

there was isolated 50 mg. of catechol, m.p. and mixed m.p. 101–103°, from the reaction product.

A mixture of 0.34 g. of VIII, m.p. 149°, 0.66 g. of hexachlorocyclopentadiene and 2 ml. of benzene was heated in a sealed tube at 155–160° for 21 hours. The mixture was taken up in 10 ml. of benzene and passed through a short column of alumina to remove much of the color. Concentration and addition of a little Skellysolve C yielded a total of 0.80 g. (85%) of crystalline X, m.p. 198–203°. Recrystallization from Skellysolve B containing a little benzene afforded a good yield of a fairly pure isomer, m.p. 200.0–200.6°, of the cyclic carbonate of 5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydro-1,4-epoxy-5,8-methanonaphthalene-2,3-diol (X).

Anal. Calcd. for $C_{12}H_6O_4Cl_6$: C, 33.8; H, 1.4; Cl, 49.8. Found: C, 33.7; H, 1.4; Cl, 49.8.

f. Anthracene.—A mixture of 0.52 g. of pure anthracene 2.06 g. of I and 4 ml. of dry benzene was sealed in a tube and heated at 160–170° for 12 hours. After removal of unchanged I by distillation there was obtained 0.68 g. (88%) of adduct, m.p. 254–257° by crystallization from benzene

Skellysolve B. The analytical sample of the cyclic carbonate of *cis*-9,10-dihydro-9,10-ethanoanthracene-11,12-diol formed colorless needles, m.p. 259.0–259.6°.

Anal. Calcd. for $C_{17}H_{12}O_3$: C, 77.2; H, 4.6. Found: C, 77.3; H, 4.8.

On hydrolysis of this adduct with warm 40% sodium hydroxide for one hour there was obtained a quantitative yield of *cis*-9,10-dihydro-9,10-ethanoanthracene-11,12-diol, m.p. 201.9–202.7°. ²⁵

Anal. Calcd. for $C_{16}H_{14}O_3$: C, 80.7; H, 5.9. Found: C, 80.9; H, 6.0.

Oxidation of 0.13 g. of diol at 13–17° for 5 hours and at 0° for 11 hours with acid dichromate¹⁸ afforded a small yield of *cis*-9,10-dihydroanthracene-9,10-dicarboxylic acid,²⁴ m.p. 281–284°.

(23) All melting points for analytical samples are corrected. Analyses by Galbraith and Clark Analytical Laboratories.

(24) J. Mathieu, *Ann. chim.*, [11] **20**, 215 (1945), gives m.p. 283°.

COLUMBUS 10, OHIO

[CONTRIBUTION NO. 334 FROM THE CHEMICAL DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY]

Synthesis and Polymerization of Vinyl Sulfonates¹

BY J. C. SAUER AND J. D. C. WILSON

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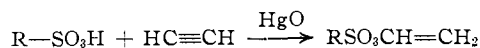
Monomeric vinyl sulfonates have been prepared by the direct vinylation of the sulfonic acid with acetylene in yields of 50–75%. Vinyl methanesulfonate has been homopolymerized and copolymerized with a variety of vinyl monomers.

Esters of vinylsulfonic acid (I), in which R is an alkyl group, and their polymers are known.² However, monomeric vinyl esters of sulfonic acids (II) have not hitherto been reported.



Copolymers of vinyl sulfonates (II) have been prepared indirectly by partially esterifying a preformed polyvinyl alcohol or a hydrolyzed ethylene/vinyl acetate copolymer with a sulfonyl chloride.³ Homopolymers of vinyl sulfonates (II) or other copolymers have not been reported, due to the inaccessibility of the monomeric vinyl esters needed for such an investigation.

It has been found that monomeric vinyl sulfonates II can be prepared by the direct vinylation of a sulfonic acid with acetylene in an ether solvent in the presence of mercuric oxide catalyst.⁴



The R group can be methyl, butyl, phenyl or *p*-tolyl, and the yields range from 50 to 75%.

An ether solvent such as dioxane or dibutyl ether has given best results in this synthesis; oxonium salt formation of the sulfonic acid with the ether group may be involved. Attempts to isolate vinyl esters in the absence of solvent or in the presence of benzene were unsuccessful.

(1) Presented at the Cincinnati Meeting of the American Chemical Society, March, 1955.

(2) Abstracts of the September, 1950, meeting of the American Chemical Society at Chicago, p. 10-J. V. V. Alderman and W. E. Hanford, U. S. 2,348,705 (1944). Z. Földi, *Ber.*, **53B**, 1836 (1920).

