[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF ILLINOIS INSTITUTE OF TECHNOLOGY]

The Effect of a Cyclopropyl Group on a Displacement Reaction at an Adjacent Saturated Carbon Atom. I. The Ethanolysis of Cyclopropylmethyl Benzenesulfonate[1]

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Cyclopropylmethyl benzenesulfonate isomerizes readily to a mixture which contains mainly 3-butenyl benzenesulfonate. It reacts with ethanol by a first order process to yield chiefly cyclopropylmethyl ethyl ether. The rate is faster than that of allyl or 3-butenyl benzenesulfonate by a factor of 10 and 10^3, respectively, at 20°. Therefore, in its effect upon displacement reactions at an adjacent carbon atom, the cyclopropyl group cannot be taken as a simple though less polarizable analog of a vinyl group. The implications of these results are discussed.

The interaction of cyclopropyl groups with other functional groups within a molecule has been clearly demonstrated to be analogous to the behavior of vinyl groups by a variety of experimental observations including comparison, using suitable derivatives, of the ultraviolet spectra,[3] electric polarizabilities[3b,4] and chemical reactions.[5] Recent studies of the displacement reactions undergone by derivatives of *i*-cholesterol[6] stimulated our interest in a study of the displacement reactions of simple analogs of these compounds. To this end cyclopropylmethyl benzenesulfonate was prepared and its alcoholysis in absolute ethanol was studied.[7]

Cyclopropylmethanol[8] was converted to the benzenesulfonate by a carefully controlled reaction of the alcohol with benzenesulfonyl chloride in the solvent 2,4,6-collidine.[9] The isolation of cyclopropylmethyl benzenesulfonate was complicated by its thermal instability. The compound could not be distilled, at 10^{-4} mm. in a molecular still, without causing considerable isomerization of the product. It was therefore necessary to study the product which was purified by extraction with methylene chloride followed by evaporation of the volatile solvent at diminished pressure. This gave a product which contained approximately 90% of the ester, the solvent being incompletely removed in the allotted time.

Cyclopropylmethyl benzenesulfonate isomerizes to a mixture which consists predominantly of 3-butenyl benzenesulfonate. A sample of the ester, stored over anhydrous K_2CO_3 at 20°, was 90% isomerized in 24 hours. The infrared absorption spectrum of the isomerized ester was compared with that of 3-butenyl benzenesulfonate prepared from 3-buten-1-ol. All absorption peaks found in the spectrum of 3-butenyl benzenesulfonate appear in the spectrum of the isomerized cyclopropylmethyl benzenesulfonate. This suggests that it consists mainly of the former substance. However, the absorption peaks at 11.1 and 11.7 microns show the presence of an additional substance. It must be isomeric with 3-butenyl benzenesulfonate because of the excellent agreement between the data for the elementary analysis and the saponification equivalent weight with those calculated for butenyl benzenesulfonate. A likely candidate for this unidentified species is cyclobutyl benzenesulfonate. This identification is suggested by the findings of Roberts and Mazur[10] that both cyclopropylmethyl chloride and cyclobutyl chloride are formed in the reaction of cyclopropylmethanol with thionyl chloride. Further support for this interpretation of the identity of the products of isomerization is obtained from kinetic data. (See later discussion.)

The reaction of the isomerized cyclopropylmethyl benzenesulfonate with sodium ethoxide in absolute ethanol yielded 3-butenyl ethyl ether and 1,3-butadiene. A small amount of another ether, possibly cyclopropylmethyl ethyl ether, was indicated.

From the reaction of undistilled cyclopropylmethyl benzenesulfonate with a solution of sodium ethoxide in absolute ethanol, cyclopropylmethyl ether was isolated. This was identified by a comparison of its physical properties and its infrared spectrum with that of a sample prepared by the alkylation of sodium cyclopropylmethoxide. The spectra are identical except for a weak absorption peak at 8.2 μ which is not present in the authentic sample. The correspondence in spectra excludes the presence of an appreciable quantity of any substance other than cyclopropylmethyl ethyl ether.

Rate Studies.—To further explore the mechanism of the alcoholysis of cyclopropylmethyl benzenesulfonate, the kinetics of the reaction was examined and a comparison made with the kinetics of alcoholysis of two related compounds, allyl benzenesulfonate and 3-butenyl benzenesulfonate. In each of these compounds the benzenesulfonate group is attached to a primary carbon atom, and the predominant mode of reaction was expected to be of the S_N2 type, particularly in an alcoholic solution of sodium ethoxide.[11]

Cyclopropylmethyl benzenesulfonate reacts more rapidly than allyl benzenesulfonate with ethanol or water. The first order rate constant in absolute alcohol was $6.0 \pm 0.4 \times 10^{-5}$ sec.$^{-1}$ at 20.1°.

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(1) Presented at the 119th Meeting of the American Chemical Society, Boston. Mass., April 4, 1951.

(2) From the dissertation of Clarence G. Bergstrom, submitted in partial fullfilment of the requirements for the Ph.D. degree at Illinois Institute of Technology.

(3) (a) I. M. Klotz, THIS JOURNAL, **66**, 88 (1944); (b) M. T. Rogers, *ibid.*, **69**, 2544 (1947); (c) J. F. Music and F. A. Matsen, *ibid.*, **72**, 5256 (1950); (d) A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

(4) M. T. Rogers and J. D. Roberts, THIS JOURNAL, **68**, 843 (1946).

(5) E. P. Kohler and J. B. Conant, *ibid.*, **39**, 1404 (1917).

(6) Studies in the laboratory of Professor Byron Riegel. *Cf.* R. M. Dodson and B. Riegel, *J. Org. Chem.*, **13**, 427 (1948).

(7) After this study was well under way, we learned that Professor John D. Roberts of the Massachusetts Institute of Technology was engaged in an extended study of the reactions of cyclopropylmethyl chloride. Occasional conversations and exchange of correspondence with him proved of value in our study.

