quency measurements with a high degree of accuracy. Chemical shifts between the *cis* and *trans* isomer calculated from measurements on the pure compounds agreed well with the same shifts measured with spectra of 50–50 mixtures of the same compounds.

The high temperature spectra were measured with the Varian model V-4340 variable temperature probe and the model V-4331-THR Dewar insert. Solutions of *cis*-1,2-diphenylcyclopentane in carbon tetrachloride (30% by volume) in 2.5 mm. i.d. Pyrex tubes were degassed and then sealed under prepurified nitrogen and inserted in 5-mm. tubes. Tetramethylsilane (0.3–3% by volume) was used as an internal standard. Spectra of the pure liquid *cis*-diphenylcyclopentane were also examined at higher temperatures and gave results similar to those obtained with the solutions. *cis*-3,4-Diphenylcyclopentanone was examined in carbon tetrachloride (11% by volume) and care was taken to protect it from light. The temperature was maintained by a flow of hot air and the insert temperature was calibrated for a range of settings from 25–185° using a dummy sample tube containing a thermocouple— the temperature of the insert jacket being monitored by means of a copper–constantan thermocouple located in it. The temperatures are considered reliable to about ±1°. As a check on chemical stability and reproducibility of the spectra, the spectra at 25° were re-run after the samples had been examined at 152 and 182°. Although a slight yellowish discoloration was noticed with the carbon tetrachloride solution after heating, the spectra obtained before and after heating were essentially superimposible and no new peaks were evident in any sample. Positions of n.m.r. maxima are presented in Table III.

TABLE III

α- AND AROMATIC PROTON RESONANCE OF *cis* AND *trans* ISOMERS IN CARBON TETRACHLORIDE SOLUTION (τ-VALUES)

Compound	Aromatic protons (Phenyl positions) *trans*	*cis*	*c* − *t*	α-Protons (Benzylic positions) *trans*	*cis*	*c* − *t*
1,2-Diphenylcyclopropanes	2.87[a]	3.04[a]	0.17	7.87[a]	7.55[a]	−0.32
1,2-Diphenylcyclopentanes	2.99[a]	3.19[a]	.20	7.07[a]	6.67[a]	− .40
	3.01[b]	3.22[b]	.21	7.00[b]	6.68[b]	− .32
3,4-Diphenylcyclopentanones	2.83[c]	3.10[c]	.27	6.52[c]	6.17[c]	− .35
Stilbenes	2.62[a]	2.79[a]	.17	2.97[a]	3.47[a]	− .50
Azobenzenes	2.52[a]	3.09[a]	.57			

[a] Calculated from value obtained from extrapolation of infinite dilution in carbon tetrachloride at 40 Mc. in p.p.m. relative to water by the addition of 5.22 p.p.m.[35] [b] Value in carbon tetrachloride measured from tetramethylsilane as an internal standard at 60 Mc. [c] Value of 5% solution in deuteriochloroform using tetramethylsilane as an internal standard.

(35) Value suggested by G. V. D. Tiers in his "Tables of τ-Values for a Variety of Organic Compounds," Minnesota Mining and Manufacturing Co. Report, 1958.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY, LAFAYETTE, IND.]

Transmission of Electrical Effects through Homoallylic Systems. V. The Nature of the Bonding in Ions Derived from Cyclopropylcarbinyl and Cyclobutyl Derivatives[1a]

BY RICHARD A. SNEEN, KENNETH M. LEWANDOWSKI,[1b] ISSAM A. I. TAHA[1b] AND BILLY RAY SMITH[1b]

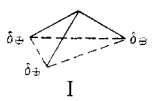
RECEIVED JULY 12, 1961

Synthesis of the crystalline β-naphthalenesulfonate esters of cyclopropylcarbinol, of *cis*- and *trans*-2-phenylcyclopropylcarbinol and of cyclobutanol is reported. The rates of solvolysis of the three cyclopropylcarbinyl esters were determined in 90 volume per cent. aqueous dioxane at 25°. The unsubstituted ester proved to be intermediate in reactivity (k_{rel} = 1.00) between the slower *cis*- (0.62) and the faster *trans*-2-phenylcyclopropylcarbinyl β-naphthalenesulfonate (2.19). This insensitivity to phenyl substitution is interpreted as evidence that, whatever the nature of the intermediate derived on solvolysis of cyclopropylcarbinyl systems, little positive charge is dispersed to the methylene carbon atoms of the cyclopropyl ring. Kinetic salt effects on solvolysis of cyclopropylcarbinyl β-naphthalenesulfonate were carried out with results confirming Roberts' suggestion[2,22] that such reactions are accompanied by internal return. Finally, the trifluoroacetate esters of *cis*- and *trans*-2-phenylcyclopropylcarbinol have been prepared and their rates of solvolysis in 60 volume per cent. aqueous dioxane have been measured.

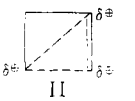
In spite of the general interest which was aroused by the original solvolytic studies[2–4] on cyclopropylcarbinyl and cyclobutyl derivatives, the nature of the bonding in the intermediate ions and, indeed, even the number of such intermediates involved in these ionization reactions has not yet been unequivocally established. The facts which must be accounted for are these: both cyclopropylcarbinyl and cyclobutyl derivatives react at rates abnormally fast when compared with appropriate model compounds. Further, both cyclopropylcarbinyl and cyclobutyl derivatives give rise to essentially the same distribution of solvolysis products, consisting of derivatives containing the cyclopropylcarbinyl, the cyclobutyl and the allylcarbinyl nuclei.

