$$R_fCF_2R'_f \longrightarrow R_fCF_2\cdot + R'_f\cdot \xrightarrow{X_2} R_fCF_2X + R'_fX$$
$$\downarrow$$
$$R_f\cdot + CF_2 \xrightarrow{X_2} R_fX + CF_2X_2$$

Since only CF_2X_2 and no other disubstituted fluorocarbon was obtained, it must be concluded that CF_2X_2 was formed most probably *via* CF_2 elimination from the fluorocarbon radical fragment followed by reaction with the carrier gas.

On the basis of these results it is believed that "unzippering" of a fluorocarbon chain may very probably occur *via* CF_2 elimination rather than *via* $CF_2{=}CF_2$ elimination. The work of Simons, *et al.*, however, must be repeated using the improved methods of analysis such as gas chromatography and nuclear magnetic resonance before one can conclude with considerable certainty that this is indeed the true mode of decomposition.

It is intended that the decomposition of very thin films of polytetrafluoroethylene in an evacuated system be re-examined in such a way that the primary reactive fragments pass directly to a mass spectrometer or are quenched on the walls of the apparatus before secondary reactions can occur to give the usual stable end products.

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

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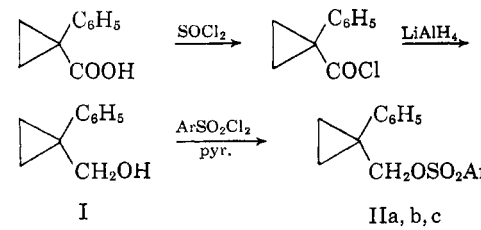
1-Phenylcyclopropylcarbinol (I) and its benzene-, *p*-bromobenzene-, and *p*-toluenesulfonate derivatives (II) were prepared. The acetolysis of these sulfonates showed first-order kinetics, with rate constants only slightly larger than that reported for cyclopropylcarbinyl benzenesulfonate itself. The sulfonates showed greatly different activation parameters, reflecting the difference in leaving groups. When the acetolysis of the *p*-toluenesulfonate ester was performed in the presence of sodium acetate, 1-phenylcyclobutyl acetate (IV) was the only product (100%). The slight relative rate acceleration found with these arenesulfonates is discussed in terms of possible ground state energy differences, while the formation of but one product, with little or no internal return, is interpreted in terms of a localized, more classical ion in these cases. Transformations within the 1-phenylcyclobutyl system are also reported.

Our interest in ring size effects in the neophyl rearrangements[4] led to the study of the acetolysis of the neophyl-like 1-phenylcycloalkylcarbinyl arenesulfonates. The cyclopropyl member of this series of compounds[5] showed such different behavior from the others that we thought it sensible to communicate the results on it separately.

That cyclopropylcarbinyl compounds are endowed with special reactivity in carbonium ion processes is beyond doubt. But just why and in what way this special reactivity occurs is still being discussed, notwithstanding the intensive and revealing work of Roberts and his group.[6] While we do not wish to enter the arena with new mechanistic proposals, we do wish to note the consequences of a phenyl substituent at the 1-ring position in this system and to suggest how these consequences might be accommodated by present theory.[7]

1-Phenylcyclopropylcarbinol (I, m.p. 32.5–33°) was obtained in high yield from the corresponding acid chloride by reduction with lithium aluminum hydride. The arenesulfonate derivatives (II) were



I IIa, b, c

prepared through reaction of the alcohol I with the appropriate arenesulfonyl chloride in pyridine. The benzenesulfonate (IIa. Ar = C_6H_5—, dec. 48°, 89%) and *p*-bromobenzenesulfonate (IIb. Ar = *p*-BrC_6H_4—, dec. 35°, 46%) were white crystal-

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

(2) Taken from the Ph.D. dissertation of D. D. R., Loyola University, February, 1962. Some of this material was presented at the 140th National Meeting of the American Chemical Society, Chicago, Illinois, September 3–8, 1961, p. 10Q of the abstracts.