(8) L. I. Smith and S. McKenzie, Jr., *J. Org. Chem.*, **15**, 74 (1950).

(9) C. G. Bergstrom and S. Siegel, THIS JOURNAL, **73**, in press (1951).

(10) J. D. Roberts and R. H. Mazur, *ibid.*, **73**, 2509 (1951).

(11) E. D. Hughes, *Trans. Faraday Soc.*, **37**, 603 (1941).

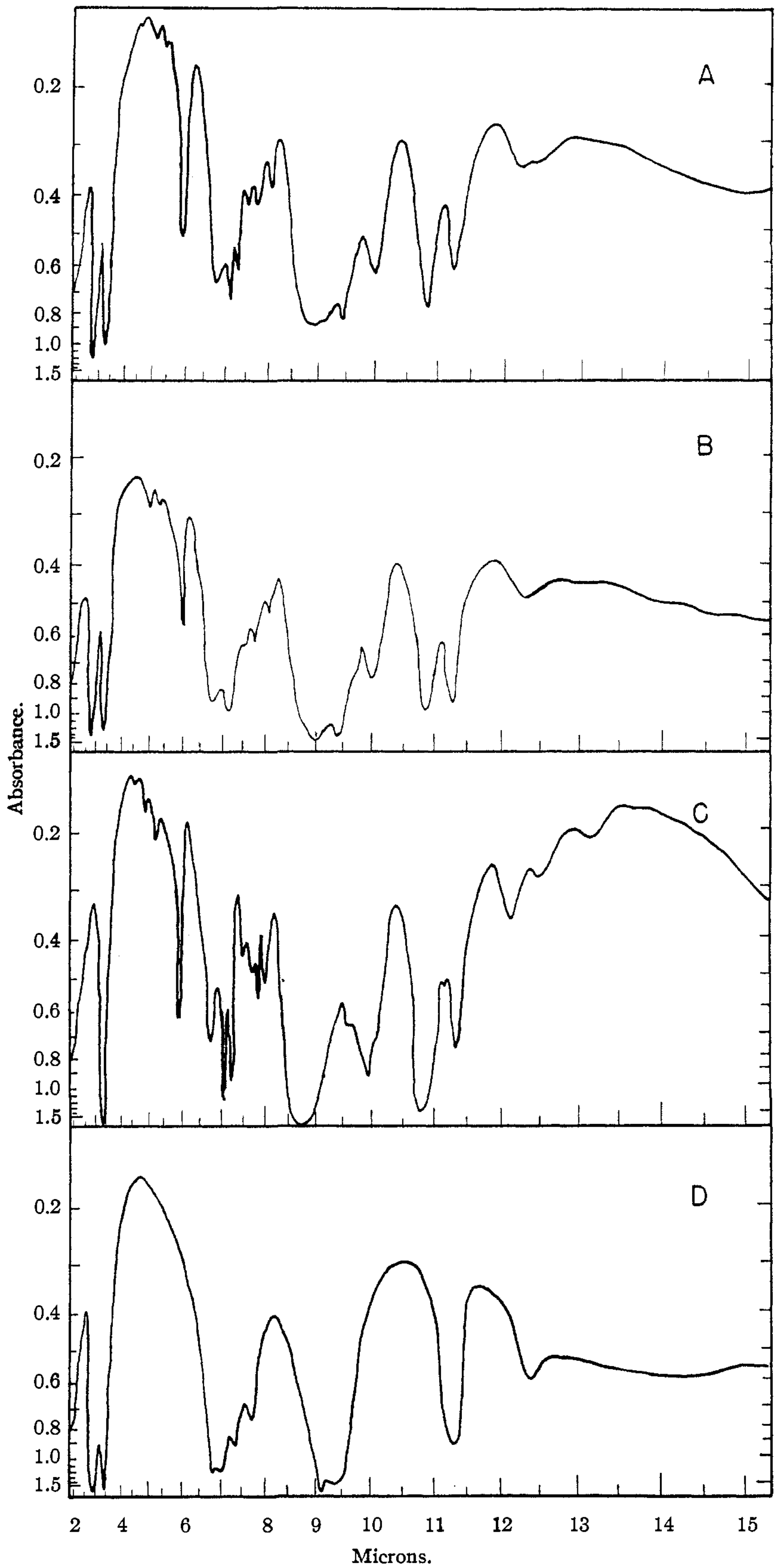

Fig. 1.—Infrared spectra: A, ether–ethyl alcohol mixture obtained from the ethanolysis of "isomerized cyclopropylmethyl benzenesulfonate"; B, mixture of 3-butenyl ethyl ether and ethanol; C, 3-butenyl ethyl ether; D, ethanol.

The rate remained first order in a solution containing approximately equivalent concentrations of ester and sodium ethoxide, although it was somewhat faster (7.1×10^{-5} sec.$^{-1}$). These results indicate the predominance of the S_N1 type of reaction. No attempt was made to obtain data from which activation energies for the solvolysis could be calculated because of the limited accuracy in the measurements of the rate constants.

