[CONTRIBUTION FROM THE PURDUE RESEARCH FOUNDATION AND THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Monomers and Polymers. VIII. Alkylthiostyrenes and Alkylsulfonylstyrenes[1]

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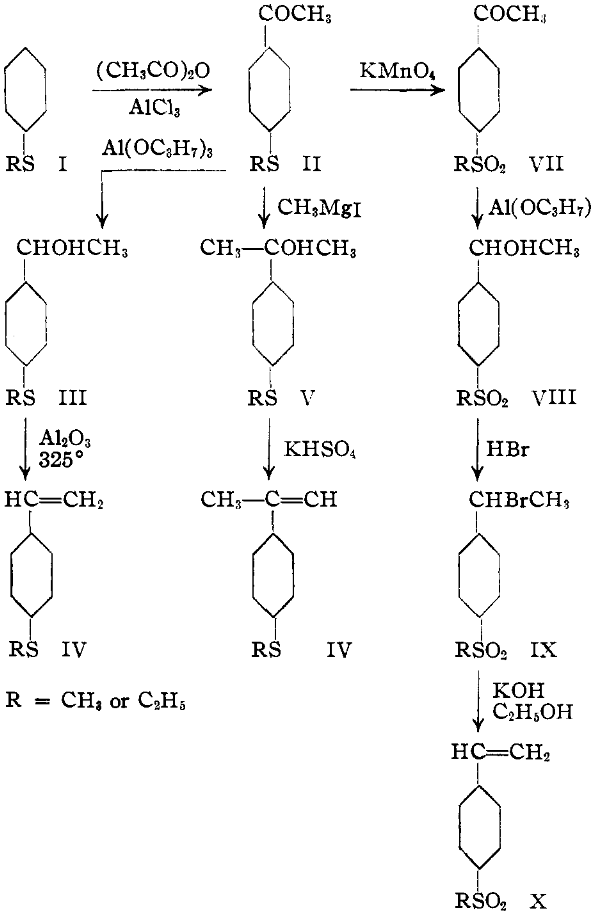
The syntheses of four new styrenes and α-methylstyrenes with sulfide and sulfone groups substituted on the aromatic nucleus are described. It has been found that the sulfide group permits free-radical-catalyzed polymerization and copolymerization. However, *p*-methylsulfonylstyrene yields only viscous oils under the same conditions.

No previous investigators have reported the synthesis and polymerization of monomeric styrenes and α-methylstyrenes containing sulfide and sulfone groups substituted on the aromatic nucleus. We have undertaken the preparation of some typical examples of these compounds in order to observe their polymerization behavior. The compounds prepared are: *p*-methylmercaptostyrene, *p*-methylsulfonylstyrene, *p*-methylmercapto-α-methylstyrene, and *p*-ethylmercapto-α-methylstyrene. The synthetic scheme employed is outlined.

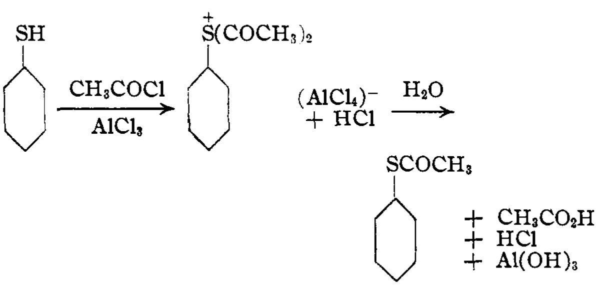


The position occupied by the acetyl group in II was confirmed by performing a haloform reaction with II and comparing the melting point of the acid product with that of *p*-methylmercaptobenzoic acid as reported by Gattermann.[2]

It is interesting to note that VII, because of its almost complete insolubility in ether, failed to react with methylmagnesium iodide. All attempts to dehydrate VIII, directly, failed. This compound was converted to the corresponding bromide which was dehydrobrominated successfully to the desired *p*-methylsulfonylstyrene.

An attempt was made to prepare *p*-mercaptostyrene from *p*-mercaptoacetophenone by reduction and then dehydration. However, we were unable to obtain the latter compound by acetylating thiophenol under Friedel–Crafts conditions. More than twenty experiments were run using various temperatures (0–150°), solvents (CS_2, $C_6H_5NO_2$, petroleum ether), catalysts ($AlCl_3$, BF_3, $SnCl_4$), ratios of reactants, and orders of addition of the reactants. Phenyl thioacetate was formed quite readily, but no other reaction occurred unless the temperature was raised to 150° or higher, at which point only tars were formed. From these none of the desired product could be isolated.

The above resistance of thiophenols to nuclear acetylation has not been adequately emphasized in the chemical literature,[3] although it has been reported by Auwers and Arndt[4] that *p*-thiocresol does not undergo a ketone synthesis when subjected to the usual Friedel–Crafts conditions. Kastner[5] has pointed out that the nuclear acetylation of phenyl esters by boron fluoride catalysts is more difficult than the reaction with phenols and phenyl ethers. Similarly, phenyl thioesters would be expected to be more resistant to acetylation than the corresponding thiophenols. However, the great resistance of the esters here encountered was unexpected. The simplest way to account for this deactivation of the nucleus would be to assume that the mercapto group is converted to an electron-withdrawing group capable of deactivating the nucleus sufficiently to prevent its reaction with acylating agents. A possible mechanism for this involving the formation of a sulfonium ion might be



It is difficult, however, with such a mechanism, to understand why the alkyl mercaptobenzenes should not behave similarly to thiophenol. Actually methylmercaptobenzene acetylates readily in

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(1) From the Ph.D. thesis of C. L. Carlson, Purdue University.

