow cooling gave 1-phenylcyclopropylcarbinol (I) in high yield [m.p. 32–32.5°, no depression when admixed with I, a depression to under 30° when admixed with 1-phenylcyclobutanol (V)].

Preparation of Reference Materials. 1-Phenylcyclobutanol (V) was prepared as reported[11] from cyclobutanone (Aldrich Chemical Co.) and phenyllithium (65%, m.p. 39–41°, lit.[11] m.p. 42°). Its infrared spectrum was in accord with its proposed structure.

1-Phenylcyclobutyl acetate (IV) resulted when acetyl chloride (1.57 g., 20 mmoles) was added dropwise to the alcohol V (2.5 g., 16.9 mmoles) stirred in cold pyridine (5 ml.). After refrigeration for 12 hr., the material was acidified with dilute hydrochloric acid and extracted with ether. The ester IV (again containing some olefin) was isolated as described above (2.15 g., b.p. 90–93° at 2 mm., $n^{26}D$ 1.5198, d^{20}_4 1.045). The ultraviolet spectrum (λ^{max}_{alc} 255 mμ, ε 2375) indicated 17% 1-phenylcyclobutene (VI) to be present, again presumably because of thermal cracking.

Anal. Calcd. for $C_{12}H_{14}O_2$(83%)–$C_{10}H_{10}$(17%): C, 78.52; H, 7.45. Found: C, 78.52; H, 7.61.

1-Phenylcyclobutene (VI) was prepared as reported[11] by the dehydration of 1-phenylcyclobutanol (V) (93%, b.p. 68–70° at 3.5 mm., $n^{26}D$ 1.5657, d^{20}_4 0.967, λ^{max}_{alc} 255 mμ (ε 13,850), lit.[11] b.p. 74–75° at 3.5 mm., $n^{25}D$ 1.5639) as well as by the pyrolysis of the ester IV (from either the acetolysis or the acetyl chloride reaction) in the gas chromatograph. Ester IV (three 0.3-ml. samples of acetyl chloride–produced ester) was injected into the instrument (Hercoflex column, 150°, helium flow 54 ml./min.). The higher temperature of the injector block (about 300°) pyrolyzed the ester and the olefin VI (retention time 20 min.) was trapped (0.53 g., b.p. 43–44° at 1.5 mm., λ^{max}_{alc} 252 mμ (ε 14,000). From two injections of acetolysis-produced ester IV (0.3 ml. each) the olefin was also obtained (0.3 g., λ^{max}_{alc} 251 mμ (ε 13,850), retention time 20 min. as before). The infrared spectrum[26] showed among its many peaks a strong absorption at 1695 cm.$^{-1}$ in the aromatic overtone-combination region as well as three sharp peaks in the olefin region (1621, 1603, 1580 cm.$^{-1}$). The spectra of all samples of the olefin prepared above matched peak for peak. 1-Phenylcyclobutene set to a soft jelly-like polymer upon storage in an ampoule (small void) in a fortnight. The polymer showed decreased absorption at 1695 and 1621 cm.$^{-1}$ and probably results from self-addition across the strained double bond. This unusual behavior for an α,β-substituted styrene[27] is probably explainable in terms of strain. The **nitrosochloride derivative (VII)** of 1-phenylcyclobutene was readily prepared as reported[11] (m.p. 97–98°, lit.[11] m.p. 98° dec.). All samples of the olefin gave identically-melting nitroso chlorides and their mixture m.p. were not depressed. It was found convenient to generate the nitrosyl chloride used in these reactions by adding sodium nitrite (1 part) to warm phosphorus pentachloride (3 parts) and condensing the gas evolved at −30°. The nitrosyl chloride was then added to the olefin in diethylene glycol dimethyl ether.

Stability of 1-Phenylcyclobutene in the Acetolysis Mixture. A solution (*ca.* 0.35 *M*) of olefin VI (0.228 g., 1.75 mmoles) was prepared in acetic acid (4.8 ml.) and allowed to stand 30 min. at room temperature with no decrease in olefin concentration (g.l.p.c.). *p*-Toluenesulfonic acid (monohydrate, 0.323 g., 1.70 mmoles) was then added, causing the solution to color immediately. Gas chromatographic analysis showed 15% of the olefin remaining after 15 min., and at most a trace after 45 min.

(26) We thank Prof. J. D. Roberts and Dr. E. I. Snyder of the California Institute of Technology for unpublished information on this olefin.

(27) C. Walling, "Free Radicals in Solution," John Wiley & Sons, New York, 1957, pp. 127–130.

Ring Size Effects in the Neophyl Rearrangement. IV.[1] The Acetolysis of 1-Phenylcycloalkylcarbinyl Arenesulfonates[2,3]

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The rate constants and activation parameters of the acetolysis of 1-phenylcycloalkylcarbinyl arenesulfonates indicated the expected anchimeric assistance by phenyl, as well as an accelerating "ring size effect" in the order seven > six > four > five-membered ring. Olefins, produced exclusively with phenyl migration and comprising endo- and exocyclic isomers, made up the reaction product and were formed quantitatively.