3-Butenyl benzenesulfonate solvolyzes much more slowly than cyclopropylmethyl benzenesulfonate and a bimolecular rate constant for its reaction with sodium ethoxide was easily measured (4.5×10^{-4} l. mole^{-1} sec.$^{-1}$ at 34.8°). The rate of solvolysis at 20° (5×10^{-8} sec.$^{-1}$) was extrapolated by the use of the Arrhenius equation from the data obtained at 35 and 55°. The cyclopropylmethyl benzenesulfonate, therefore, solvolyzes at a rate over 10^3 times as rapidly as the 3-butenyl ester. The ratio compares well with that estimated by Roberts and Mazur for the ratio (10^3–10^4) of the rates of solvolysis in aqueous ethanol of cyclopropylmethyl chloride and 3-butenyl chloride.[10]

Experimental[12]

Cyclopropanemethanol.—Cyclopropanemethanol was prepared according to the method of Nystrom and Brown,[13] by the reduction of cyclopropanecarboxylic acid (86 g.) with $LiAlH_4$ (47.5 g.) dissolved in 50 ml. of absolute ether. (See also ref. 8.) The alcohol was separated from the reaction mixture by steam distillation. The average yield for nine preparations was 69 ± 2% of the theoretical yield; b.p. 121–123°. The alcohol was purified by fractionation through a 12 × 915 mm. Todd column packed with glass helices. The properties of the material used were: b.p. 124°, n^{25}_D 1.4308 and d^{25}_4 0.911.

Cyclopropylmethyl α-naphthylurethan was prepared in the usual way.[14] After it was recrystallized twice from carbon tetrachloride, it melted at 118–119°. *Anal.* Calcd. for $C_{15}H_{15}O_2N$: N, 5.67. Found: N, 5.88.

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[12] Elementary analyses were performed by the Micro-Tech Laboratory, Skokie, Illinois.

[13] R. F. Nystrom and W. G. Brown, THIS JOURNAL, **69**, 2648 (1947).

[14] R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," Second Edition, John Wiley and Sons, Inc., New York, N. Y., 1940, p. 136.

Cyclopropylmethyl 3,5-dinitrobenzoate was prepared in pyridine from the alcohol and 3,5-dinitrobenzoyl chloride.[15] The product was recrystallized twice from alcohol and obtained in the form of brown plates, m.p. 97.5–99.0°. *Anal.* Calcd. for $C_{11}H_{10}O_6N_2$: N, 10.53. Found: N, 10.41.

3-Buten-1-ol.—3-Buten-1-ol was prepared by treating an ethereal solution of allylmagnesium chloride with gaseous formaldehyde. The alcohol boiled at 112–115° (lit. 112.5–113.5°).[16]

3-Butenyl Benzenesulfonate.—The conversion of 3-buten-1-ol to 3-butenyl benzenesulfonate was performed in the manner described for the preparation of allyl benzenesulfonate.[9] The properties of the ester were: b.p. 110° (1 mm.); $n^{20}D$ 1.5157; d^{20}_4 1.173. *Anal.* Calcd. for $C_{10}H_{12}O_3S$: C, 56.58; H, 5.70; S, 15.10; sapn. equiv., 212.3. Found: C, 56.60; H, 5.73; S, 14.63; sapn. equiv., 212.8.

Cyclopropylmethyl Benzenesulfonate.—The preparation of this ester was patterned after the procedure described for allyl benzenesulfonate.[9] However, chloroform used to extract allyl benzenesulfonate could not be removed effectively by vacuum distillation at room temperature and methylene chloride was a useful substitute for the chloroform. A mixture (26.4 ml.) of 2,4,6-collidine and cyclopropanemethanol (7.92 g.) was cooled to −5°, and freshly distilled benzenesulfonyl chloride (17.6 g.) was added. The rate of addition was such that the temperature was maintained between 0 and 5°. When all of the benzenesulfonyl chloride had been added (2 hours), 10 ml. of methylene chloride was added to give the mixture greater fluidity. The temperature was allowed to rise to 12° and was held there for one hour. The collidine was neutralized by 25 ml. of 10 *N* sulfuric acid, and the temperature did not rise above 18°. The two phases present were separated and the aqueous layer was extracted with methylene chloride. The combined extract was washed repeatedly with 2.5 *N* sulfuric acid and dried over anhydrous potassium carbonate. The solvent was removed under vacuum (0.5 mm.) at room temperature. The ester thus obtained was placed over anhydrous potassium carbonate and stored at −78° until it was used. The yield of ester was 70 ± 8%. Weighed samples of the ester were hydrolyzed in water at the reflux temperature and provided an estimate of its purity; hydrolysis equivalent weight, calcd.: 212.3. Found: 228.5.

The ester could not be distilled in a molecular still[17] at 10^{-4} mm. because of a tendency to decompose which caused the material to splatter. It decomposed more rapidly when ordinary methods of low pressure distillation were attempted.