These facts were early interpreted in terms of a single so-called tricyclobutonium ion (I),[3,5] an intermediate assumed common to both ring structures. Such a structure would presumably account not only for the observed product distributions but also, if it is stabilized with respect to more classical ions, the enhanced rates of reaction.

More recently Roberts and co-workers[6] have shown that the highly symmetric tricyclobutonium ion cannot, at least simply, explain the results of C-14 experiments in the closely-related reaction, the decomposition of cyclopropylcarbinyl diazonium ion. Thus, although each of the three methylene carbons of the product cyclobutanol contained C-14, equilibration was not complete. These results led Roberts to propose a somewhat less



I



II

(1) (a) Presented in part at the 138th Meeting of the American Chemical Society, New York, N. Y., September 13, 1960, Abstracts of Papers, p. 34-P. (b) Abstracted from theses submitted by K. M. L., I. A. I. T. and B. R. S. in partial fulfillment of the requirements for the degree of Master of Science.

(2) J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 2509 (1951).

(3) C. G. Bergstrom and S. Siegel, *ibid.*, **74**, 145 (1952).

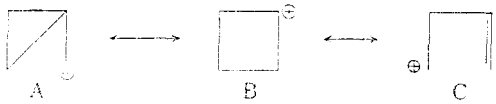
(4) H. C. Brown and M. Borkowski, *ibid.*, **74**, 1894 (1952).

(5) J. D. Roberts and R. H. Mazur, *ibid.*, **73**, 3542 (1951).

(6) R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver and J. D. Roberts, *ibid.*, **81**, 4390 (1959).

symmetric bicyclobutonium ion, II, as the non-classical intermediate formed on solvolysis of cyclopropylcarbinyl and cyclobutyl systems. The incomplete scrambling observed in the C-14 experiments was assumed to result from isomerization of the initially-formed ion to isotopically distinct but otherwise identical bicyclobutonium ions at a rate comparable with that of solvolysis.

Essentially this bicyclobutonium ion, although assumed to be a true intermediate, has structural features generally associated with a Wagner–Meerwein transition state. Roberts' electronic description of the bicyclobutonium ion II is equivalent to the valence bond picture of a resonance hybrid of the structures



A B C

A time-honored technique which has been often used to probe the electronic distribution in transition states leading to intermediates is the study of the effect of substituents on the rates of the reaction in question. It occurred to us that such a technique, applied to cyclopropylcarbinyl systems, might aid in the assessment of the relative importance of the forms (A ↔ B ↔ C) and thus in the determination of the electron distribution in their equivalent, the hybrid ion, II. In particular it seemed of interest to study the effect of substitution at a ring methylene carbon atom of the cyclopropylcarbinyl system since the contribution of form C should be strongly dependent on such substitution.

It was with these thoughts in mind that the present research was begun and in this paper we report the preparation and solvolytic behavior of the crystalline β-naphthalenesulfonate esters of cyclopropylcarbinol, of *cis*- and *trans*-2-phenylcyclopropylcarbinol and of cyclobutanol. In the course of this work several tangential points of interest developed and these are also reported in this paper.

Results

Synthesis of β-Napthalenesulfonates.—In addition to our central interest in the bonding in cyclopropylcarbinyl-derived ions we wished to prepare a solid, crystalline, solvolyzable derivative of cyclopropylcarbinol since results of earlier studies with this system were somewhat clouded by the uncertain purity of the liquid derivatives used, the chloride[2] and benzenesulfonate.[3] Attempts to prepare solid samples of the usual sulfonate esters (tosylate, brosylate, *p*-nitrobenzenesulfonate, benzenesulfonate) were uniformly fruitless. However the β-naphthalenesulfonate[7] of cyclopropylcarbinol proved to be a crystalline solid of m.p. 53–54°.[8]

Our initial attempts to prepare crystalline β-naphthalenesulfonates of *cis*- and *trans*-2-phenylcyclopropylcarbinol[12] were unsuccessful and only after repeated attempts were solid derivatives obtained. In retrospect, the reasons for our difficulties became apparent: the esters, when in the solid phase, proved to be extraordinarily unstable thermally at ordinary temperatures.[15] They could be kept, however, for several days at −78°.

In view of the extreme thermal instability of these esters, with its implications of facile rearrangements, we were anxious to establish their structures with certainty. Microanalytical determination of carbon and hydrogen in *cis*-2-phenylcyclopropylcarbinyl β-naphthalenesulfonate checked fairly well the expected values, although thermal instability of the *trans*-ester precluded its analysis. Further, the near infrared spectra of both the *cis*- and *trans*-esters as well as of several synthetic precursors showed absorption at 1.63–1.64 μ, an absorption band reported by Washburn and Mahoney[16] to be characteristic and quite definitive for the cyclopropyl ring. Finally the kinetic data, as shown below, support the structural assignments.[17]

Kinetic Data.—Rates of solvolysis of the β-naphthalenesulfonates in 90 volume per cent aqueous dioxane were determined by titration of liberated acid and these data are given in Tables I and II. Table I contrasts the reactivity of the various esters, each of which was found to react with good first-order kinetics. The three cyclopropyl esters were solvolyzed at 25.0° whereas the rate of the slower-ionizing cyclobutyl β-naphthalenesulfonate was measured at higher temperatures and extrapolated to 25.0° for comparison purposes. The unsubstituted cyclopropyl ester was found to liberate, reproducibly, only 81.0 ± 1.0% of the theoretical acid after ten half-lives and this percentage was essentially unchanged after 20 half-lives. The rate constants for this ester have been calculated from the experimental infinity and thus measure the sum of the rates of all processes for the destruction of this ester. A sample run has been included in the Experimental as Table V.