The question whether the ring size effect previously noted in the radical neophyl rearrangement[4] would persist in the carbonium ion process led to our investigation of this rearrangement in some neophyl-like arenesulfonates. To extend the study so that more information on ring size effects in this rearrangement might be gained, not only the five-

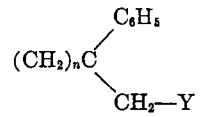
(1) For paper III, see J. W. Wilt and D. D. Roberts, *J. Org. Chem.*, **27**, 3430 (1962).

(2) This report is taken from the doctoral dissertation of D. D. R., February, 1962. Some of this work was presented at the 140th National Meeting of the American Chemical Society, Chicago, September 3–8, 1961, p. 10-Q of the abstracts.

(3) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(4) J. W. Wilt and Bro. H. Philip, F.S.C., *J. Org. Chem.*, **24**, 441 (1959); **25**, 891 (1960).

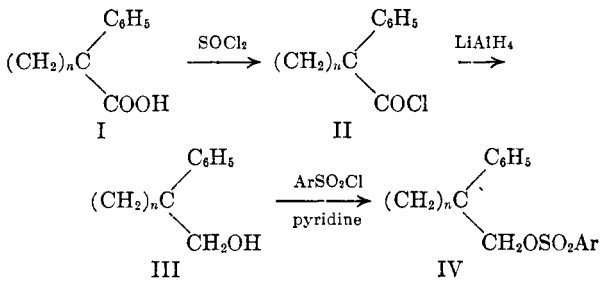
and six-membered ring substances were investigated, but also the three-, four-, and seven-membered ring analogs of the general structure shown.



$n + 1$ = 3, 4, 5, 6, 7 (ring size)
Y = arenesulfonate

As the means of carbonium ion generation, we chose the process of solvolysis, specifically, acetolysis, following the well-worn path described in the literature.[5] Of the rings studied, the cyclopropyl analog formed a class apart (as might be expected) and the much different results on it have been reported separately.[1] The remaining rings showed some differences which are, by and large, interpretable in terms of known concepts. The present paper is concerned with these substances.

The syntheses shown below of the starting compounds IV presented little novelty, although, somewhat surprisingly considering their simple structure, the alcohols III appear to be new. The acids I have been well characterized for years,[6] except the cycloheptyl compound.[7]

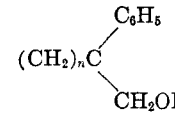


$n + 1$ = 4, 5, 6, 7 (no II $n + 1 = 7$)
Ar = C_6H_5—, p-$CH_3C_6H_4$—, p-BrC_6H_4—

The work on the cycloheptyl system was hampered by the lack of a large-scale synthesis for 1-phenylcycloheptanecarboxylic acid (X).[8] The synthesis of the higher homolog, (1-phenylcycloheptyl)-acetic acid, was achieved in other work[9] and will be reported in detail later. Its conversion to the desired acid X by a Barbier–Wieland degradation was effected, though poorly, and therefore this ring size was so inaccessible that our data on it are meager and less compelling.

The properties of the several acids I and the acid chlorides II are given elsewhere[4] while those of the carbinols III are collected in Table I.

TABLE I
1-PHENYLCYCLOALKYLCARBINOLS (III)



Ring size ($n + 1$)	M.p., °C.	Yield %	Calcd. C	Calcd. H	Found C	Found H
4	60–60.5	94	81.44	8.70	81.10	8.69
5	43–44	91	81.77	9.15	81.49	8.90
6	63–64	97	82.06	9.53	81.97	9.48
7	Oil	100	...	...	...	...

Use of the appropriate arenesulfonyl chloride on a pyridine solution of the carbinols III led in high yield (>90%) to the sulfonate esters IV. All these compounds were white, crystalline solids except those in the cycloheptyl instance. Here only crude esters, largely contaminated with unchanged alcohol, were isolated. Limited material made attempts at purification senseless, and the kinetic data later given is subject to the error of a decidedly impure starting compound in this ring size. The arenesulfonate data are summarized in Table II.

With these sulfonates in hand, a study of their solvolysis in glacial acetic acid was made. The kinetic and activation parameter data are shown in Table III.

The relative acetolysis rates of these substances were calculated from the data in Table III and some of these are grouped in Table IV, with the cyclopentyl compound as the standard.

While some discussion of these relative rate data will be given later, it is noteworthy that the same relative rate situation exists in these acetolyses with the five- and six-membered ring compounds as was found in the decarbonylation reaction involving the corresponding radicals[4]—a point that was the actual goal of this work.

To complete the kinetic picture with these sulfonates, comparative data were desired that would show the effect of ring size on the anchimeric ability of phenyl in this rearrangement ("ring size effect") and data that would show the rate effect of placing phenyl on these various rings ("phenyl effect"). The comparison of the rate data found here with that of the parent neophyl compound itself[10] would suffice for the ring size effect. The necessary data to compile the phenyl effect were not available for the cyclobutylcarbinyl and cycloheptylcarbinyl systems, however, and this necessitated the synthesis and study of these alicyclic arenesulfonates (XI and XII).

NOTE ADDED IN PROOF: Compound XII has been prepared by G. Leny [*Compt. rend.*, **251**, 1526 (1960)] but no data are given.

(5) A. Streitwieser, Jr., *Chem. Rev.*, **56**, 606 (1956).