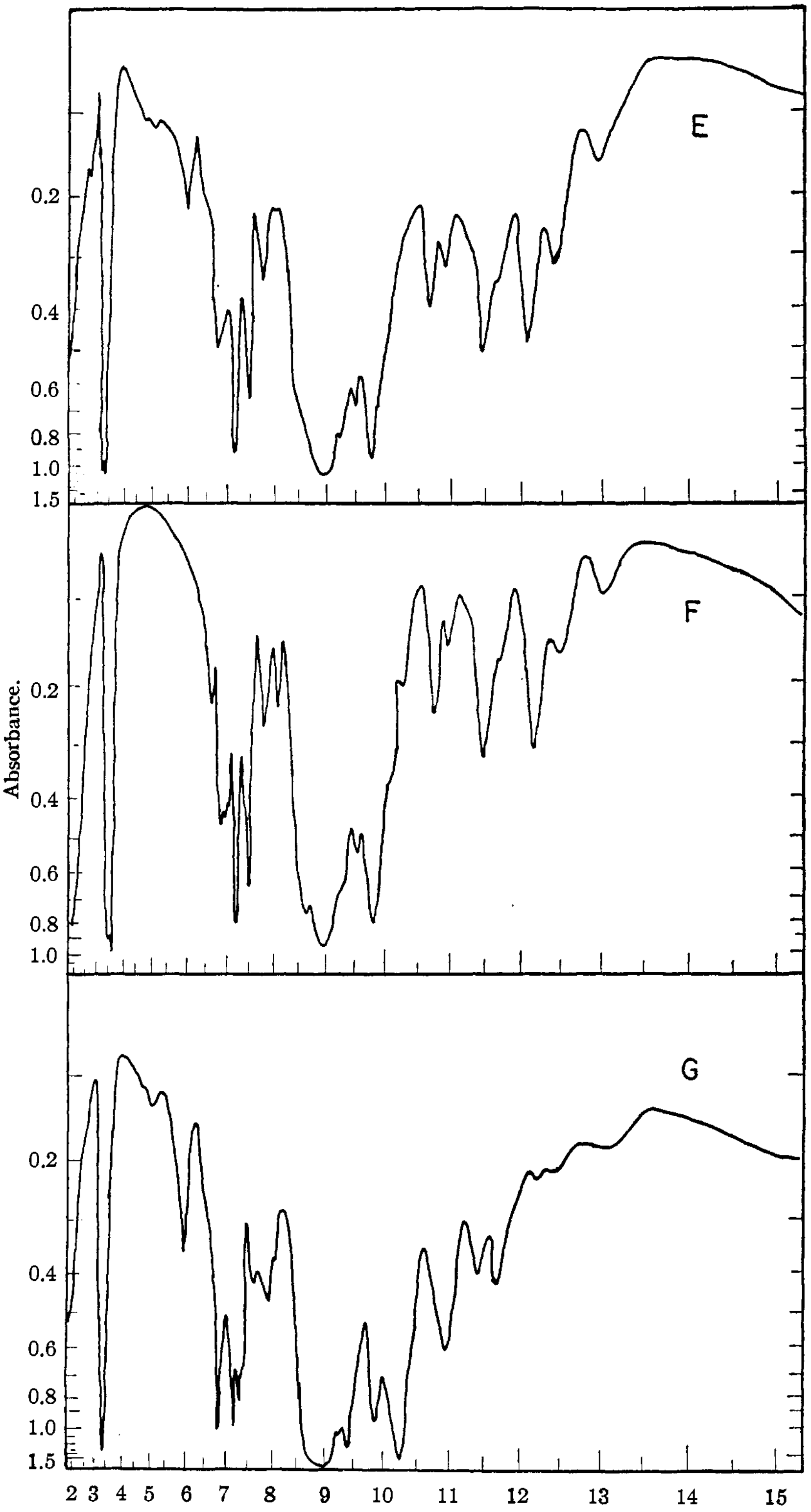

Fig. 2.—Infrared spectra: E, cyclopropylmethyl ethyl ether; F, the ether obtained in the ethanolysis of cyclopropylmethyl benzenesulfonate; G, crotyl ethyl ether.

The Isomerization of Cyclopropylmethyl Benzenesulfonate.—A chloroform solution of the product (obtained by the method described for allyl benzenesulfonate[9]) was dried over anhydrous potassium carbonate for 24 hours. After the solvent was removed under vacuum (20 mm.) the concentrate was distilled in approximately 5-g. portions from a 10-

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(15) *Ibid.*, p. 138.

(16) H. Pariselle, *Compt. rend.*, **148**, 849 (1909).

(17) J. R. Matchett and J. Levine, *Ind. Eng. Chem., Anal. Ed.*, **16**, 580 (1944).

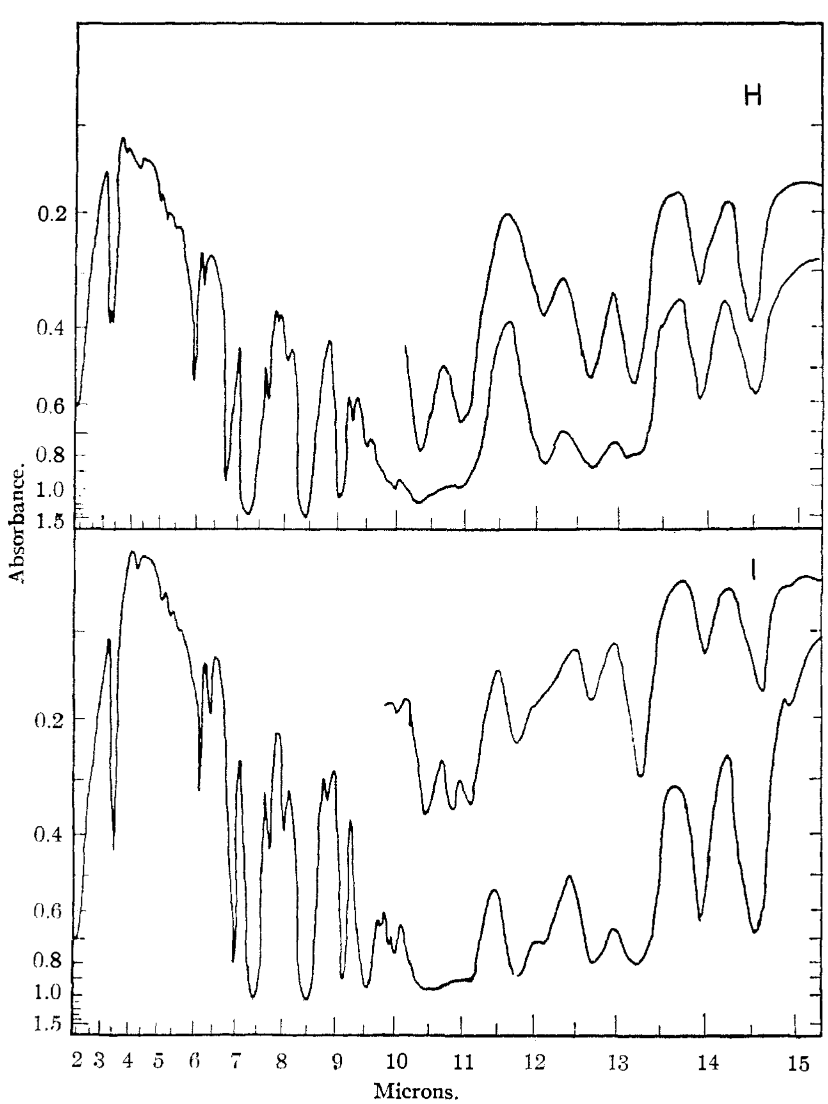

Fig. 3.—Infrared spectra: H, 3-butenyl benzenesulfonate; I, "isomerized cyclopropylmethyl benzenesulfonate." The upper curves were obtained from thin films.