(3) Grateful 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 ref. 1 deal with ring size effects in the radical neophyl rearrangement. A study of such effects in the carbene neophyl rearrangement has been completed and will be reported soon (J. Kosturik).

(5) For the 1-phenylcyclobutyl- through 1-phenylcycloheptylcarbinyl systems, see J. W. Wilt and D. D. Roberts, *ibid.*, **27**, 3434 (1962).

(6) For a recent study, one of many from that laboratory, see M. S. Silver, M. C. Caserio, H. E. Rice, and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 3671 (1961).

(7) R. A. Sneen, K. M. Lewandowski, I. A. I. Taha, and B. R. Smith, *ibid.*, **83**, 4843 (1961), have reported the kinetic consequences of a phenyl group (*cis* and *trans*) at the 2-ring position of this system, using β-naphthalenesulfonates and trifluoroacetates.

TABLE I

ACETOLYSIS RATES OF 1-PHENYLCYCLOPROPYLCARBINYL ARENESULFONATES[a]

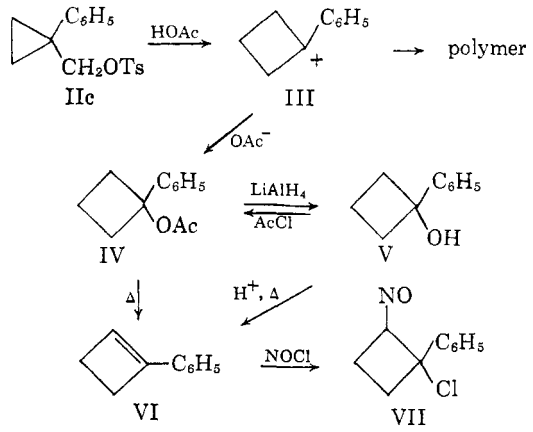
-Sulfonate	Conc. (10^2 M)	Temp., °C.	k_1[b] (10^4 sec.$^{-1}$)	ΔH^*[c] (kcal.)	ΔS^*[d] (e.u.)
Benzene- (IIa)[e]	2.82	13.0	1.10 ± 0.06	24.2 ± 0.4	7.7 ± 1.5
	2.92	18.0	1.82 ± 0.06		
	2.88	25.0	6.18 ± 0.24		
p-Bromobenzene- (IIb)[f]	2.96	12.0	1.52 ± 0.04	32.7 ± 0.5	38.6 ± 1.5
	2.84	15.0	3.05 ± 0.14		
	1.76	18.0	5.12 ± 0.24		
p-Toluene- (IIc)[g]	2.85	10.5	0.54 ± 0.04	17.9 ± 0.4	−14.9 ± 2.0
	2.73	18.0	1.53 ± 0.01		
	3.00[h]	18.0	1.63 ± 0.02		
	3.00	25.0	2.65 ± 0.10		

[a] Solvent was glacial acetic acid (99.9%). The determinations were continued to 52–95% completion and were cleanly first order. All the compounds, however, showed prerun conversions due to the inevitable delay between solution and immersion in the constant temperature device. The data for IIa and IIb particularly are subject to this error (see Experimental). [b] Calculated from the expression $k_1 = 2.303/t \times \log a/a - x$. The values given are ± standard deviation. [c] Obtained from the Arrhenius activation energy using the relation $\Delta H^* = E^a - RT$ (as well as other ways, see Experimental). The uncertainties given are two standard deviation units from the mean. [d] Derived from the expression $\Delta S^* = 2.303\ R \log k_1 h/kT + \Delta H^*/T$ (as well as other ways, see Experimental). The uncertainties given are as in *c*. [e] 97% pure by infinity titer; initial concentrations calculated on this basis. [f] 99% pure by infinity titer; initial concentrations calculated on this basis. [g] Analytically pure; weighed concentrations. [h] Acetolysis in the presence of 0.0510 M sodium acetate.

line solids that were stable for less than thirty minutes at room temperature. The white crystalline *p*-toluenesulfonate (IIc. Ar = *p*-$CH_3C_6H_4$—, dec. 52°, 86%) was a bit more stable, decomposing to a purple mass in about an hour at 25°. In spite of this difficulty, it proved feasible to study these substances. Accordingly, the acetolysis of these sulfonate esters was carried out as described in the literature[8] and the results are summarized in Table I.