(6) Among others, F. Case, *J. Am. Chem. Soc.*, **56**, 715 (1934); A. W. Weston, *ibid.*, **68**, 2345 (1946); and R. E. Lyle and G. G. Lyle, *ibid.*, **74**, 4061 (1952).

(7) N,N-Diethylaminoethyl 1-phenylcycloheptanecarboxylate has been reported in the patent literature by H. Martin and F. Häfliger (to J. R. Geigy A.-G.), U. S. Patent 2,404,588, July 23, 1946 (*Chem. Abstr.*, **40**, 6501[2] (1946). The acid itself is not described in the abstract.

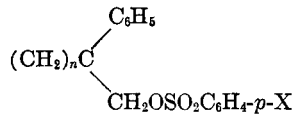
(8) The obvious route by cyclization techniques[6] as used for the lower homologs gave 2–4% yields of a nitrile which was never successfully hydrolyzed to the acid X by us.

(9) J. W. Wilt and J. Zawadzki, to be published.

(10) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *J. Am. Chem. Soc.*, **74**, 1113 (1952).

TABLE II

1-PHENYLCYCLOALKYLCARBINYL ARENESULFONATES (IV)



Ring size (n + 1)	X	Code	M.p., °C.	Calcd. C	Calcd. H	Found C	Found H
4	H	4-OBz	80.5–81.5	67.52	6.00	67.73	6.11
	Br	4-OBs	108–108.5	53.54	4.49	53.60	4.43
	CH_3	4-OTs	97–98	68.32	6.37	68.50	6.31
5	H	5-OBz	57–58	68.32	6.37	68.65	6.52
	Br	5-OBs	114.5–115	54.69	4.84	54.43	4.93
	CH_3	5-OTs	115–116	69.06	6.71	69.14	6.57
6	H	6-OBz	57–58	69.06	6.71	68.80	6.71
	Br	6-OBs	92.5–93.5	55.75	5.17	55.50	5.22
	CH_3	6-OTs	91–92	69.73	7.02	69.71	7.24
7	Br	7-OBs	Oil[a]	...	...	...	...
	CH_3	7-OTs	Oil[a]	...	...	...	...

[a] Crude material (see text).

TABLE III

ACETOLYSIS DATA FOR SULFONATES IV[a]

Compound	Neophyl OTs[b]	4 OBz	4 OBs	4 OTs	5 OBz	5 OBs	5 OTs	6 OBz	6 OBs	6 OTs	7 OBs[c]	7 OTs[c]
k_1^{25} (10^7 sec.$^{-1}$[d])	0.282[e]	1.75	3.73	1.09	1.02	2.10	0.62	5.40	10.0	3.22	28.6	...
k_1^{35} (10^7 sec.$^{-1}$)		7.90	16.0	4.92	4.70	9.53	2.89	22.5	41.2	13.6	118.	23.1
				5.62[f]			3.42[f]			16.1[f]		
k_1^{45} (10^7 sec.$^{-1}$)		29.8	62.2	19.6	17.6	37.2	10.9	84.0	148.	52.8	503.	...
ΔH^* (kcal./mole)[g]	25.7	26.0	25.9	26.6	26.2	26.6	26.3	25.3	24.9	25.7	26.4	...
ΔS^* (e.u.)[h]	−6.5	−2.2	−1.1	−1.1	−2.6	0.0	−3.3	−2.5	−2.7	−2.0	4.5	...

[a] In glacial acetic acid. Initial concentration of all sulfonates was 0.03 M, except 7-OBs and 7-OTs (see footnote c). [b] Data of ref. 10 (see text). [c] Initial concentrations were calculated from the amount of sulfonic acid liberated after ten half-lives and were *ca.* 3–15 × 10^{-3} M. [d] Values are precise to within 3% (errors calculated as standard deviations). [e] Extrapolated value (by us). [f] Acetolysis performed in the presence of sodium acetate (0.051 M for 4-OTs and 6-OTs; 0.052 M for 5-OTs). [g] All values precise to within 0.5 kcal. mole^{-1}. [h] Values are precise to only about 1 e.u.

TABLE IV

RELATIVE ACETOLYSIS RATES (*p*-BROMOBENZENESULFONATES[a])

Compound	k_{rel}^{acet} (25°)
4-OBs	1.78
5-OBs	1.00
6-OBs	4.76
7-OBs	13.6[b]

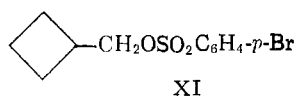
[a] Comparable data can be obtained for the other arenesulfonates. [b] Less accurate because of the lack of purity.

TABLE V

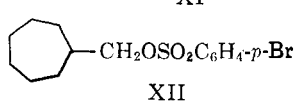
RING SIZE AND PHENYL EFFECTS

Ring size (x)	Ring size effect[a] (35°)	Phenyl effect[b] (°C.)
4	3.2	2 (60°)
5	1.9	34 (80°)
6	8.9	652 (80°)
7	15.	523 (65°)

[a] Rate of x-OTs relative to neophyl *p*-toluenesulfonate. [b] Rate of x-OBs relative to the unsubstituted cycloalkylcarbinyl *p*-bromobenzenesulfonate.