(3) D. D. Reynolds and W. O. Kenyon, *THIS JOURNAL*, **72**, 1584 (1950); W. H. Sharkey, U. S. Patent 2,395,347 (1946).

(4) J. C. Sauer, U. S. 2,667,469 (1954).

A convenient procedure for carrying out the synthesis involved injecting acetylene at 7–18 atmospheres pressure into a rocker bomb containing the sulfonic acid, solvent, and catalyst heated to 50–60°. Acetylene was repressured as required. The vinyl esters were isolated by distillation. These products were characterized by spectral and elemental analyses, hydrogen number and saponification number. In addition, vinyl benzenesulfonate was hydrogenated to ethyl benzenesulfonate which was compared with an authentic sample.

Polymerization studies were carried out mainly with vinyl methanesulfonate. A low softening homopolymer was obtained in conversions up to 30% in aqueous medium using a persulfate-bisulfite initiator. Vinyl methanesulfonate was also found to copolymerize with a variety of vinyl monomers yielding compositions containing vinyl methanesulfonate in a wide range of proportions. However, the yields, inherent viscosities, and stick temperatures of the copolymers decreased with increasing vinyl methanesulfonate content.

Vinyl benzenesulfonate was converted into viscous, tacky homopolymers with polymerization initiators of the ionic or free radical types.

During the course of this work, one of us developed a sensitization to unidentified substances. Several other persons who worked with the vinyl sulfonates were not affected. Although the adverse physiological effects have not been definitely assigned to the vinylsulfonates, care should be used in handling them.

Experimental

Source and Purification of the Materials.—Methanesulfonic acid was purchased from the Eastman Kodak Company and was purified by distillation at the lowest pressure

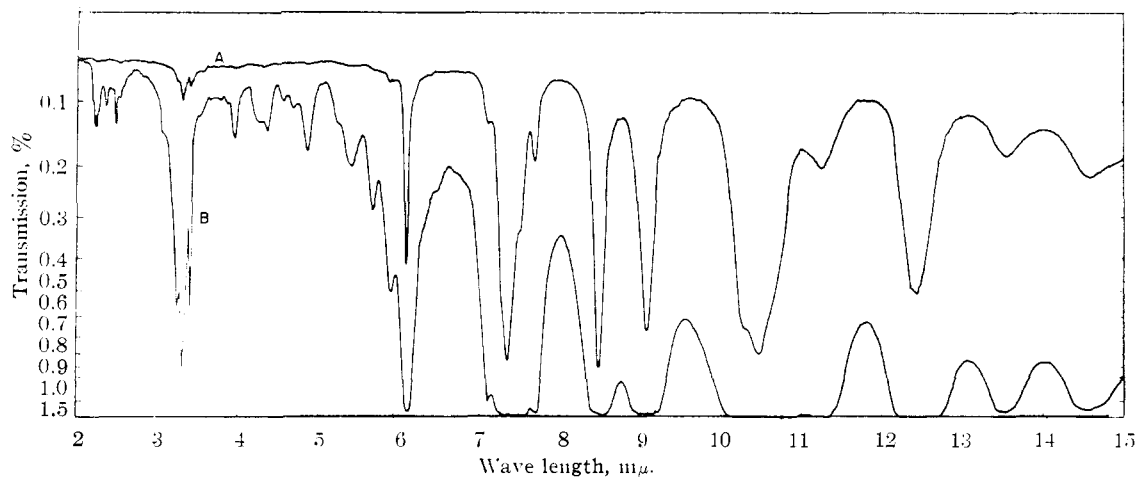


Fig. 1.—A, vinyl methanesulfonate; spectrum determined on thin layer between plates without spacers. B, vinyl methanesulfonate; spectrum determined on sample contained in 0.04 mm. cell.

of the oil pump, b.p. 131° (0.5 mm.), using a simple vapor bath apparatus with xylene as the heating vapor. *Anal.* Calcd. for $\text{CH}_3\text{O}_2\text{S}$: neut. equiv., 96. Found: neut. equiv., 96.5. Benzene and *p*-toluenesulfonic acids were purchased from the Eastman Kodak Company as the monohydrates and were dehydrated by heating in a bath at 60 – 80° for 6–10 hours under a vacuum of 1 mm. The butanesulfonic acid was an impure grade obtained through the chlorosulfonation of a hydrocarbon gas mixture containing mainly *n*-butane; the exact purity of this sulfonic acid mixture was not determined. Dioxane was commercial grade purified by distillation from sodium. Commercial grade acetylene obtained from the Air Reduction Company was passed through a series of scrubbers containing, in order, Fieser solution, calcium chloride, activated alumina and sodium hydroxide pellets. The infrared spectra were determined on a Perkin-Elmer Model 21 double beam spectrometer. The yields of the vinyl sulfonates are based on the amount of sulfonic acid consumed.