In Table II are collected the kinetic results of solvolyses of cyclopropylcarbinyl and of cyclo-

(7) The generic name, nosylate, is the logical abbreviation for this class of esters, a name which, for reasons of euphony, we prefer not to use.

(8) Indeed we have subsequently found that many alcohols, the usual sulfonate esters of which are liquids or low-melting solids, form higher-melting crystalline β-naphthalenesulfonates. In general, the latter derivative is found to have a melting point *ca.* 15–20° higher than that of the corresponding *p*-toluenesulfonate ester.[9,10] β-Naphthalenesulfonate esters appear to be intermediate in solvolytic reactivity[9] (0.8) between benzenesulfonates[11] (1.0) and *p*-toluenesulfonates[11] (0.6).

(9) Unpublished work.

(10) Private communication from H. C. Brown and S. Nishida.

(11) A. Streitwieser, Jr., *Chem. Revs.*, **56**, 654 (1956).

(12) These alcohols were prepared in turn by the method of Burger and Yost[13] which involves, as the key step, the reaction between styrene and ethyl diazoacetate. The stereoisomers were separated by fractional crystallization from hot water of the derived carboxylic acids. Structural assignments are securely based on the work of de Waal and Perold.[14]

(13) A. Burger and W. L. Yost, *J. Am. Chem. Soc.*, **70**, 2198 (1948).

(14) H. L. de Waal and G. W. Perold, *Ber.*, **85**, 574 (1952).

(15) As an example, the *trans*-ester decomposed spontaneously, turning black and evolving heat, in the short period of time required to bring the material to room temperature prior to microanalysis (perhaps 5–10 minutes).

(16) W. H. Washburn and J. J. Mahoney, *J. Am. Chem. Soc.*, **80**, 504 (1958).

(17) In particular, the fact that the *cis*- and *trans*-2-phenylcyclopropylcarbinyl esters solvolyzed at different rates requires that they be different compounds. They therefore cannot both be the, perhaps, most reasonable rearranged isomer, phenylallylcarbinyl β-naphthalenesulfonate, a compound with no possibilities of *cis–trans* isomerism.

TABLE I

RATES OF SOLVOLYSIS IN 90 VOLUME PER CENT. AQUEOUS DIOXANE

β-Naphthalenesulfonate	[Ester] × 10²	Temp., °C.	k, sec.⁻¹ × 10⁵	Infinity,[b] %
Cyclopropylcarbinyl[a]	0.765–1.90	25.0	5.47 ± 0.07	81.0 ± 1.0[c]
cis-2-Phenylcyclopropylcarbinyl	1.068	25.0	3.56 ± .10	92.5
	1.109	25.0	3.20 ± .09	95.1
trans-2-Phenylcyclopropylcarbinyl	0.654	25.0	11.92 ± .35	97.5
	1.038	25.0	12.06 ± .18	96.5
Cyclobutyl	2.008	65.0	3.01 ± .04	99.8
	1.968	55.0	1.08 ± .02	99.7
	...	25.0	0.014[d]	..

[a] Average of four separate runs. [b] Percentage of the theoretical acid liberated after 10 half-lives. [c] After 20 half-lives, 81.1 ± 1.5%. [d] Extrapolated from data at higher temperatures.

TABLE II

SOME RATES OF SOLVOLYSIS IN 90 VOLUME PER CENT. AQUEOUS DIOXANE IN THE PRESENCE OF SALTS

β-Naphthalenesulfonate	[Ester] × 10²	Salt	[Salt] × 10²	k, sec.⁻¹ × 10⁵	Infinity, %
Cyclopropylcarbinyl[a]	0.765–1.80	.....	..	5.47 ± 0.07[c]	81.0 ± 1.0
	1.28	LiOAc	0.94	6.12 ± .12	74.5
	1.22	LiOAc	1.95	6.77 ± .15	69.7
	1.15	$LiClO_4$	0.14	5.82 ± .16	85.5
	1.37		0.52	6.38 ± .16	85.7
	1.26		1.02	6.73 ± .15	88.7
	1.18		1.94	6.82 ± .14	90.1
	1.25		2.80	8.01 ± .17	92.5
	1.37	NaOBz	1.02	5.49 ± .24	77.0
	1.57		2.00	5.38 ± .12	70.1
	1.74		3.97	6.37 ± .22	67.0
Cyclobutyl[b]	2.01	.....	..	3.01 ± .04	99.8
	1.92	NaOBz	4.12	3.87 ± .06	81.7

[a] At 25.0°. [b] At 65.0°. [c] Average of four separate runs.

butyl β-naphthalenesulfonate, carried out in the presence of varying concentrations of lithium acetate, sodium benzoate and lithium perchlorate.

Product Studies.—Products of the solvolysis in aqueous dioxane of cyclopropylcarbinyl and of cyclobutyl β-naphthalenesulfonate were investigated by vapor phase chromatographic techniques and the results are compiled in Table III.