ml. distilling flask containing 0.2 g. of potassium carbonate. A clear, almost colorless distillate was obtained; b.p. 124° (0.9 mm.). The infrared spectrum was similar to that of 3-butenyl benzenesulfonate. *Anal.* Calcd. for $C_{10}H_{12}O_3S$: C, 56.58; H, 5.70; S, 15.10; sapn. equiv., 212.3. Found: C, 56.28; H, 5.64; S, 15.13; sapn. equiv., 211.9.

A portion of this ester was stored for 11 days at 55° over anhydrous potassium carbonate. It distilled in a molecular still when heated 50°(0.001 mm.); $n^{20}{}_D$ 1.5160; $d^{20}{}_4$ 1.183. Its infrared spectrum had many features in common with that of 3-butenyl benzenesulfonate. *Anal.* Calcd. for $C_{10}H_{12}O_3S$: C, 56.58; H, 5.70; S, 15.10. Found: C, 56.54; H, 5.65; S, 15.46. These data suggest that cyclopropylmethyl benzenesulfonate isomerizes readily whenever an attempt is made to distil it.

The rate of alcoholysis of the ester provided a method for its analysis. (See Rate Studies.) A freshly prepared sample of cyclopropylmethyl benzenesulfonate, in contact with anhydrous potassium carbonate at 20°, was 90% isomerized in 24 hours.

The Reaction of Cyclopropylmethyl Benzenesulfonate with a Solution of Sodium Ethoxide in Absolute Alcohol.—A solution of sodium ethoxide (200 ml., 1.7 *M*) was mixed with cyclopropylmethyl benzenesulfonate (38.1 g.; 93% by weight as determined by measurement of its hydrolytic equiv. wt.) and heated at 35° for 11 days. The alcoholic solution was fractionated through a 12 × 915 mm. glass helix packed Todd column. After 89 ml. of distillate (b.p. 76.3–78.4°) had been taken, a further quantity of absolute alcohol (100 ml.) was added to the still pot (to prevent bumping). A total of 140 ml. of distillate was collected. It had an odor characteristic of the butenyl ethers. None of these fractions reacted with bromine in the manner of the butenyl ethyl ethers.

One-half of the distillate was diluted with water (300 ml.) and the mixture extracted with four 50-ml. portions of carbon bisulfide. The extract was dried over potassium carbonate. The dry solution was fractionated through an 8 × 915 mm. nickel spiral-packed Todd column. After removal of the carbon bisulfide, the product distilled at 95.7–99.4° (5.2 g.), mainly at 99.0–99.4° (2.8 g.). The infrared spectrum of the latter fraction was identical with that of cyclopropylmethyl ethyl ether prepared independently. The infrared spectrum of the fore fraction showed in addition, the presence of carbon bisulfide. The yield of cyclopropylmethyl ethyl ether is 65% of the theoretical.

The Reaction of "Isomerized Cyclopropylmethyl Benzenesulfonate" with a Solution of Sodium Ethoxide in Absolute Alcohol.—The "isomerized cyclopropylmethyl benzenesulfonate" (17.1 g.), purified by distillation, and an alcoholic solution of sodium ethoxide (100 ml. of 1.4 *M*) were combined in a round-bottomed flask. The mixture of esters was not completely soluble in this medium. The flask was attached immediately to an 8 × 915 mm. nickel spiral-packed Todd column. The openings of the column were connected by rubber tubing and led into a trap held in Dry Ice. The temperature of the flask was raised until liquid refluxed in the column. The mixture was heated for five hours. A small amount of liquid (0.5 g.) condensed in the trap. It was transferred to a gas holder and an infrared spectrum of the vapor was obtained. Except for weak absorption bands characteristic of ethyl ether, the spectrum was identical with that reported for 1,3-butadiene.[18]

The reaction mixture was cooled and filtered to remove the large amount of solid which had separated from the solution. The crystalline material was washed with absolute alcohol, the washings were combined with the filtrate. The filtrate was returned to the still pot and 40 ml. of 1-hexanol (b.p. 158.0–159.5°) was added to serve as a "chaser." Distillate was obtained which boiled in the range 74–79° (120 g.). There was no appreciable intermediate fraction boiling between 79 and 158°. The amount of unsaturated ether present in the 74–79° fraction was measured by bromination, and the yield of unsaturated ether was 36%.

The first fraction taken, b.p. 74–78° (8.85 g.), contained approximately one-third by weight (2.9 g.) of an unsaturated ether. The infrared spectrum was identical with that of a synthetic mixture of one part 3-butenyl ethyl ether and two parts ethanol. The later fractions b.p. 78–79° (33.1 g.) contained less unsaturated ether (estimated by analysis for unsaturation, 1 g.). The solution was too dilute to provide a significant infrared spectrum. The ether was isolated by the procedure described above for the isolation of cyclopropylmethyl ethyl ether from an alcoholic solution. The product distilled at 92–95° (0.40 g.); $n^{20}{}_D$ 1.4010. Its infrared spectrum was almost identical with that of 3-butenyl ethyl ether. The fraction is therefore mainly 3-butenyl ethyl ether.

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[18] R. S. Rasmussen and R. R. Brattain, *J. Chem. Phys.*, **15**, 131 (1947).