Vinylation of Methanesulfonic Acid.—A mixture of 130 g. of methanesulfonic acid, 100 ml. of dibutyl ether and 6 g. of yellow mercuric oxide was transferred to a 500-ml. stainless steel rocker bomb which had been previously flushed with nitrogen. The bomb was pressure tested with nitrogen at 36 atmospheres pressure, then cooled in a Dry Ice-methanol cooling bath and evacuated to about 10 mm. pressure. The equipment was installed behind a heavy barricade, and all operations with acetylene were controlled from the outside. With a bomb temperature slightly under 0° , acetylene at 8 atmospheres pressure was introduced and the reaction mixture was heated to 60° . When this temperature was reached, additional acetylene pressure was applied until the bomb gage reached 16 atmospheres. The pressure was maintained at 16–17 atmospheres by periodic repressuring with acetylene for 3 hours. The bomb was then cooled to room temperature, pressure released and the contents removed. The reaction mixture was washed with 10% aqueous potassium carbonate and the oily layer was dried over anhydrous potassium carbonate. After removing the dibutyl ether, the residual liquid distilled at 64 – 65° (5 mm.). There was obtained 117 g. of vinyl methanesulfonate, 71% yield, n_D^{20} 1.4271. Redistillation through a helix-packed fractionating column of 25 theoretical plates gave a product boiling at 36° (1 mm.), 71° (10 mm.), n_D^{20} 1.4273.

To gain some insight into the thermal stability of vinyl methanesulfonate, samples were thoroughly flushed with nitrogen and heated in an atmosphere of nitrogen. The ester underwent no detectable decomposition in 20 hours heating at 73° . At 175° a sample darkened almost immediately and underwent very vigorous decomposition accompanied by a rapid rise in temperature. Addition of powdered sodium carbonate did not improve the thermal stability at 175° . *Anal.* Calcd. for $\text{C}_3\text{H}_5\text{O}_2\text{S}$: C, 29.5; H, 4.9; S, 26.3; sapon. no., 460. Found: C, 29.8, 29.8; H, 5.0, 4.9; S, 26.6, 26.6; sapon. no., 481, 486. Infrared spectral data are shown in Fig. 1.

Vinylation of Butanesulfonic Acid.—A solution containing 50 g. of butanesulfonic acid, 100 ml. of dioxane and 4 g. of yellow mercuric oxide was treated with acetylene under a gage pressure of 7–11 atmospheres during 3.9 hours at 20 – 33° . The reaction mixture was taken up in ether, washed with aqueous potassium carbonate and the oily layer was dried over anhydrous potassium carbonate. After removing the ether and dioxane, a crude cut distilling at 35 – 79° (1 mm.) (27.2 g.) was composited with 11.4 g. of crude vinyl ester from another run. From the composited sample there was obtained 27.5 g. of product in 5 fractions distilling at 111 – 119° (24–25 mm.). The sulfur analyses of these fractions varied from 15.53–18.59%. A careful redistillation of these fractions gave 10 g. of a central fraction, boiling point 98 – 98.2° (15 mm.), n_D^{20} 1.4390. *Anal.* Calcd. for $\text{C}_4\text{H}_9\text{O}_2\text{S}$: C, 43.8; H, 7.3; S, 19.5. Found: C, 44.5; H, 7.9; S, 19.4.

Vinylation of Benzenesulfonic Acid.—A mixture of 100 g. of benzenesulfonic acid, 50 g. of dioxane and 5 g. of mercuric oxide was treated with acetylene under a gage pressure of 7–14 atmospheres for 9.5 hours at 35 – 65° . The crude reaction mixture was taken up in ether, washed with aqueous potassium carbonate, dried over anhydrous potassium carbonate and subjected to a crude, rapid distillation at 5–10 mm. The distillate thus obtained was redistilled and the fraction distilling at 95° (0.5 mm.) to 101° (1.5 mm.) weighed 61.7 g., n_D^{20} 1.5161 (53% yield). *Anal.* Calcd. for $\text{C}_8\text{H}_9\text{O}_2\text{S}$: C, 52.2; H, 4.3; S, 17.4; sapon. no., 306; H_2 no., 0.0108. Found: C, 52.5, 52.7; H, 5.0, 4.8; S, 17.2, 17.6; sapon. no., 317.8, 318.8; H_2 no., 0.0107, 0.0109; d_4^{20} 1.2263.