TABLE III

PRODUCTS OF THE SOLVOLYSES OF CYCLOPROPYLCARBINYL AND CYCLOBUTYL β-NAPHTHALENESULFONATE IN 90 VOLUME PER CENT. AQUEOUS DIOXANE

β-Naphthalenesulfonate	Time, half-lives	Products, % Cyclopropylcarbinol	Cyclobutylcarbinol	Allylcarbinol
Cyclopropylcarbinyl[a]	10	58	42	Trace
	20	56	44	Trace
Cyclobutyl[b]	10	54	46	Trace
	20	49	51	Trace

[a] 25°. [b] 65°.

Trifluoroacetate Esters.—Our initial failures to isolate crystalline β-naphthalenesulfonate esters of the phenylcyclopropylcarbinols led us to prepare the corresponding trifluoroacetate esters and to study their rates of solvolysis in 60 volume per cent. aqueous dioxane at 25.0°. The usual titrimetric technique was complicated by the extraordinary sensitivity of these esters to what is, presumably, a base-catalyzed acyl–oxygen fission reaction. It was accordingly necessary to develop a two-phase carbon tetrachloride–water quench system under which conditions good first-order kinetics were obtained. The data are given in Table IV.

TABLE IV

RATES OF SOLVOLYSIS OF TRIFLUOROACETATE ESTERS IN 60 VOLUME PER CENT. AQUEOUS DIOXANE AT 25.0°

Trifluoroacetate	[ROTFA] × 10²	k, sec.⁻¹ × 10⁵	Infinity, %
Cyclopropylcarbinyl	..	6.7[a]	...
cis-2-Phenylcyclopropylcarbinyl	1.96	2.50 ± 0.08[b]	97.4[b]
trans-2-Phenylcyclopropylcarbinyl	1.89	6.83 ± .16[b]	95.1[b]
	2.08	7.14 ± .24[c]	81.4[c]

[a] This is a very crudely determined rate constant, calculated on the basis of only four separate points. [b] Undistilled ester. [c] Distilled ester.

Discussion

The data of Table I, which relate to the kinetic effect of phenyl substitution into cyclopropylcarbinyl β-naphthalenesulfonate, give additional insight into the nature of the bonding in ions derived from the cyclopropylcarbinyl group. It is apparent that the total spread in rate constants for the cyclopropyl series is less than a factor of four. Furthermore, the unsubstituted ester proved to be intermediate in reactivity between the faster *trans*-phenyl ester and the slower *cis*-phenyl ester. Such a small kinetic effect implies that in these solvolysis transition states little excess positive charge is concentrated at the ring methylene carbon atoms of the cyclopropylcarbinyl systems. The conclusion would then seem inescapable that, to the extent that the ion under discussion is properly described as a hybrid of (A ⟷ B ⟷ C), form C contributes in only a minor way. Accordingly, the electronic description of the bicyclobutonium ion can be simplified to[18]

≡ (A⟷B)

Another point of interest which emerges from the data of Table I is the fact that only 81.0 ± 1.0% of the theoretical acid was liberated after ten half-lives of solvolysis of cyclopropylcarbinyl β-naphthalenesulfonate. This behavior is reminiscent of that reported by Roberts[2] for solvolyses of cyclopropylcarbinyl chloride and which was interpreted by him as evidence for internal return from ion pairs to less reactive isomeric chlorides. An alternative interpretation of the data seemed, if improbable, at least possible: that the isomeric

(18) In our opinion this conclusion also follows from the recently reported results of Borčić, Nikoletić and Sunko,[19] who found the isotope effect on acetolysis of α,α-dideuteriocyclopropylcarbinyl benzenesulfonate to be 1.34 whereas 2,2,3,3-tetradeuteriocyclopropylcarbinyl benzenesulfonate underwent this reaction with an immeasurably small isotope effect. On the other hand, a recent paper by Walborsky and Plonsker[20] reports that the rates of acid-catalyzed ring opening reactions of benzoylcyclopropanes depend rather strongly on the nature of substituents in the cyclopropyl ring. Although these reactions bear a superficial resemblance to solvolyses of cyclopropylcarbinyl systems, the processes are apparently quite different mechanistically.

(19) S. Borčić, M. Nikoletić and D. E. Sunko, *Chemistry & Industry*, 527 (1960).

(20) H. M. Walborsky and L. Plonsker, *J. Am. Chem. Soc.*, 83, 2138 (1961).

chlorides, reported by Roberts to be present in the solvolysis mixtures, had been present as impurities in the starting material and were not formed by internal return, an interpretation made plausible by the method of preparation of the liquid cyclopropylcarbinyl chloride.[21] Since our experiments utilized a pure, crystalline cyclopropylcarbinyl derivative, they erase any doubts about the correctness of Roberts' original interpretation and one can conclude with certainty that cyclopropylcarbinyl derivatives do indeed undergo solvolysis accompanied by internal return.[23]

It is further interesting to compare the rates of solvolysis of cyclopropylcarbinyl and cyclobutyl β-naphthalenesulfonates (Table I): the former compound is the more reactive by a factor of 390 under our conditions, an order of magnitude larger than the factor of 27 reported by Roberts[2] for the corresponding chlorides on solvolysis in 50 volume per cent. aqueous ethanol at 50°.