XI



XII

These new substances were prepared by straightforward routes and characterized. Their acetolysis was studied in the same way as with the other sulfonates, yielding their rate constants: XI (60°) 1.99 × 10^{-5} sec.$^{-1}$; XII (65°) 1.15 × 10^{-6} sec.$^{-1}$. With these results, plus literature data on neophyl *p*-toluenesulfonate,[10] cyclopentylcarbinyl,[11] and cyclohexylcarbinyl[11] *p*-bromobenzenesulfonates, the comparative rates given in Table V were determined.

The products of the acetolyses of the sulfonates IV were structurally rearranged olefins, formed in quantitative yield as established by gas chromatography. Isolated yields were lower (50–77%), though no attempt was made to maximize them. The composition of the olefinic product was determined also by gas chromatography and checked by ultraviolet spectroscopy. The product data are given in Table VI.

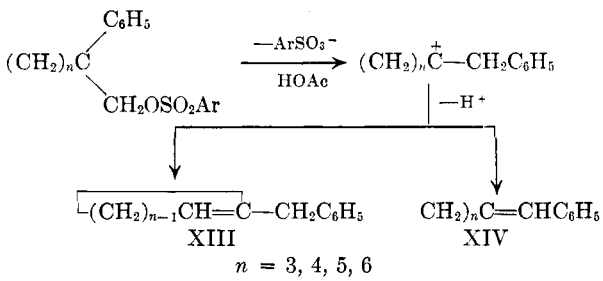
The formation of these products can be envisioned as shown.

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

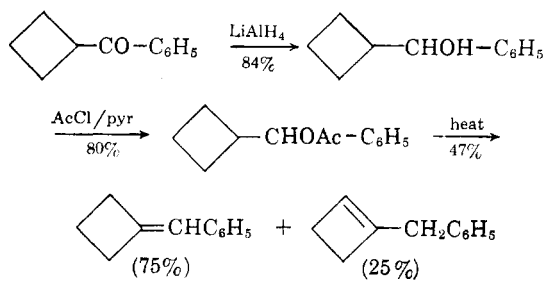
TABLE VI
ACETOLYSIS PRODUCTS (35°)

Compound	Product composition, %[a] 1-Benzylcycloalkene (XIII)	Benzalcycloalkane (XIV)
4-OTs	5 (8)	95 (92)
-OBz	5	95
-OBs[b]	35	65
5-OTs	80 (74)	20 (26)
-OBz	73	27
-OBs[b]	67	33
6-OTs	80 (81)	20 (19)
-OBz	76	24
-OBs[b]	75	25
7-OTs	71	29

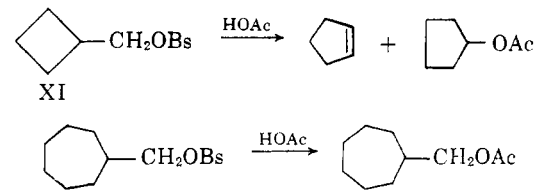
[a] The olefin yields were uniformly over 97% and were determined after 57–73% acetolysis. The percentage composition of product was determined by gas chromatography. The values in parentheses indicate the composition as calculated from ultraviolet spectra (see Experimental). [b] Data given for experiments performed at 45° after six half-lives.



In all but one instance mixtures of these olefins were available by the dehydration of the appropriate 1-benzylcycloalkanol.[12] Authentic mixtures so prepared were used to obtain gas chromatographic and spectral (both infrared and ultraviolet) comparison data. The previously unreported benzalcyclobutane and 1-benzylcyclobutene were prepared by the pyrolysis of cyclobutylphenylcarbinyl acetate as shown,



The acetolysis of cyclobutylcarbinyl *p*-bromobenzenesulfonate was anchimerically assisted[13] and led to cyclopentene and cyclopentyl acetate. The reaction of cycloheptylcarbinyl *p*-bromobenzenesulfonate was not so assisted and yielded cycloheptylcarbinyl acetate. The absence of the olefin-stabilizing phenyl group in these compounds probably accounts for the decreased elimination and increased ester formation.



As a final point, the normal salt effect (14–18% rate increase) was found in the acetolyses of the neophyl-like compounds when they were performed in the presence of excess sodium acetate (see Table III). No investigation of products, however, was carried out under these conditions.

Discussion

From Table IV, the rate order (in terms of ring size) of 7 > 6 > 4 > 5 is interesting. This order is quite different from that observed when the cationic site is *on* the ring,[14] and points up the different steric requirements of the neophyl rearrangement. We feel that the rate difference between 6-OBs and 5-OBs (4.76-fold) reflects the same restriction to rotation of the phenyl ring as was proposed earlier[4] to explain the difference in rearrangement ability of the corresponding radicals. This emphasizes the fact that the electronic state of the migration terminus is of minor importance in these rearrangements. As a matter of fact, there is quantitative agreement (perhaps fortuitous, but nevertheless disturbingly close) between the two studies.[15] It is perhaps also true that in the six-, as well as the seven series, rearrangement is facilitated by the relief of the axial strain present in the parent structures. The relative importance of these two steric effects is difficult to judge, although another study[16] has shown that restricted rotation is a sufficient explanation.[17] The close similarity in the rates of the 4- and 5-arenesulfonates possibly results also from this restricted rotation phenomenon. When the hindrance to rotation is gone, and the rearranged ion is free of Pitzer strain too,[18] the rate should be greatest. These two conditions are met

(12) K. von Auwers and W. Treppmann, *Ber.*, **48**, 1218 (1915); Y. I. Denisenko, *ibid.*, **69B**, 1668 (1936); and N. V. Elagina and N. D. Zelinskii, *Compt. rend. acad. sci. URSS*, **30**, 728 (1941), *Chem. Abstr.*, **37**, 616[8] (1943).