Additional Characterization of Vinyl Benzenesulfonate.
(a) **Molecular Refractivity.**—The *M_R* value for the SO_3 function in sulfonates apparently has not been reported in the literature. However, by substituting known values in ethyl benzenesulfonate, the SO_3 function was determined by difference to be 9.53. Using this value, the theoretical *M_R* for vinyl benzenesulfonate is 45.28 and the found value is 45.33.

(b) **Hydrogenation of Vinyl Benzenesulfonate.**—Fifteen grams of vinyl benzenesulfonate was dissolved in 40 ml. of dioxane, 0.05 g. of platinum-on-charcoal catalyst was added, and the solution was hydrogenated at room temperature and 1000 lb./sq. in. hydrogen pressure. The ethyl benzenesulfonate thus obtained distilled at 107° (0.9 mm.), n_D^{20} 1.5067. An authentic sample of ethyl benzenesulfonate purchased from Eastman Kodak Company distilled at 107° (0.9 mm.), n_D^{20} 1.5070.

Care must be used in the distillation of vinyl benzenesulfonate. Occasionally vigorous decomposition took place, particularly during the final stages of the distillation. No difficulties of this nature were noted with the aliphatic sulfonates.

Vinylation of *p*-Toluenesulfonic Acid.—The procedure outlined above was used; a mixture of 60 g. of *p*-toluenesulfonic acid, 50 ml. of dioxane and 4 g. of yellow mercuric oxide was treated with acetylene during 3.3 hours at 32 – 55° at a

gage pressure of 7–18 atmospheres. There was obtained 39.6 g. of vinyl ester distilling at 106.2–107.5° (0.3 mm.), n_D^{20} 1.5187 (57%). *Anal.* Calcd. for $C_9H_{10}O_2S$: C, 54.6; H, 5.1; S, 16.1. Found: C, 55.3, 55.0; H, 5.4, 5.3; S, 16.0, 16.1.

Polymerization of Vinyl Methanesulfonate (VMS).—A round-bottomed flask equipped with stirrer, thermometer and reflux condenser, was flushed with nitrogen and charged with 150 ml. of deoxygenated water, 10.0 g. of vinyl methanesulfonate, 0.2 g. of potassium persulfate and 0.4 g. of sodium bisulfite. The mixture was stirred without external heating. It became milky after 20 minutes with no rise in temperature. Stirring was stopped after 8 hours. Coagulation by addition of 15 ml. of alum solution⁵ and steaming yielded a white polymer, which was washed with methanol. It was then dissolved in acetone and reprecipitated in methanol twice. After drying over P_2O_5 for 30 minutes, the polymer had discolored slightly in several spots and was stored in Dry Ice. At this time it was a white solid, weighing 2.2 g. (yield 22%). Relative viscosity of a 0.46% cyclohexanone solution at 25° was 1.121; inherent viscosity, 0.25. *Anal.* Calcd. for $(C_3H_5O_3S)_x$: S, 26.3. Found: S, 25.2, 25.4.

Transparent films, which softened just above room temperature, were pressed at 25°. When dry, the polymer darkened rapidly, but it could be stored under water indefinitely without discoloration, regardless of the acidity of the water.

Mechanism of Decomposition of Polyvinyl Methanesulfonate.—The infrared spectrum of a polyvinyl methanesulfonate film was recorded at successive time intervals in an effort to determine the chemical changes taking place during decomposition. Absorption bands characteristic of ethylenic double bonds were found at 6.0 μ , and this absorption increased in succeeding spectra. This has been interpreted as being caused by increasing carbon-carbon unsaturation. An absorption band developed at 9.5 μ where ionic sulfonates absorb. This band was not visible in the first spectrum but became quite definite in later spectra. A band at 2.9 μ appeared to be developing in the later spectra. This is in a region where hydroxyl absorbs and may corroborate the formation of sulfonic acid groups. Strong absorption bands

(5) The alum solution was prepared by dissolving 200 g. of aluminum potassium sulfate in 200 cc. of concentrated HCl and diluting with 2 l. of H_2O .

at about 7.5 and 8.5 μ , which are characteristic of $-SO_3-$, did not change noticeably. These results are interpreted as indicating that during the decomposition of polyvinyl methanesulfonate, methanesulfonic acid is eliminated with the introduction of ethylenic linkages into the polymer.