The experiments summarized in Table II were undertaken in an attempt to uncover ion pair phenomena in this system of the sort described by Winstein and co-workers,[24] particularly in solvent acetic acid. A careful analysis of the data, however, indicated that all of the experimental facts can be accounted for in terms of a simple ionization scheme involving only dissociated ions and intimate ion pairs; there is no positive evidence for solvent-separated ion pairs. Thus each of the salts investigated, lithium acetate, sodium benzoate and lithium perchlorate, produced a moderate positive kinetic salt effect of a sort expected to accompany a change in ionic atmosphere. Lithium acetate and sodium benzoate on the one hand, and lithium perchlorate on the other affected the percentage infinity (*i.e.*, the amount of acid produced after ten half-lives) in opposite but not unexpected ways. With the former salts, presumably, the stoichiometry of acid production is changed by the formation of acetate and benzoate esters at the expense of alcohols.[25] With lithium perchlorate the increased infinity undoubtedly results from an ionic atmosphere-induced change in the relative rates of dissociation of and return from intimate ion pairs.

The product studies reported in Table III conform to the pattern reported by Roberts[2] for the corresponding chlorides where both cyclopropylcarbinyl and cyclobutyl chloride were found to solvolyze in water to furnish the same mixture of carbinols, consisting of about equal parts of cyclopropylcarbinol and cyclobutanol and a trace of allylcarbinol. It will be noted that the composition of the product mixture resulting from solvolysis of cyclobutyl β-naphthalenesulfonate changed somewhat between 10 and 20 half-lives, suggesting product instability with this slower solvolyzing ester. Extrapolation of the data to zero time indicates that both sulfonate esters furnish, within experimental error, the same initial distribution of products.

Finally the experiments reported in Table IV were undertaken in view of our initial failures to prepare crystalline sulfonate derivatives of the phenylcyclopropylcarbinols, since it had been shown that sufficiently reactive secondary[26] and tertiary[27] trifluoroacetate esters solvolyze by an alkyl–oxygen fission reaction of the SN1 type. Unactivated primary trifluoroacetate esters, on the other hand, solvolyze by an "uncatalyzed" process involving, presumably, acyl–oxygen fission.[28] And from the rate data of Table IV it would appear that the behavior of cyclopropylcarbinyl trifluoroacetates parallels that of other primary systems; for it can be shown that these esters solvolyze at a rate much faster than would be predicted for reaction by mechanism SN1.[29] It is interesting, however, to note that the order of increasing reactivity found with the corresponding β-naphthalenesulfonate esters, *cis*-phenyl < unsubstituted < *trans*-phenyl, follows that of the corresponding trifluoroacetate esters. Indeed the ratio of rates of the *trans*- to *cis*-esters in the sulfonate series, 3.55, is similar to the corresponding ratio in the trifluoroacetate series, 2.80. Since these two series of compounds solvolyze, presumably, by different mechanistic processes, the similar effects of phenyl substitution are probably not of electronic origin and thus may reflect a small amount of steric interaction common to both series of reactions.

Experimental

Cyclopropylcarbinol.—In a 2-l. flask were placed 14.2 g. (0.375 mole) of lithium aluminum hydride and 500 ml. of dry ether. The solution was stirred while 25.8 g. (0.300 mole) of cyclopropanecarboxylic acid[30] in 150 ml. of dry ether was added at a rate sufficient to produce gentle reflux. After the addition (*ca.* 2 hours) the reaction mixture was stirred for 1 hour and then cooled in an ice-bath while 73 g. of sodium potassium tartrate in 97 ml. of water was added slowly. The aqueous layer formed a thick paste, the ether was removed by decantation and was washed twice

(21) In the course of the present work Roberts[22] reported a re-examination of this entire question, using the now-available technique of gas chromatography, and presented convincing evidence that his original interpretation had been correct.

(22) M. C. Caserio, W. H. Graham and J. D. Roberts, *Tetrahedron*, **11**, 171 (1960).

(23) This conclusion is made even more secure by the fact that, potentially, more than 81% of the theoretical acid is available on solvolysis of cyclopropylcarbinyl β-naphthalenesulfonate; for, as noted in Table II, an infinity of 92.5% was found in the run with added 2.80×10^{-2} *M* lithium perchlorate.

(24) See S. Winstein, P. E. Klinedinst, Jr., and G. C. Robinson, *J. Am. Chem. Soc.*, **83**, 885 (1961), and earlier papers in this series.

(25) The possibility that the lowered infinities observed with these salts may reflect a small SN2 component, involving attack by the anion on the neutral covalent ester, can be ruled out by the observation that, at comparable levels of sodium benzoate concentration (*ca.* 4.0×10^{-2} *M*), cyclobutyl and cyclopropylcarbinyl β-naphthalenesulfonate solvolyzed with similarly depressed infinities (82% and 67/81 = 83%, respectively).

(26) Private communication from S. Winstein.

(27) A. Moffat and H. Hunt, *J. Am. Chem. Soc.*, **81**, 2082 (1959).

(28) A. Moffat and H. Hunt, *ibid.*, **79**, 54 (1957).

(29) This conclusion follows from the following argument. Roberts[2] has reported that cyclopropylcarbinyl chloride undergoes solvolysis in 50% aqueous ethanol at 50° with a rate constant of 1.25×10^{-4} sec.$^{-1}$. Since it has been shown[26] that cyclocholesteryl-6β-yl chloride solvolyzes at a rate approximately ten times that of cyclocholesteryl-6β-yl trifluoroacetate, it can be calculated that cyclopropylcarbinyl trifluoroacetate would solvolyze by an SN1 process in 50% aqueous ethanol at 50° at a rate of approximately 1.25×10^{-5} sec.$^{-1}$. Thus the experimentally determined rates of reaction of the cyclopropylcarbinyl esters at 25° in 60% aqueous dioxane are faster than their predicted rates at 50° in the better ionizing solvent, 50% aqueous ethanol. This corresponds to a factor between the experimental and predicted rate constants of at least 50.