Of comparable importance to the rates of acetolysis of these esters is the nature and composition of the product formed.[9] Larger scale acetolyses were therefore performed on the most stable of the three compounds, the *p*-toluenesulfonate IIc. When IIc was treated with acetic acid for an extended time at 25°, no definite product resulted other than a nonvolatile, tacky, polymeric material. In the belief that polymerization was being promoted by the liberated sulfonic acid, a subsequent run was made on IIc (0.44 M) in a 0.52 N solution of sodium acetate in acetic acid at 35° for one hour. Isolated in quantitative yield was 1-phenylcyclobutyl acetate (IV), which afforded 1-phenylcyclobutanol[11] (V, m.p. 40–41°) in 95% yield when hydrolyzed with lithium aluminum hydride. Various other reactions were performed resulting in the olefin VI and its nitroso chloride VII.

The compounds IV–VII were identical with those produced from authentic alcohol V prepared from cyclobutanone and phenyllithium[11] (see Experimental). That the prepartion of IIc had not itself caused the observed ring enlargement was shown by the regeneration of the parent alcohol I upon saponification of IIc with dilute base. Also, the acetolysis of IIc in the absence of the added acetate salt had indeed produced the olefin VI which then polymerized, since VI (0.35 M in acetic acid) disappeared completely over a forty-five-minute period in the presence of *p*-toluenesulfonic acid. No change was caused by the solvent itself. Pure olefin VI, an oil of styrene-like odor, set to a gel (probably a polymer) on standing.



Some relative rate comparisons, in particular those with the parent cyclopropylcarbinyl benzenesulfonate and neophyl *p*-toluenesulfonate, are of interest. The data are collected in Table II.

Discussion

In our opinion, previously published work on the cyclopropylcarbinyl system suffers from the lack of activation parameter data. As Table I shows, these parameters even in the same parent system

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

(9) A particularly disquieting feature of previously reported work[7,10] on arenesulfonate derivatives in this system is the absence of information about products.

(10) S. Borčić, M. Nikoletić, and D. E. Sunko, *Chem. Ind.*, 527 (1960); *J. Am. Chem. Soc.*, **84**, 1615 (1962).

(11) A. Burger and R. Bennett, *J. Med. Pharm. Chem.*, **2**, 687 (1960).

TABLE II
Relative Acetolysis Rate Data

Compound	k_1 (sec.$^{-1}$, °C.)	k_{rel} (compounds)
Cyclopropylcarbinyl benzenesulfonate (VIII)	$2.24 \pm 0.04 \times 10^{-4}$ (20)[a]	1.3 (IIa/VIII)
Neophyl *p*-toluenesulfonate (IX)	2.82×10^{-8} (25)[b]	9.4×10^{3} (IIc/IX)

[a] Ref. 10. [b] Extrapolated from data given in ref. 8.

are not even similar[12] and reflect a dependence on the leaving group; the better the leaving group, the more favorable the activation entropy and the less favorable the activation enthalpy.[13] Substitution of various groups—(*e.g.*, 1-methyl[6] or 2-*cis* and *trans* phenyl[7])—into the cyclopropylcarbinyl system could also affect either or both of these parameters, so explanations of why and how these substitutions influence the solvolytic rate in the absence of this data are hazardous, albeit tempting.

For the present study, the activation enthalpy and entropy data suggest that in acetolysis the progression IIb through IIa through IIc involves increasingly concerted formation of the activated complex,[14] even though cyclopropyl anchimeric assistance is present to a high degree in each case. Presumably, cyclopropyl participation (a known phenomenon in the reaction of the ester VIII) is involved exclusively in this reaction, since, as Table II shows, a 1-phenyl ring substituent makes the rate of the benzenesulfonate only 30% faster. In further support of this view, ester IIc is indeed much faster in acetolysis than a standard case of phenyl participation, neophyl *p*-toluenesulfonate (IX). Comparable data could be cited for the sulfonates IIa and IIb also. Finally, the production in quantitative yield of the ring-enlarged acetate ester IV further demonstrates exclusive cyclopropyl participation.