Copolymers of Vinyl Methanesulfonate.—Copolymers of vinyl methanesulfonate with vinyl acetate, acrylonitrile, styrene, methyl methacrylate, methyl acrylate and allylidene diacetate were prepared by similar procedures. Acrylonitrile copolymers containing 7–74% by weight of vinyl methanesulfonate and vinyl acetate copolymers containing 11–78% by weight of vinyl methanesulfonate were examined for the effect of VMS content on physical properties. As indicated in the tables below, the yields, inherent viscosities and stick temperatures decrease with increasing vinyl methanesulfonate content.

ACRYLONITRILE/VINYL METHANESULFONATE COPOLYMERS

VMS content wt., %	Conversion, %	Inherent viscosity	Stick temp., °C.
7	85	0.90	200
22	10	.41	145
35	57	.28	115
60	36	.20	110
74	32	.13	110

VINYL ACETATE/VINYL METHANESULFONATE COPOLYMERS

VMS content wt., %	Conversion, %	Inherent viscosity	Stick temp., °C.
11	71	0.33	68
17	73	.11	..
50	28	.08	49
78	34	.04	36

Polymerization of Vinyl Benzenesulfonate.—A solution of 5 g. of vinyl benzenesulfonate and 0.1 g. of 1,1-azodicyclohexanecarbonitrile was heated at 100° for 4 hours in an atmosphere of deoxygenated nitrogen. During this time the monomer polymerized to a soft, sticky, extremely viscous homopolymer.

Vinyl benzenesulfonate polymerized vigorously with evolution of heat when 0.1 g. of a boron trifluoride-methanol addition compound was added to 2 g. of the monomer. The resulting homopolymer was very viscous at room temperature.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, GEORGIA INSTITUTE OF TECHNOLOGY]

Decarboxylation. II. The Stereochemistry of the Transformation of *cis*-Cinnamic Acid Dibromide to β -Bromostyrene^{1,2}

BY ERLING GROVENSTEIN, JR., AND SPYROS P. THEOPHILOU

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The stereochemistry of the conversion of sodium or potassium salts of *cis*-cinnamic acid dibromide to β -bromostyrene has been studied in solvents acetone, ethanol and water. In the first two solvents the β -bromostyrene formed is found to be essentially 100% *trans*-isomer while in water about 97% *trans* and 3% *cis*. These results are compared with those obtained with *trans*-cinnamic acid dibromide and are discussed in light of probable mechanisms for the decarboxylation. Improved procedures are given for the preparation of *cis*-cinnamic acid and *cis*-cinnamic acid dibromide.

The stereochemistry and mechanism of the conversion of *trans*-cinnamic acid dibromide to β -bromostyrene has been reported earlier from this Laboratory¹ and simultaneously by Cristol and Norris.³ These studies and recent interest in related decarboxylative eliminations⁴ have prompted

(1) Paper I, E. Grovenstein, Jr. and D. E. Lee, *THIS JOURNAL*, **75**, 2639 (1953).

(2) Abstracted in part from the M.S. thesis of Spyros P. Theophilou, Georgia Institute of Technology, June, 1954.

(3) S. J. Cristol and W. P. Norris, *THIS JOURNAL*, **75**, 2645 (1953).

(4) In addition to the references given in Paper I and in ref. 3 see the following: (a) W. R. Vaughan and K. M. Milton, *ibid.*, **74**, 5623 (1952); W. R. Vaughan, M. V. Anderson, Jr., and R. Q. Little, Jr., *ibid.*, **76**, 1748 (1954); W. R. Vaughan and R. Q. Little, Jr., *ibid.*,

us to extend our studies to include *cis*-cinnamic acid dibromide.

cis-Cinnamic acid dibromide was prepared by addition of bromine to *cis*-cinnamic acid. A somewhat improved procedure for preparation of the latter from *trans*-cinnamic acid by irradiation with ultraviolet light is described in the Experimental portion. The addition of bromine to *cis*-cinnamic acid was effected in acetic acid as sol-

76, 2952 (1954); (b) W. v. E. Doering and L. H. Knox, *ibid.*, **73**, 828 (1951); (c) G. Stork and R. Breslow, *ibid.*, **75**, 3292 (1953); (d) L. J. Hals, T. S. Reid and G. H. Smith, Jr., *ibid.*, **73**, 4054 (1951); *ibid.*, **75**, 4525 (1953); (e) T. J. Brice and J. H. Simons, *ibid.*, **73**, 4017 (1951); (f) R. N. Haszeldine, *J. Chem. Soc.*, 4259 (1952).