(13) This fact prompted our checking the properties of 1-phenylcyclopentene with the olefin product from the acetolysis of 4-arenesulfonates. This ring-expanded olefin was proved to be different from the acetolysis product both by infrared spectroscopy and by comparison of the nitrosochloride derivatives (see Experimental).

(14) J. D. Roberts and V. C. Chambers, *J. Am. Chem. Soc.*, **73**, 5034 (1951).

(15) If, for instance, the rearrangement ratios obtained in the earlier study[4] reflect the different rearrangement rates of the 1-phenylcyclohexylcarbinyl and 1-phenylcyclopentylcarbinyl radicals, the result is (89/11) ÷ (63/37) = 4.76. Since this calculation employs the equation developed by F. H. Seubold, Jr. [*ibid.*, **75**, 2532 (1953)], which has been validly criticized by C. Rüchardt [*Chem. Ber.*, **94**, 2599 (1961)], this agreement may be only sentimentally satisfying.

(16) J. W. Wilt and C. A. Schneider, *J. Org. Chem.*, **26**, 4196 (1961).

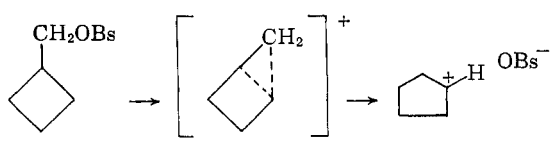
(17) A case where displacement was *not* assisted by axial strain has been reported by E. L. Eliel, *Tetrahedron Letters*, 474 (1961).

(18) See E. L. Eliel, "Substitution at Saturated Carbon Atoms" in "Steric Effects in Organic Chemistry," M. S. Newman, ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 122.

only in the seven-series, of those here studied. Even so, the exact degree of acceleration is a little hazy, since our results on 7-OBs and 7-OTs are beclouded by their lack of purity.

The increased rate due to the ring present in the esters IV relative to neophyl (the "ring size effect," Table V) is certainly not startling. The rates and activation parameters (Table III) for the sulfonates IV are uniformly similar among themselves and only a bit less so to neophyl itself. Without exception, however, the sulfonates IV did exhibit increased anchimeric assistance by phenyl, as evidenced by their augmented rate (2–15-fold) compared to neophyl. This assistance is shown also by the production of only phenyl-rearranged products (XIII, XIV). This ring size effect appears to be entropic in origin, possibly a consequence of the greater strain in the esters IV, relatively speaking. The slightly negative ΔS^* values (excepting 7-OBs and our data here do not warrant detailed mechanistic interpretation) indicate an activated complex still more rigid than the reactant, as would be a phenonium ion. But the difference in rigidity is less in the cases here studied than in neophyl and this entropic factor could explain the acceleration of their acetolyses.

The "phenyl effect" (Table V) simply illustrates the added impetus given these acetolyses in comparison to the unsubstituted cycloalkylcarbinyl compounds by the anchimerically active phenyl group. Both the cyclobutyl (this study) and cyclopentyl[11] rings anchimerically assist the departure of leaving groups from the carbinyl position in acetolysis and the driving force added by the phenyl group is less here than in the other two rings systems, neither of which themselves assist such a reaction. The very low phenyl effect in the four-series is reminiscent of the similarly small effect of the 1-phenyl group in the three-series.[1] The latter effect was ascribed to phenyl stabilization of the reactant, but such is not felt to be the case in the former, since the pi-character of the ring bonds in cyclobutane is most certainly less than that of these bonds in cyclopropane. More probably, the relief of ring strain attending acetolysis of XI lowers its activation energy to near that of 4-OBs, for which the better migrating phenyl group stabilizes the activated complex.



The products of these acetolyses (Table VI) were the olefins expected from phenyl rearrangement, normally with a preponderance of the more stable endocyclic isomer XIII.[19] Because the reaction medium was acidic, the product distribution obtained probably represents the equilibrium ratio of endo and exo olefin, generally about 3:1. Interesting exceptions are the cyclobutyl homologs. Here, when the product composition was determined at 35° between one and two solvolytic half-lives, the exocyclic isomer greatly predominated. Even after six half-lives at 45°, this isomer was favored 2:1. Such results are in accord with other work with methylenecyclobutane and 1-methylcyclobutene which indicated less preference for the endocyclic isomer at equilibrium for these olefins than for their higher homologs.[20] The shift in the other olefin ratios at 45° may reflect only the temperature dependence of the equilibrium, giving more of the less stable component.

Current work involves similar investigations of the analogous radicals (of which the results in two ring sizes have been reported earlier[4]) and the analogous carbenes. We plan to report on this work shortly.