(30) "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 221.

with a saturated sodium chloride solution. To the thick paste were added 200 ml. of saturated sodium chloride solution and 100 ml. of water, and the resulting mixture was extracted three times with ether. The ethereal solutions were combined and dried over Drierite. The ether was removed and the product distilled, furnishing 16 g. (70%) of cyclopropylcarbinol, b.p. 123°, $n^{20}D$ 1.4313 (lit.[31] b.p. 121–123°, $n^{20}D$ 1.4308). Analysis of the product by vapor phase chromatography showed the maximum impurity to be about 0.1%.

Cyclobutanol.—Cyclopropylcarbinol (15 g.) was mixed with 13 ml. of concentrated hydrochloric acid in 10 ml. of water and the solution was refluxed for 3.5 hours. The solution was then made slightly basic with 0.6 *N* sodium hydroxide. Layers formed and were separated. The aqueous layer was extracted with ether and the extracts were combined over Drierite. The ether was removed and the products were fractionated. Analysis by vapor phase chromatography indicated material boiling above 124° to be essentially pure cyclobutanol. The lower boiling fractions were combined and refractionated; total yield of cyclobutanol 10 g., b.p. 124–126°, $n^{20}D$ 1.4376 (lit.[32], b.p. 123° (735 mm.), $n^{19}D$ 1.4339).

Allylcarbinol.—The procedure used was essentially that used for preparing cyclopropylcarbinol. To 8.0 g. (0.20 mole) of lithium aluminum hydride in ether was added 16 g. (0.186 mole) of 1-butenoic acid, giving 7.7 g. of allylcarbinol (57.7%), b.p. 113°, $n^{20}D$ 1.4205 (lit.[10] b.p. 113°, $n^{20}D$ 1.4216).

***cis*- and *trans*-2-Phenylcyclopropanecarboxylic Acid.**—These acids were prepared by the published procedure of Burger and Yost.[13] *cis*-2-Phenylcyclopropanecarboxylic acid had m.p. 105.5–107° (lit.[13] m.p. 106–107°) whereas the *trans*-acid had m.p. 92.5–93° (lit.[13] m.p. 93°).

***cis*- and *trans*-2-Phenylcyclopropylcarbinol.**—These isomeric carbinols were prepared by a modification of the method of Nystrom and Brown.[31] The following general procedure was used to prepare both carbinols. In a 1-l., three-necked flask, equipped with a mechanical stirrer, dropping funnel and reflux condenser was placed 19 g. of lithium aluminum hydride suspended in 100 ml. of anhydrous tetrahydrofuran (distilled from lithium aluminum hydride). A solution of 40.5 g. (0.25 mole) of the 2-phenylcyclopropanecarboxylic acid in 150 ml. of anhydrous tetrahydrofuran was added through the dropping funnel with stirring at such a rate as to produce gentle reflux (2 hours). After the addition was completed, the reaction mixture was refluxed for 12 hours. The excess hydride was then decomposed by the slow addition of 50 ml. of methanol dissolved in 100 ml. of tetrahydrofuran. To complete the decomposition 100 ml. of 8 *N* sodium hydroxide was added, followed by 300 ml. of water. The aqueous solution was decanted and filtered from the white gelatinous precipitate and extracted with four 200-ml. portions of ethyl ether. During the first extraction an emulsion formed which was broken with a small amount of magnesium sulfate. The combined ethereal extracts were dried over anhydrous potassium carbonate for 2 hours and the solvent was then removed by distillation through an 8-inch column packed with glass beads. The desired product was distilled through the same column at reduced pressure.

The yield of *trans*-2-phenylcyclopropylcarbinol was 29.09 g., 78.6% of theory, b.p. 90° (0.30–0.35 mm.), $n^{25}D$ 1.5507.

Anal. Calcd. for $C_{10}H_{12}O$: C, 81.08: H, 8.11. Found: C, 81.16; H, 8.33.

The 2-naphthylurethan derivative of *trans*-2-phenylcyclopropylcarbinol had m.p. 97°.

Anal. Calcd. for $C_{21}H_{19}NO_2$: C, 79.50: H, 5.99; N, 4.42. Found: C, 79.65; H, 6.06; N, 4.49.

The yield of *cis*-2-phenylcyclopropylcarbinol was 7.94 g., 87% of theory (based on 10 g. of *cis*-acid reduced, other reagent quantities reduced accordingly), b.p. 73–76° (0.10–0.15 mm.), 85–86° (0.15–0.25 mm.), $n^{25}D$ 1.5482.

Anal. Calcd. for $C_{10}H_{12}O$: C, 81.08; H, 8.11. Found: C, 81.81; H, 8.59.

Cyclopropylcarbinyl β-Naphthalenesulfonate.—Cyclopropylcarbinol (2.16 g., 0.030 mole) was dissolved in 40 ml. of anhydrous pyridine and stirred magnetically with cooling at ice–salt temperatures. β-Naphthalenesulfonyl chloride (8.0 g., 0.035 mole) was added in small portions and the reaction was allowed to proceed for 1.75 hours, after which 20 ml. of cooled water was added dropwise. The reaction mixture was then poured, with stirring, into 20 ml. of a water–ice mixture, saturated with sodium chloride and was extracted three times with ether. The ethereal layers were combined and washed first with 100 ml. of a saturated sodium chloride solution containing a small amount of sodium bicarbonate and then twice with 100-ml. portions of dilute hydrochloric acid. The ethereal layer was dried over magnesium sulfate and filtered and the volume was then reduced to about 15 ml. at which point crystallization commenced. Pentane (20 ml.) was added and, after cooling the solution in an ice–salt mixture, the crystals were removed by filtration. The crude cyclopropylcarbinyl β-naphthalenesulfonate was immediately recrystallized from 20 ml. of ether and 20 ml. of pentane. Yields ranged from 40–60%, m.p. 52–53°.