Slight, if any, internal return to kinetically slower species seemed evident in this system. After five to ten half lives, the esters IIa–c routinely liberated > 95% of the theoretical sulfonic acid based on pure arenesulfonate starting material. This result contrasts with the reports of internal return in related systems.[7,15] Possibly the pronounced carbonium ion stabilizing effect of phenyl makes the bicyclobutonium ion character[6] of the ion III smaller, giving it then more classical character than the ions produced in other systems.[16] The benzylic nature of III would then render return by the arenesulfonate ion quite unlikely[17] and its decreased bicyclobutonium ion character would also limit a return to kinetically slower compounds. In the view that the ion III *is* classical, capture by the acetate ion should then yield but one product (IV). Indeed, if one must explain this work (disregarding our earlier advice and yielding to temptation) perhaps the notable lack of phenyl rate assistance and the possible difference in number of products[9] in the esters IIa–c relative to the ester VIII reflect the change in the stability of the generated ions coupled with compensating change in the stability of the starting compounds. In the case of ester VIII an ion stabilized by its bicyclobutonium character is formed leading to a rapid acetolysis rate. In the case of the esters IIa–c this ion, now stabilized additionally by benzyl-type resonance, is again formed. If, however, the benzyl-type resonance surely present in each of the esters IIa–c lowered the ground state energy (as in phenylcyclopropane[18]) comparably to the transition state energy in acetolysis, similar rates could then result through a subtle combination of ground state energies and activation parameters. Nevertheless, since the former are difficult to estimate[19] and the latter are not yet available for VIII, no definite conclusions seem prudent. As to number of products, a possibly obvious but still worthy comment, it would seem, is that the more localized the charge in the ion engendered by the cyclopropylcarbinyl system, the fewer the products.[20]

The acetolysis of ester IIc was subject to a normal salt effect as expected. The rate increase from Table I (about 7%) yields a "b-value"[21] for acetate ion of 1.4. The normal salt effect "b-values" reported are from about 0.5 to 4. Special

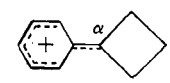
(12) Admittedly, the temperature range over which these reactions were studied was not large and the activation parameters given could be inaccurate to some degree. Nonetheless, a decided difference exists among these substances with regard to their kinetic behavior relative to temperature.

(13) The generally useful ratios of reactivity associated with various arenesulfonates (*e.g.*, that *p*-bromobenzenesulfonates are about threefold faster in solvolysis than are *p*-toluenesulfonates) were found to obtain here also. The actual ratio of reactivity, as may be seen from Table I, is quite dependent on temperature, of course.

(14) P. D. Bartlett and R. R. Hiatt, *J. Am. Chem. Soc.*, **80**, 1398 (1958), have shown that occasionally a reaction more concerted in one analog than in another will be characterized by lower ΔH^* and ΔS^* values. For more discussion, see J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955).

(15) J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 2509 (1951); E. F. Cox, M. C. Caserio, M. S. Silver, and J. D. Roberts, *ibid.*, **83**, 2719 (1961).

(16) More exactly, resonance with the aromatic ring would increase the *cyclobutyl* character of III, as shown, making site α most receptive



to nucleophilic attack.

(17) The product would be a benzylic, tertiary arenesulfonate and would undoubtedly be kinetically faster than the original reactant. Only one tertiary alcohol arenesulfonate is apparently known to be stable, *cf.* D. J. Cram and G. S. Hammond, "Organic Chemistry," McGraw-Hill Book Co., Inc., New York, p. 246.

(18) For a discussion, see L. L. Ingraham, *Steric Effects on Certain Physical Properties* in "Steric Effects in Organic Chemistry," edited by M. S. Newman, John Wiley and Sons, New York, 1956, pp. 518–522.