Experimental

The experimental work in this study paralleled that reported for the cyclopropyl analog.[1] For this reason, some description of this work will be omitted and reference to the other study will be made. The analytical data are from the Galbraith Microanalytical Laboratories, Knoxville, Tennessee. All constants are uncorrected for stem exposure. The instrumentation used has been described.[1]

1-Phenylcycloalkylcarbinols (III).—The corresponding acids were prepared as reported,[6] converted to their acid chlorides[4] (the cycloheptyl homolog was converted to its methyl ester), and reduced in the usual manner with lithium aluminum hydride. A detailed preparation has been given.[1] The carbinols were white, crystalline solids with a characteristic floral odor that became objectionable in the higher analogs. The yield and property data for these carbinols are given in Table I. **1-Phenylcycloheptanecarboxylic acid** was obtained from (1-phenylcycloheptyl) acetic acid[9] (5.0 g., 21.5 mmoles) by a sequence commencing with its conversion to the methyl ester (4.79 g., 91%, b.p. 144–146° at 1.5 mm.) with diazomethane. The ester in dry ether (20 ml.) was added to phenylmagnesium bromide (81 mmoles) in ether (50 ml.) and the mixture stirred at reflux for 12 hr. The reaction mixture was cooled and poured into an ice–sulfuric acid mixture. After separation of the acidic layer and its extraction with ether (2 × 30 ml.), the reaction ether layer was combined with these extracts, dried, and the ether removed by distillation. The pale yellow oil remaining was dehydrated at reflux in benzene (100 ml.) containing *p*-toluenesulfonic acid monohydrate (1 g.), using a water separator. The reaction mixture was washed with water (50 ml.), dried over potassium carbonate, and freed of benzene by vacuum distillation. Into a stirred solution of the viscous residue dissolved in isoöctane (16 ml.) and acetic acid (37.5 ml.) was added chromium trioxide (7 g., 70 mmoles) in water (5.2 ml.) and acetic acid (56 ml.) at a rate such that the temperature remained below 50°. After the addition, the reaction was completed by stirring at 48° for 90 min., followed by concentration to half its volume. The mixture was next diluted with water (100 ml.) and extracted with ether (4 × 40 ml.). The combined ether extracts were washed with water (2 × 30 ml.) and then treated with aqueous sodium hydroxide (10%, 2 × 50 ml.). The acid was finally obtained by treatment of this alkaline solution with

(19) This preference for the endocyclic isomer over the conjugated exocyclic isomer has been commented on by E. L. Eliel, J. W. McCoy, and C. C. Price, *J. Org. Chem.*, **22**, 1533 (1957).

(20) E. Gil-Av and J. Hepling, *Tetrahedron Letters*, 27 (1961).

excess, cold, dilute hydrochloric acid, followed by refrigeration overnight. Recrystallization from methanol–water (1:7) afforded the acid as a white, crystalline solid (m.p. 85.5–86°, 0.986 g., 21%).

Anal. Calcd. for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.83; H, 8.38.

1-Phenylcycloalkylcarbinyl Arenesulfonates (IV).—These derivatives were prepared in yields over 90% from the carbinols III and the appropriate arenesulfonyl chloride in pyridine, as described.[1] The reactions were allowed to stand overnight in the refrigerator before isolation of the products. The sulfonates were white, nicely crystalline solids that were stable over a period of days at room temperature, allowing their accurate preparation as solutions in acetic acid. Table II lists their melting points and analyses. The 7-OBs and 7-OTs samples so prepared resisted solidification, remaining as viscous oils. Infrared analysis indicated unchanged alcohol (3350 cm.$^{-1}$) in both instances, as well as sulfonate (1355 and 1175 cm.$^{-1}$) and titration of the sulfonic acid liberated after several half-lives gave purities of 11 and 34.5% for 7-OBs and 7-OTs, respectively. Both compounds yielded olefin in acetolysis to these same percentages, substantiating the purities mentioned.

Cyclobutylcarbinyl *p*-Bromobenzenesulfonate (XI).—Cyclobutylcarbinol (73% from cyclobutanecarboxylic acid (Aldrich Chemical Co.) and lithium aluminum hydride, b.p. 141–143° at 742 mm., lit.,[21] b.p. 142–143° at 750 mm.) was converted to its *p*-bromobenzenesulfonate as described above. The sulfonate XI was an oil, freezing slightly below room temperature. It formed pretty needles from petroleum ether (30–60°) in the refrigerator (21%).

Anal. Calcd. for $C_{11}H_{13}BrO_3S$: C, 43.29; H, 4.29. Found: C, 43.07; H, 4.06.

Cycloheptylcarbinyl *p*-Bromobenzenesulfonate (XII).—Cycloheptylcarbinol (58% from cycloheptanecarboxylic acid[22] and lithium aluminum hydride on a 12-mmole scale, $n^{25}D$ 1.4723, lit.,[23] $n^{25}D$ 1.4730) was converted by the usual procedure to its *p*-bromobenzenesulfonate (white needles from low-boiling petroleum ether, 27.5%, m.p. 50–51°).

Anal. Calcd. for $C_{14}H_{19}BrO_3S$: C, 48.42; H, 5.51. Found: C, 48.50; H, 5.47.