Anal. Calcd. for $C_{14}H_{14}SO_3$: C, 64.12; H, 5.34. Found: C, 64.37; H, 5.44.

***cis*- and *trans*-2-Phenylcyclopropylcarbinyl β-Naphthalenesulfonate.**—The following general method was followed for each isomeric ester. A glass-stoppered 25-ml. erlenmeyer flask, equipped with a magnetic stirring bar and containing a solution of 1.68 g. (11 mmoles) of the 2-phenylcyclopropylcarbinol in 10.7 g. (100 mmoles) of anhydrous 2,6-lutidine, was placed on a magnetic stirrer in a cold room regulated at 1°. To this cooled solution 2.27 g. (10 mmoles) of recrystallized β-naphthalenesulfonyl chloride (m.p. 76°) was added in small increments with stirring over a period of 20 to 30 minutes. The reaction mixture was stirred at this temperature for a period of 6 hours. It was then poured into a beaker containing 50–60 g. of ice and 8.3 ml. of concentrated hydrochloric acid. The aqueous mixture was extracted with three 30-ml. portions of ethyl ether and the combined ethereal extracts were washed with one 30-ml. portion of 5% sodium bicarbonate solution and one 30-ml. portion of water. After drying over anhydrous potassium carbonate for 10–15 minutes, the solution was filtered and concentrated under reduced pressure to a volume of 3–5 ml. On addition of 30 ml. of pentane, a white solid appeared at −78°, which became an oil on warming to room temperature. After three to four recrystallizations from ether–pentane at −78°, a white solid was obtained at room temperature.

The yield of *trans*-2-phenylcyclopropylcarbinyl β-naphthalenesulfonate was 1.10 g., 31.6% of theory, m.p. 39–40° with decomposition at 44°. This material decomposed, turning black and generating heat, when allowed to stand at room temperature for only a few minutes. It was stored at −78°. Attempted microanalysis was unsuccessful because of its extreme thermal instability.

The yield of *cis*-2-phenylcyclopropylcarbinyl β-naphthalenesulfonate was 2.00 g., 57.5% of theory, m.p. 48–50° with decomposition at 50°. This material was also stored at −78°. It was found to decompose in 1 to 2 hours at room temperature.

Anal. Calcd. for $C_{20}H_{18}SO_3$: C, 71.0; H, 5.32. Found: C, 70.50; H, 5.37.

Cyclobutyl β-naphthalenesulfonate was prepared by the method used for the preparation of cyclopropylcarbinyl β-naphthalenesulfonate. Yields ranged from 40–60%, m.p. 75–76° (lit.[10] m.p. 75–76°).

***cis*- and *trans*-2-Phenylcyclopropylcarbinyl Trifluoroacetate.**—The same general procedure was used for preparing each of the isomeric esters. A solution of trifluoroacetic anhydride (3.15 g., 15 mmoles; Matheson, Coleman and Bell) in 2.5 ml. of anhydrous 2,6-lutidine (distilled from calcium hydride) was cooled to 0° and added dropwise with stirring (by means of a magnetic stirring assembly) to a cooled solution of 1.48 g. (10 mmoles) of the 2-phenylcyclopropylcarbinol in 2.5 ml. of 2,6-lutidine. The temperature was maintained by means of an ice-bath. The addition required approximately 30 to 45 minutes. The reaction mixture was then poured into a beaker containing 50 g. of ice and 25 ml. of 5% sodium bicarbonate solution. The aqueous mixture was then extracted with three 30-ml. portions of methylene chloride–ethyl ether (2:1 by volume), and the combined extracts were washed with three 30-ml. portions of 5% hydrochloric solution and one 30-ml. portion of water. The organic layer was dried for 20 minutes

(31) R. F. Nystrom and W. G. Brown, *J. Am. Chem. Soc.*, **69**, 2648 (1947).

(32) N. J. Demjanov and M. Dojarenko, *Ber.*, **40**, 2596 (1907).

over anhydrous magnesium sulfate and filtered and the solvent was then removed by distillation at water-pump pressure. The ester was distilled in a micro-distillation apparatus at reduced pressure.

The yield of *trans*-2-phenylcyclopropylcarbinyl trifluoroacetate was 1.885 g., 76.2% of theory, b.p. 55–58° (0.10–0.15 mm.), $n^{25}D$ 1.4621.

Anal. Calcd. for $C_{12}H_{11}F_3O_2$: C, 59.0; H, 4.53; F, 23.26. Found: C, 58.96; H, 4.72; F, 23.08.

The yield of *cis*-2-phenylcyclopropylcarbinyl trifluoroacetate was 2.006 g., 82% of theory, b.p. 44–45° (0.10 mm.), $n^{25}D$ 1.4570.

Lithium Perchlorate Trihydrate.—To 36 g. (0.5 mole) of lithium carbonate in water sufficient to form a slurry was added about 60 g. (0.4 mole) of 70% perchloric acid. After the addition had been completed the reaction mixture was stirred for 8 hours to ensure complete reaction of the acid. The excess carbonate was filtered off and the resulting solution evaporated at water-pump pressure until crystallization occurred. The salt was then recrystallized twice from water. It was air dried at room temperature to furnish lithium perchlorate trihydrate (50%), m.p. 96°.