TABLE I

PROPERTIES OF ETHYL ETHERS PREPARED IN THIS STUDY

Ethyl ether	B.p., °C.	$n^{20}\mathrm{D}$	$d^{20}{}_4$	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Cyclopropylmethyl[a]	99.5–100.8	1.4050	0.816	71.95	71.50	12.08	11.80
3-Butenyl[b]	90.7–90.8	1.3978	.779	71.95	71.72	12.08	11.57
Crotyl[c]	102–103	1.4036	.777	71.95	71.95	12.08	11.80

[a] Michiels[21] reports b.p. 98–101° for the ether obtained from the reaction of cyclopropylmethyl iodide and alcoholic potassium hydroxide. [b] Pariselle[22] prepared this ether from allylmagnesium bromide and chloromethyl ethyl ether; b.p. 90°; $n^{17}\mathrm{D}$ 1.396. [c] *trans*-Crotyl ethyl ether[23]; b.p. 100.4–100.5; $n^{20}\mathrm{D}$ 1.4040; $d^{20}{}_4$ 0.7846.

3-Butenyl Ethyl Ether.—This ether was prepared by the reaction of the sodium salt of 3-buten-1-ol and diethyl sulfate. The salt was obtained from the reaction of the alcohol with "sodium naphthalene" in dioxane.[19]

To a mixture of carefully purified dioxane (250 ml.), and naphthalene (36 g.) maintained in an inert atmosphere, small lumps of sodium (6 g.) were added. The mixture was slowly heated to the reflux temperature. At the end of 20 hours, all of the sodium was dissolved and a brown sludge had separated from the solution. The solution was cooled in ice and 3-buten-1-ol (18.9 g.) was added cautiously. This was followed by 41.5 g. of diethyl sulfate. The mixture was allowed to stand at room temperature overnight.

The reaction mixture was distilled rapidly through a 12 × 915 mm. Todd column. The material boiling below 100° was purified by extraction with dilute sodium hydroxide and dried over Drierite. Fractionation of the material yielded a product of b.p. 90–91° (10.0 g., 26% of the theoretical). A central fraction had the properties given in Table I.

Cyclopropylmethyl Ethyl Ether.—Using the techniques described above, the lithium salt of cyclopropanemethanol was prepared from the alcohol (14.4 g.), and lithium hydride (1.59 g.) in butyl ether (100 ml.). A voluminous white precipitate formed when the flask was heated on a steam-bath for one-half hour. The mixture was heated for two hours longer and then cooled. Diethyl sulfate (30.0 g.) diluted with 25 ml. of *n*-butyl ether was added over a period of 40 minutes. The mixture was heated on the steam-bath and as the reaction proceeded more *n*-butyl ether was added to maintain a fluid mixture. The reaction was completed with the reaction flask attached to an 8 × 915 mm. nickel spiral-packed Todd column, and the material which boiled in the range 68–140° was collected (21.8 g.). The crude product was dried over solid sodium hydroxide and refractionated. The ether forms an azeotrope with ethyl alcohol; b.p. 78.0–78.1°; $n^{20}\mathrm{D}$ 1.3749. After the removal of the azeotrope (6.0 g.), cyclopropylmethyl ethyl ether distilled at 99.5–100.8° (5.0 g.); $n^{20}\mathrm{D}$ 1.4050. The properties of the product which was redistilled from sodium are given in Table I. Cyclopropylmethyl ethyl ether reacts slowly with bromine in carbon tetrachloride.

Crotyl Ethyl Ether.—This ether was prepared from crotyl chloride and sodium ethoxide in the way described by Roberts, Young and Winstein.[20] The properties are reported in Table I.

Rate Studies.—The rate of reaction of 3-butenyl benzenesulfonate with sodium ethoxide in anhydrous ethanol was performed in the manner described for allyl benzenesulfonate.[9] The reactants were contained in volumetric flasks immersed in thermostats controlled to ±0.05°. Samples were removed by pipet for analysis. For the solvolysis of esters performed at 55° or followed for periods longer than 24 hours at 35 or 55°, the procedure was varied to avoid volatilization of materials. Aliquots were transferred to test-tubes and sealed using the usual techniques.

For the reaction of 3-butenyl benzenesulfonate with sodium ethoxide, the second-order rate constants calculated for sequential points in a run did not show a trend (Table II). However, "isomerized cyclopropylmethyl benzenesulfonate" (*e.g.*, cyclopropylmethyl benzenesulfonate which had been allowed to stand at room or higher temperature for a day or more and then distilled) did not react with sodium ethoxide according to any simple reaction order. The calculated bimolecular rate constants decreased as the reaction proceeded (Table III) but was of the same order of magnitude as that of 3-butenyl benzenesulfonate. This may be explained if the isomeric esters include one such as cyclobutyl benzenesulfonate which would be expected to react more slowly with sodium ethoxide than the 3-butenyl ester.

TABLE II

RATE OF REACTION OF 3-BUTENYL BENZENESULFONATE WITH NaOEt IN ABSOLUTE ETHANOL AT 34.8°

3-Butenyl benzenesulfonate, 0.0289 *M;* sodium ethoxide 0.0472*M*

Time, min.	Reacted, %	$k_2 \times 10^4$(l. mole^{-1} sec.$^{-1}$)
210	22.0	4.55
479	40.2	4.42
710	52.6	4.60
1392	71.3	4.43
1643	76.2	4.48
1990	80.6	4.40
2200	82.0	4.23
2843	88.9	4.53
3099	92.1	5.03
	Average	4.52
	Weighted av.	4.55

TABLE III

RATE OF REACTION OF "ISOMERIZED CYCLOPROPYLMETHYL BENZENESULFONATE" WITH NaOEt IN ETHANOL AT 34.8°

Ester 0.0253 *M;* NaOEt 0.0446 *M*

Time, min.	Reacted, %	$k_2 \times 10^4$ (l. mole^{-1} sec.$^{-1}$)
354	26.1	3.47
1290	55.3	2.85
1798	62.5	2.60
2740	71.9	2.37
3314	75.4	2.20
4254	80.6	1.97
4722	79.8	1.83
8854	91.7	1.77

The Reaction of Cyclopropylmethyl Benzenesulfonate with Ethanol.—Since this ester hydrolyzes more rapidly than allyl benzenesulfonate, a modification was made in the quenching technique. A mixture of 25 ml. of carbon tetrachloride and 50 ml. of water was chilled in ice and made just basic to phenolphthalein. The

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(19) (a) R. G. Stevens and S. A. V. Deans, *Canada J. Research*, **17B**, 290 (1939); (b) N. D. Scott, J. F. Walker and V. L. Hansley, THIS JOURNAL, **58**, 2442 (1936).