Rate Determinations.—The solvent, indicator, and titrant employed and the methods used to evaluate the rate, the rate constant and the activation parameters have been described.[1] Initial concentrations of 0.03 *M* were obtained by weighing precisely the sulfonates into exactly 25 ml. of solvent. Exact 2-ml. portions were then placed into ten ampoules, sealed, and thermostated. However, note the initial concentrations of 7-OTs (35°), 0.015 *M;* 7-OBs (25°), 0.007 *M;* (35°), 0.003 *M*. The reactions were continued to 50–70% completion and seven kinetic points were obtained at each temperature for the determination of the rate constant. Excellent linearity for a first-order reaction was obtained in all the experiments, though the samples colored badly above 70% completion when sodium acetate was not present. The reactions with sodium acetate present were treated as follows: Exact 2-ml. aliquots were withdrawn at specific times and *p*-toluenesulfonic acid (0.0558 *M*, 2.000 ml.) in acetic acid added. The excess acid was then titrated with sodium acetate.

Product Determinations.—1. Solutions (*ca.* 0.35 *M*) of the sulfonates IV were prepared at room temperature and held at 45° for six half-lives. The olefin content was then determined by gas chromatography, employing calibration curves obtained with authentic olefin samples from plots of peak area against micromoles injected. A Perkin-Elmer 154C instrument with a copper tubing column (8 ft. × 1/4 in.) packed with Hercoflex 600[24] (20%) on Celite was used. The column temperature was 190° (7-system, 205°) and the helium pressure 20 p.s.i. (7-system, 25 p.s.i.). The retention times in minutes of the olefins formed were as follows, listing the *ring size*, benzyl isomer (XIII) retention time and benzal isomer (XIV) retention time: *4*, 12, 17; *5*, 13, 21; *6*, 21, 24. The olefin yields were above 98%.

Solutions of 4-OBs, 5-OTs, and 6-OTs were used also to isolate the olefins by adding them after the heating period to crushed ice. The melt was extracted with ether and the ether extracts washed and dried. After the ether was removed by distillation, the residual olefins were purified by vacuum distillation. Their properties are collected in Table VII along with those of the olefins prepared as standards. The acetolysis products showed unsaturation at 1630, 1652, and 1655 cm.$^{-1}$. 2. The products of the 7-OTs and 7-OBs acetolyses were determined by combining the mixtures from the kinetic experiments with these substances (total, 100 ml.) and neutralizing them with aqueous saturated sodium bicarbonate. Ether extraction and subsequent removal of solvent from the washed and dried extracts left the olefins which were identified by gas chromatographic comparison with the authentic mixture (see Table VII). Retention times of 16 and 20 min. for the 1-benzylcycloheptene and benzalcycloheptane, respectively, were observed and the olefins were formed in yields close to theory (11% for 7-OBs, 34.5% for 7-OTs—the purities of these arenesulfonates). 3. Sulfonates XI and XII (0.03 *M* each) were thermostated at 60° and 80°, respectively, for over six kinetic half-lives. Gas chromatographic analysis of the solutions (neutralized to the bromphenol blue endpoint with sodium acetate) showed the presence of cyclopentene (confirmed with standard) and either cyclobutylcarbinyl acetate or cyclopentyl acetate (same retention times) from XI and cycloheptylcarbinyl acetate (confirmed with standard) from XII. However, as the acetolysis of XI appeared anchimerically assisted—XI was over 17-fold faster than XII—cyclopentyl acetate is believed to be the more likely companion to the cyclopentene from XI.

Preparation of Reference Olefins and Esters.—In most cases the olefins were obtained as reported[12] by the iodine-catalyzed dehydration of the known 1-benzylcycloalkenol. The preparation of the olefins for comparison with those from the acetolyses of the 4-arenensulfonates is described later. The yields and properties of the olefins so prepared are gathered in Table VII, along with the acetolysis products. They compare very favorably. In addition, the infrared spectra of the olefins from both sources were the same, though the absorbances differed at times due to the different compositions in terms of exo and endocyclic isomers.

The **benzalcyclobutane–1-benzylcyclobutene** mixture was procured from cyclobutylphenylcarbinol (b.p. 112–114° at 3 mm., $n^{20}D$ 1.5390, d^{20}_4 1.104, lit.,[25] b.p. 257–259° at 750 mm.) by conversion to its acetate in the usual fashion employing acetyl chloride in pyridine (80%, b.p. 106–108° at 2 mm., $n^{20}D$ 1.5200, d^{20}_4 1.052).

Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.44; H, 7.89. Found: C, 76.31; H, 7.76.

Its infrared spectrum was in accord with the structure proposed. The acetate (five 0.5-ml. portions) was pyrolyzed in the gas chromatograph [column temperature 206°, injector block probably ~100° higher, 54 ml./min. helium flow, Hercoflex 600 column (see earlier)]. The olefin eluate was collected and distilled, see Table VII.

Anal. Calcd. for $C_{11}H_{12}$: C, 91.61; H, 8.39. Found: C, 91.66; H, 8.14.

The nitroso chloride derivative was prepared in low yield using the technique earlier reported[1] (m.p. 93–94° dec.). This is probably the derivative of the predominant benzal isomer, though this was not proved.

Anal. Calcd. for $C_{11}H_{12}ONCl$: C, 63.01; H, 5.77. Found: C, 62.97; H, 5.66.

(21) N. J. Demjanow, *Ber.*, **40**, 4959 (1907).

(22) E. Buchner and A. Jacobi, *ibid.*, **31**, 2008 (1898).

(23) W. J. Bailey and F. H. Hale, *J. Am. Chem. Soc.*, **81**, 654 (1959).