Lithium Acetate.—To 0.5 mole of lithium carbonate in enough water to form a slurry was added 0.45 mole of acetic acid. The mixture was stirred magnetically for 10 hours, filtered and then heated, first at 100° and then at 140°, at aspirator pressures. The resulting salt was recrystallized from water and then heated at 130° (1 mm.) for 12 hours. Storage was over phosphorus pentoxide in a desiccator.

Product Studies.—Calibration was carried out with synthetic mixtures of cyclopropylcarbinol, cyclobutanol and allylcarbinol. Samples were injected into a Perkin–Elmer vapor fractometer, model 154, equipped with a 2-meter diglycerol column. The three components were resolved under these conditions and the symmetry of the peaks allowed the triangular approximation method to be used as a quantitative gauge of the ratios of alcohols. Since conditions of flow rate and temperature were difficult to duplicate from day to day, calibration was carried out whenever product studies were made. Samples (*ca.* 50 ml.) of a solvolysis reaction mixture were taken and potassium carbonate (anhydrous) was dissolved in the reaction mixture until an aqueous layer separated. This layer was removed and the organic layer dried further with anhydrous magnesium sulfate. The mixtures were then filtered and *ca.* 60-μl. samples were injected into the fractometer.

Kinetic Measurements.—Rates of solvolysis of the β-naphthalenesulfonate esters were determined in 90 volume per cent. aqueous dioxane.[33] A weighed sample (by difference) of ester was placed in a 100-ml. volumetric flask and sufficient solvent added to give a volume of 100 ml. Aliquots (5 ml.) were pipetted out at intervals, quenched in 10 ml. of acetone, and the resulting solution titrated to the phenolphthalein end-point with *ca.* 0.02 *M* sodium hydroxide. Infinity titers were measured after approximately 10 half-lives and, on occasion, also after 20 half-lives. When salts were used the sample of salt was weighed into a specially-calibrated 106-ml. volumetric flask and dissolved to 106 ml. of solution with 9:1 dioxane–water. This salt solution was then added to a weighed ester sample in another flask to give a volume of 100 ml. A 5-ml. aliquot of the excess salt solution was titrated to give the blank correction. Cyclobutyl β-naphthalenesulfonate, because of its slow rate of solvolysis, was treated at higher temperatures using the sealed ampoule technique.[34] A typical kinetic run is reproduced as Table V.

Rates of solvolysis of the trifluoroacetate esters were determined in 60 volume per cent. aqueous dioxane by the techniques described above for the sulfonate esters. However, the use of acetone as a quench solvent resulted in rapidly fading end-points. Accordingly, a two-phase quench system was developed. Each aliquot was pipetted into 5 ml. of carbon tetrachloride. Distilled water (10 ml.) was added and the entire mixture was titrated with dilute sodium hydroxide to the phenolphthalein end-point while stirring was carried out by means of a magnetic stirrer. A typical kinetic run is reproduced as Table VI.

TABLE V

SOLVOLYSIS OF 1.068×10^{-2} *M* *cis*-2-PHENYLCYCLOPROPYL CARBINYL β-NAPHTHALENESULFONATE IN 90 VOLUME PER CENT. AQUEOUS DIOXANE AT 25.0°

[NaOH] = 2.377×10^{-2} *M*; blank = 0.043 ml.; theoretical infinity titer = 2.245 + 0.043 = 2.288 ml.; % of theory (2.120 − 0.043)/2.245 × 100 = 92.5%.

Time, sec.	Base, ml.	k, sec.$^{-1}$ × 10^5
....	0.137	..
5220	.475	3.57
7500	.625	3.78
14400	.937	3.58
20100	1.150	3.56
23100	1.265	3.64
29040	1.410	3.53
37020	1.600	3.61
40680	1.672	3.65
68040	1.920	3.37
86880	2.005	3.28
237840(∞)	2.130	..
290760(∞)	2.120	..
323160(∞)	2.110	..
	Av.	3.56 ± 0.10

TABLE VI

SOLVOLYSIS OF 1.89×10^{-2} *M* *trans*-2-PHENYLCYCLOPROPYLCARBINYL TRIFLUOROACETATE IN 60 VOLUME PER CENT. AQUEOUS DIOXANE AT 25.0°

[NaOH] = 2.35×10^{-2} *M*; blank = 0.027 ml.; theoretical infinity titer = 4.019 + 0.027 = 4.046 ml.; % of theory (3.849 − 0.027)/4.019 × 100 = 95.1%.

Time, sec.	Base, ml.	k, sec.$^{-1}$ × 10^5
....	0.110	..
1195	.410	6.98
2372	.655	6.66
3572	.905	6.69
4802	1.135	6.68
6607	1.435	6.63
8447	1.725	6.69
10287	2.020	6.95
11816	2.210	6.98
16722	2.700	7.06
19662	2.895	6.95
58907(∞)	3.855	..
74432(∞)	3.815	..
120012(∞)	3.860	..
207232(∞)	3.865	..
	Av.	6.83 ± 0.16

Acknowledgment.—This work was supported in part by a grant from the Army Research Office (Durham) and this assistance is gratefully acknowledged.

(33) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1941, p. 369.

(34) See, for example, R. A. Sneen, *J. Am. Chem. Soc.*, **80**, 3977 (1958).