(20) J. D. Roberts, W. G. Young and S. Winstein, *ibid.*, **64**, 2157 (1942).

(21) L. Michiels, *Bull. soc. chim. Belg.*, **24**, 396 (1910).

(22) H. Pariselle, *Compt. rend.*, **150**, 1056 (1910).

(23) M. Lepingle, *Bull. soc. chim. France*, [4] **39**, 865 (1926).

sample tube was removed from the thermostat and at a recorded time 10 ml. of cold carbon tetrachloride was added to the tube. The contents of the tube were transferred quantitatively to the cold carbon tetrachloride–water mixture. The solution was titrated with 0.04 *M* sodium hydroxide. Because the end-point fades rather rapidly the rate of fading was measured and used to extrapolate the buret reading to the time of mixing of the reactants with water.

Because of the thermal instability of the ester, it was not obtained in a purity greater than about 90%. The remainder was probably solvent which was not removed. The initial concentration of the ester in a kinetic run was therefore calculated from the value of the titer of the reaction mixture which was attained at the end of eight to nine times the approximate half time for the reaction. If the sample of ester used had contained as much as 20% of either 3-butenyl benzenesulfonate or the mixture obtained when cyclopropylmethyl benzenesulfonate isomerizes, then the acid produced by their solvolysis would cause an error of about 1% in the calculated initial concentration of cyclopropylmethyl benzenesulfonate. Since the samples of ester used contained approximately 85% of cyclopropylmethyl benzenesulfonate, the error in the estimated initial concentration due to the presence of isomeric esters is less than one per cent.

The uncertainty caused by the incomplete quenching of the reaction provides a larger error, about 2 to 5% in the calculated rate constant and the probable uncertainty in the rate constants for the solvolysis of cyclopropylmethyl benzenesulfonate is estimated to be 10%. A typical run is given in Table IV.

TABLE IV

THE SOLVOLYSIS OF CYCLOPROPYLMETHYL BENZENESULFONATE IN ANHYDROUS ETHYL ALCOHOL

Concentration of ester from "infinity" titer, 0.0160 *M*; unrearranged ester in sample, 84.0%

Time, min.	Reacted, %	$k_1 \times 10^5$ (sec.$^{-1}$)
21	9.4	(7.8)
34	15.0	(8.0)
59	22.5	7.2
97	31.9	6.7
161	46.8	6.5
246	61.2	6.5
326	72.5	5.5
441	83.7	6.7
1430	100.0	...
	Average	6.5 (6.8)
	Weighted av.	6.3

Calculation of Rate Constants.—The bimolecular rate constants (k_2) were calculated from the equation

$$k_2 = \frac{2.303}{(a - b)t} \times \log \frac{b(a - x)}{a(b - x)}$$

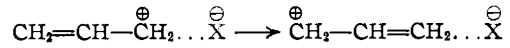
where a and b are the initial concentrations of the ester and the sodium ethoxide, respectively, and x is the concentration of ester which has reacted at the time t.

The first order rate constant is a weighted average of all of the individual values for k. The initial concentration of ester is represented by a, the other symbols are as given above. The rate constants which are listed in Table V are weighted averages for each run.

Significance of Results

The data support the conclusion that cyclopropylmethyl benzenesulfonate solvolyzes in absolute alcohol by a process of the S_N1 type. The reactivity of the ester is remarkable, its rate of alcoholysis being greater than that of allyl benzenesulfonate by a factor of 10. The reverse order of reactivity was expected from considerations that the cyclopropyl group would behave as a less effective counterpart of the vinyl group in accelerating displacement reactions at an adjacent saturated carbon atom. The expected order of reactivity apparently is found for the S_N2 type of reaction.

Similar explanations have been offered to account for the enhanced reactivity toward solvolysis of allyl[24] and cyclopropylmethyl[10,25] halides relative to the solvolysis of saturated alkyl halides. The transition state for the solvolysis of an allyl halide is said to be stabilized by the contribution of the resonance forms I and II.



$$\underset{\text{I}}{CH_2{=}CH{-}\overset{\oplus}{C}H_2 \ldots \overset{\ominus}{X}} \longrightarrow \underset{\text{II}}{\overset{\oplus}{C}H_2{-}CH{=}CH_2 \ldots \overset{\ominus}{X}}$$

I II

The analogous forms for the solvolysis of cyclopropylmethyl halide are

TABLE V

REACTION RATES OF THE BENZENESULFONATES IN ABSOLUTE ETHANOL

Benzenesulfonate	Temp., °C.	Ester, mole/l.	NaOEt, mole/l.	k_1, sec.$^{-1}$	k_2, l./mole-sec.
3-Butenyl	34.79	0.0289	0.0472	....	4.55×10^{-4}
3-Butenyl	34.79	.0217	.0417	....	4.38×10^{-4}
3-Butenyl	34.79	.0298	....	2.2×10^{-7}	....
3-Butenyl	55.30	.0221	....	2.3×10^{-7}	....
3-Butenyl	55.30	.0198	....	2.0×10^{-7}	....
Cyclopropylmethyl	20.13	.0204	....	5.7×10^{-5}	....
Cyclopropylmethyl	20.13	.0160	....	6.3×10^{-5}	....
Cyclopropylmethyl	20.13	.0175	.0266	7.2×10^{-5}	....
"Isomerized cyclopropylmethyl"	34.79	.0215	....	7×10^{-7}[a]	....
Allyl	20.1	....	....	4.2×10^{-6}[b]	2.7×10^{-3}

[a] Apparent first order rate constant for early part of the reaction. [b] Constants are taken from reference 9.