(24) An ester prepared from pentaerythritol and mixed C_{12} acids and available from the Hercules Powder Co., Wilmington, Delaware.

(25) W. H. Perkin and W. Sinclair, *J. Chem. Soc.*, **61**, 64 (1892).

TABLE VII
OLEFIN PRODUCTS (XIII, XIV)

Source of olefin	B.p.	Mm.	$n^{20}D$	d^{20}_4	Yield, %	XIII,[a] %
Cyclobutylphenylcarbinyl acetate	67–68	1.3	1.5655	0.975	47[b]	25
4-OBs	64–64.5	1	1.5660	.975	47	35
1-Benzylcyclopentanol	83–84	1.8	1.5452	.968	34	78
5-OTs	80–81	1.5	1.5450	.968	70	75
1-Benzylcyclohexanol	85–86	1	1.5411	.963	50	87
6-OTs	83–84	1	1.5410	.962	77	80
1-Benzylcycloheptanol	106–107	1.7	1.5415[c]	.971	31	68

[a] Percentage of benzyl isomer in olefin product as determined by g.l.p.c. and ultraviolet. [b] Polymerization lowered the yield. [c] At 26°.

The possibility that the acetolysis of the 4-arenesulfonates involved ring expansion was disproved through the preparation of 1-phenylcyclopentene.[26] The nitroso chloride of this olefin (m.p. 93–94° dec.), while showing the same melting point as that from the olefins described above, exhibited a melting point depression (83–87°) when the two were admixed. The olefins also possessed considerably different infrared spectra.

Nitroso chloride derivatives were also formed (again in low yields of usually under 10%) from the 5-olefin mixture (m.p. 109–110° dec., lit.,[27] m.p. 109.5–110.5° dec.) and the 6-olefin mixture (m.p. 110–111°). The latter, a previously unreported compound, was analyzed.

Anal. Calcd. for $C_{13}H_{16}ONCl$: C, 65.68; H, 6.78. Found: C, 65.59; H, 6.84.

All nitroso chlorides were prepared also from the acetolysis-produced olefins. They were identical to those above.

Cyclobutylcarbinyl acetate (b.p. 152–153°, $n^{26}D$ 1.4316, d^{20}_4 0.904, lit.,[28] b.p. 150° at 741 mm., $n^{25}D$ 1.4245, d^{20}_{20} 0.950) was prepared from the carbinol[21] with acetyl chloride in pyridine (63%). In like fashion were prepared **cyclopentyl acetate** (76%, b.p. 152–153°, $n^{26}D$ 1.4368, d^{20}_4 0.924, lit.,[29] $n^{23}D$ 1.4358) and **cycloheptylcarbinyl acetate** (18%, b.p. 62° at 1.5 mm., $n^{26}D$ 1.4490, lit.,[23] b.p. 77° at 3.5 mm., $n^{25}D$ 1.4517). Cyclopentene was used as received from the Aldrich Chemical Co., Milwaukee, Wisconsin.

Separation of Benzalcyclopentane and 1-Benzylcyclopentene.—The separation of this pair of olefins has caused problems in other work[27] and we wish to report their facile separation on the Hercoflex column at 190° and 25 p.s.i. helium pressure. The benzal isomer (t_r 6 min.) had infrared maxima (neat) at 964, 827, and 784 cm.$^{-1}$. The benzyl isomer (t_r 10 min.) possessed maxima at 1016, 909, and 861 cm.$^{-1}$, as reported.[30] These absorption maxima were absent in the spectrum of the possible ring expanded product, 1-phenyl-cyclohexene,[31] a point established because this olefin possessed a retention time identical to that of benzalcyclopentane.

Ultraviolet Spectral Determinations.—The data following gives the *ring size* of the olefin pair produced in the acetolysis of the *p*-toluenesulfonates as described earlier (A) or dehydration (D); λ^{max}_{alc} in mμ; and ϵ: *4* (A), 256, 15,800, (D), 256, 13,170; *5* (A), 256, 4950, (D), 256, 4450; *6* (A), 246, 3850, (D), 246, 2715; *7* (D), 256, 5000. The assumptions were made that the benzal isomers XIV possessed ϵ 17,150 as for benzalcyclopentane (at 248 mμ[30]) and the benzyl isomers XIII possessed ϵ 750 as for 1-benzylcyclopentene (at 248 mμ[30]). The percentage of the benzal isomer produced in these studies was then calculated from the expression 100% x (ϵ_{obs} −750) ÷ 16,400 to give for each *ring size*: *4* (A) 92, (D) 76; *5* (A) 26, (D) 23; *6* (A) 19, (D) 12; *7* (D) 26. In spite of the gross assumptions made (or maybe because of them) the agreement between the product compositions as determined by g.l.p.c. and ultraviolet methods was within 6%.

(26) W. H. Tallent, *J. Org. Chem.*, **21**, 862 (1956).
(27) H. J. Schaeffer and C. J. Collins, *J. Am. Chem. Soc.*, **78**, 124 (1956).
(28) S. Sorel and M. S. Newman, *ibid.*, **78**, 5416 (1956).
(29) S. L. Friess and R. Pinson, *J. Am. Chem. Soc.*, **74**, 1302 (1952).
(30) Lit. ref. 19.
(31) Sample supplied by Miss J. Kosturik.