(19) No arenesulfonates were preparable from 1-phenylcyclobutanol (V). Attempts (L. Piszkiewicz) to equilibrate alcohols I and V under acidic conditions led to 1-phenylcyclobutene (ν_{max} 1695 cm.$^{-1}$) and unchanged I from pure alcohol I. Alcohol V was not certainly shown to be present.

(20) As has been mentioned by Roberts,[6] this is in accord with the postulate of G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

(21) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2763 (1956).

salt effects[22] were not investigated since internal return seemed absent.

Finally, the synthetic utility of the reactions described as points of entry into 1-arylcyclobutyl chemistry warrants mention. The yields on all steps are good and the starting compounds are accessible.

Experimental

All melting points (Fisher-Johns block) and boiling points are uncorrected for stem exposure. Infrared spectra were recorded on a Perkin-Elmer Model 21 instrument using sodium chloride optics. Ultraviolet spectra were obtained on a Beckman Model DK-2 instrument. A Perkin-Elmer Model 154C gas chromatography instrument was used for this work, and a column (8 ft. × 1/4 in.) packed with 20% Hercoflex 600[23] on Celite was employed. All microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

1-Phenylcyclopropylcarbinol (I).—1-Phenylcyclopropylcarboxylic acid (64.8 g., 0.4 mole, m.p. 86–87.5°, lit.[24] m.p. 86–87°) was converted to its acid chloride with thionyl chloride in the usual way (68.6 g., 95%, b.p. 75–76° at 1 mm., $n^{20}D$ 1.547, d^{20}_4 1.169). The acid chloride was a colorless oil that soon developed a pink cast. As soon as possible after its preparation, the acid chloride (57.7 g., 0.32 mole) in dry ether (200 ml.) was added dropwise over a 60-min. period to a cold, stirred suspension of lithium aluminum hydride (12.5 g., 0.32 mole) in dry ether (800 ml.). After the addition was completed, the grey mixture was allowed to warm to room temperature and then refluxed for 2 days. The reaction mixture was then hydrolyzed by adding cold water (15 ml.), aqueous sodium hydroxide (4 *N*, 30 ml.), and lastly water (50 ml.). The ether layer was filtered and the remaining inorganic salts continuously extracted (Soxlet) for 24 hr. with ether (250 ml.). The ether was partly removed by atmospheric distillation from the combined ether solutions and the remainder of the solvent removed by evaporation under an air stream. The alcohol remaining was afterwards recrystallized from hexane (46 g., 97%, m.p. 32.5–33°). The alcohol posseses a floral odor and easily supercools.

Anal. Calcd. for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 81.21; H, 7.91.

1-Phenylcyclopropylcarbinyl Arenesulfonates (IIa–c).—These derivatives were prepared from the alcohol I (30–45 mmoles) in pyridine (5–7 ml.) by the portionwise addition of the appropriate arenesulfonyl chloride (45–50 mmoles) with stirring at 0°. After the addition of reagent, the reaction was held at 0° for the following times: 20 min. for IIa; 15 min. for IIb; 2 hr. for IIc. The mixtures were then acidified with cold dilute hydrochloric acid and the precipitated solids recrystallized from heptane–benzene mixtures to give as a colorless solid; **1-phenylcyclopropylcarbinyl benzenesulfonate** (IIa, 89%, m.p. 48° dec.),

Anal. Calcd. for $C_{16}H_{16}O_3S$: C, 66.64; H, 5.60. Found: C, 65.66; H, 5.68.

1-Phenylcyclopropylcarbinyl *p*-bromobenzenesulfonate (IIb, 46%, m.p. 35° dec., too unstable for combustion analysis) and **1-phenylcyclopropylcarbinyl *p*-toluenesulfonate** (IIc, 86%, m.p. 52° dec.) were obtained as colorless solids.

Anal. Calcd. for $C_{17}H_{18}O_3S$: C, 67.52; H, 6.00. Found: C, 67.60; H, 6.08.