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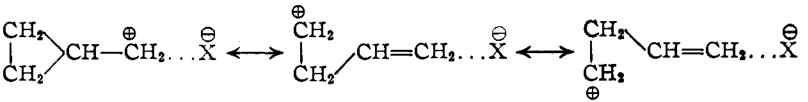
(24) M. Polanyi, *Trans. Faraday Soc.*, **37**, 377 (1941).

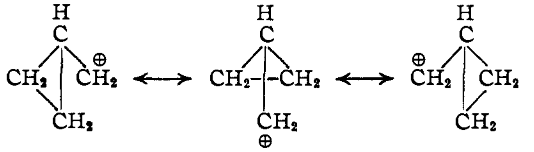
(25) J. D. Roberts, W. Bennett and R. Armstrong, THIS JOURNAL, **72**, 3329 (1950).



III IV V

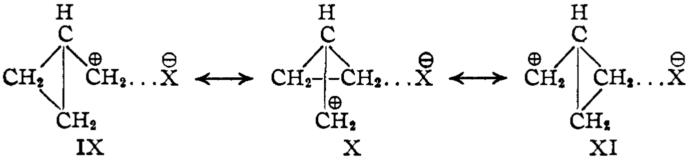
The hyperconjugation which can be represented for saturated alkyl halides is thought to provide lesser stabilization of the transition state. Clearly, these formulations are intended to describe the interaction between an unsaturated center and a positive charge. Judging from the relative displacement of ultraviolet absorption bands for vinyl- and cyclopropylcarbonyl compounds,[3a] or benzenes,[3c] the interaction between a vinyl group and a positive center should be the more effective.

The remarkable facility with which cyclopropylmethyl benzenesulfonate solvolyzes, therefore, requires an explanation in which the cyclopropyl group is taken to be something other than a simple though less polarizable analog of the vinyl group. A clue to this problem may be gained from an examination of a possible structure for the cyclopropylmethyl carbonium ion represented by the hybrid VI—VII. The structure of this resonance hybrid is noteworthy for its symmetry, suggesting that the three methylene groups are equivalent. To gain this symmetry the bond angles and distances must be changed from those present in the parent compound. The importance of the symmetry factor in resonance stabilization of an ion has been stressed previously.[26]



VI VII VIII

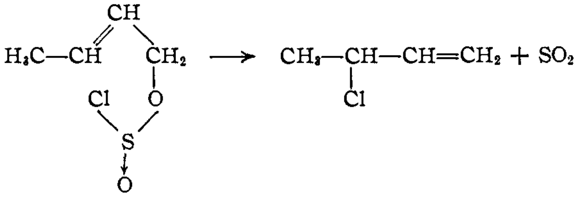
The above argument for the structure of the carbonium ion can be transposed to a discussion of the transition state for solvolysis. In the transition state the structures IX → XI would be considered. Only two of the structures are equivalent but the third approaches the energy of the other two as the ions separate during the solvolysis.



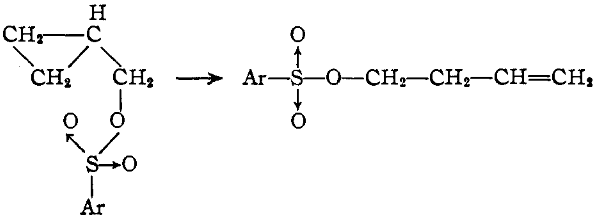
IX X XI

This hypothesis explains why the cyclopropyl group is able to accelerate the S_N1 type of replacement at a neighboring carbon atom more effectively than it can accelerate the S_N2 type of mechanism. It also explains the predominant formation of ethyl cyclopropylmethyl ether in the solvolysis; attack of a molecule of solvent at any one of three carbon atoms would lead to identical products. It does not exclude the possibility for rearranged products, for example an attack of the solvent at the carbon atom bearing only one hydrogen atom would yield a cyclobutane derivative.

The thermal isomerization of cyclopropylmethyl benzenesulfonate yields chiefly 3-butenyl benzenesulfonate. The ease with which this is accomplished suggests a mechanism of intramolecular rearrangement similar to the one postulated by Roberts, Young and Winstein[22] for the conversion of crotyl chlorosulfite XII to methylvinylcarbinyl chloride XIII. The geometry of the molecules of cyclopropylmethyl benzenesulfonate is so related as to suggest a common mechanism XIV → XV.



XII XIII



XIV XV

Acknowledgment.—We are indebted to Mrs. Lorna Patterson of the Armour Research Foundation who determined most of the infrared absorption spectra. The infrared spectrum of 1,3-butadiene was determined by Dr. Richard Bernstein. We are also grateful for his assistance in the interpretation of the spectra.

Infrared Spectra.—The infrared spectra were determined with a Perkin-Elmer Model 12C single beam recording spectrophotometer. The mechanical slit drive was used and the cell length was 0.025 mm. Used in this way, the ordinate, absorbance, approximates a linear scale of per cent. transmission and the plot is suitable for "fingerprinting" compounds.

CHICAGO, ILLINOIS RECEIVED JANUARY 31, 1951

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(26) L. Pauling, "Nature of the Chemical Bond," Second Edition, Cornell University Press, Ithaca, New York, 1945, p. 214.