All three arenesulfonates decomposed to purple masses readily at 25° on standing: IIa within 30 min.; IIb within 15 min.; IIc within 1–2 hr. The purity of the substances was further checked each time they were made by infinity titrations. Weighed amounts of IIa–c were placed in acetic acid and held for 4–6 hr. at 25°. Titration (see later) of the liberated sulfonic acid indicated purities ranging from 91–100%, calculated on the basis of the initial weights. These figures were then used to correct the weighed-in initial concentrations (when necessary) for the kinetic runs made with these samples. On two occasions infinity titers indicated purities of 75 and 83% for IIb. These samples of IIb were discarded.

Rate Determinations.—The technique of Winstein and co-workers[8] was used. The solvent was glacial acetic acid (J. T. Baker reagent grade, 99.9% min.) and the indicator was Bromphenol Blue. The titrant was sodium acetate in glacial acetic acid (about 0.05 *N*). Although the esters IIa and IIb showed appreciable prerun acetolysis (41–77%) due to the time required for initial solution, their kinetics thereafter were cleanly first order to 80–95% completion. The *p*-toluenesulfonate IIc was more reliable, showing less prerun acetolysis and its rate constant is considered the most accurate. The data given in Table III is typical of the behavior of IIc. A 2.000-ml. aliquot was titrated.

TABLE III

ACETOLYSIS DATA FOR IIc, 0.0273 *M*, 18.0°

Time, min.	Ml. titrant (0.050 *N*)	% IIc reacted	2.303 log $a/a-x$	k_1 (10^3 min.$^{-1}$)
0	0.130	12.0	...	...
40	0.430	39.5	0.368	9.22
60	0.535	49.2	0.553	9.22
90	0.662	61.0	0.812	9.04
120	0.772	71.0	1.108	9.25
				Av. 9.18 ± 0.096 (σ)

Some darkening occurred in the materials at the higher conversions. When sodium acetate was present, however, the material remained water-white throughout. The darkening was probably connected with the side reaction involved in the polymerization of VI.

Treatment of Kinetic Data.—In addition to the methods given in Table I for obtaining the rate constants, ΔH^* and ΔS^*, the latter two parameters were also obtained by least squares treatments and by IBM 704 computer regression analyses.[25] All these methods agreed within the standard deviation of each and therefore only the one value is given in Table I.

Product Studies.—A portion (25 ml.) of a solution of ester IIc (0.44 *M*) in acetic acid containing sodium acetate (0.52 *N*) was thermostated at 35° for 1 hr. The material was added to ice water (200 ml.) and extracted with ether (2 × 50 ml.). The ether extract was washed with saturated sodium bicarbonate (5 × 10 ml.), then with water (10 ml.), and finally dried over sodium sulfate. The ether was removed by distillation and the residual ester (2.18 g., 100%) vacuum distilled to give a mixture of **1-phenylcyclobutyl acetate** and **1-phenylcyclobutene** (IV and VI, respectively, about 2 g., b.p. 97–99° at 5 mm., $n^{26}D$ 1.5190). The infrared spectrum was identical with that of the authentic olefin ester mixture (see below). The ultraviolet spectrum (λ^{max}_{alc} 255 mμ, ε 1850) indicated the presence of *ca.* 13% olefin (using the λ^{max}_{alc} for the pure olefin given below) and was very similar to that of the authentic mixture also. The olefin is believed to arise during the distillation of the ester IV for two reasons: The infrared spectrum of the undistilled product showed no olefin unsaturation and the yield of alcohol V in the following hydrolysis was very high.

Hydrolysis of Acetolysis Product.—The acetolysis product from another experiment identical to that just described (undistilled, 2.1 g., 11 mmoles if all ester IV) was

(22) A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2767 (1956).

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

(24) A. W. Weston, *J. Am. Chem. Soc.*, **68**, 2345 (1946).

(25) These analyses were performed through the courtesy of the Statistical Department of the American Oil Co., Whiting Research Laboratories, Whiting, Indiana. For the complete data, the dissertation of D. D. R. should be consulted.

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.

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