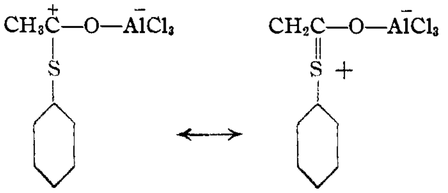
(2) Gattermann, *Ann.*, **393**, 226 (1912).

(3) Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1941, p. 369.

(4) Auwers and Arndt, *Ber.*, **42**, 537 (1909).

(5) Kastner, Thesis, Marburg, 1937; "Newer Methods of Preparative Organic Chemistry," Interscience Publishers, Inc., New York 1, N. Y., 1948, p. 283.

87% yield under mildest conditions. Alternatively it may be postulated that the catalyst coördinates with the oxygen of the acetyl group to produce a resonating complex of the type



which is inactive toward further acylation because of the partial positive charge on the sulfur atom attached to the ring. We are indebted to a referee for this proposal and for the statement that phenyl thioacetate appears not to undergo the Fries rearrangement. The absence of reaction in both cases can probably be attributed to similar factors.

In a final attempt to obtain the desired acetylated product, diphenyl disulfide was treated with acetyl chloride and $AlCl_3$ in carbon disulfide solution. The products of this reaction were resinous materials and a small amount of thiophenol.

p-Methylmercaptostyrene was polymerized satisfactorily by both the emulsion and solvent techniques, and copolymerized with butadiene in an emulsion system. The two α-methylstyrenes formed rubbery copolymers with butadiene. In benzene solution *p*-methylsulfonylstyrene polymerized to a viscous oil only.

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Experimental

***p*-Methylmercaptoacetophenone.**—Acetic anhydride, 65.0 g. (0.64 mole), was added dropwise to a mixture of methyl phenyl sulfide, 98.5 g. (0.8 mole), aluminum chloride, 240 g. (1.8 mole) and 340 ml. of carbon disulfide. The mixture was stirred and heated on a steam-cone for two hours, after which time the evolution of hydrogen chloride had slackened. Distillation of the carbon disulfide followed by hydrolysis of the residue with dilute hydrochloric acid gave 92 g. (87% theory, based on the acid anhydride) of a yellow crystalline product, m.p. 82–83° (from petroleum ether). Vacuum sublimation gave a white product of the same m.p.

Anal. Calcd. for $C_9H_{10}OS$: C, 65.02; H, 6.03. Found[6]: C, 65.4; H, 6.16.

p-Ethylmercaptoacetophenone[7] was prepared by a similar procedure. From 106 g. (0.77 mole) of ethyl phenyl sulfide and 63 g. (0.62 mole) of acetic anhydride, 60 g. (33% theory, based on the anhydride) of the ketone was obtained.

***p*-Methylmercapto-α-methylstyrene.**—A solution of *p*-methylmercaptoacetophenone, 50 g. (0.3 mole), in 200 ml. of ether was added to a solution of methylmagnesium iodide prepared from methyl iodide, 50 g. (0.35 mole) 8.4 g. of magnesium and 200 ml. of ether. The mixture was refluxed $^1/_2$ hour and hydrolyzed with saturated aqueous ammonium chloride solution. Evaporation of the ether yielded a yellow solid, presumably the tertiary alcohol. This solid was refluxed with 10 g. of fused potassium bisulfate at 100 mm. for 20 minutes, and then distilled to obtain the desired product, b.p. 85° (1–2 mm.), m.p. 51°, yield 20 g. (41% theory).

Anal. Calcd. for $C_{10}H_{12}S$: C, 73.11; H, 7.36. Found[6]: C, 73.95; H, 7.73.

1-(*p*-Methylmercaptophenyl)-ethanol.—A solution containing *p*-methylmercaptoacetophenone, 16.6 g. (0.1 mole), aluminum isopropoxide, 20 g. (0.1 mole) and 100 ml. of isopropyl alcohol was distilled at the rate of 10 drops per minute for 6 hours. An additional 75 ml. of isopropyl alcohol was added during the distillation. The excess isopropyl alcohol was removed under reduced pressure, and the residual oil poured into a solution of 35 ml. of hydrochloric acid in 175 ml. of water. The organic layer was taken up in ether and dried. Evaporation of the ether yielded a brown oil which crystallized on cooling in an ice-bath. Recrystallization from petroleum ether gave 14 g. (83% yield) of white crystals, m.p. 38–40°.

Anal. Calcd. for $C_9H_{12}OS$: C, 64.2; H, 7.19. Found[6]: C, 64.3; H, 7.35.

***p*-Methylmercaptostyrene.**—A solution of 60 g. (0.36 mole) of 1-(*p*-methylmercaptophenyl)-ethanol in 75 ml. of benzene was allowed to drop slowly (3 hours) into a vertical column packed with aluminum oxide. The temperature of the column was maintained between 300 and 325°, and the pressure was approximately 30 mm. The benzene solution of the product was condensed in a series of Dry Ice traps, dried, and distilled. The product was a colorless liquid, b.p. 83–85° (3 mm.), n^{20}_D 1.6186, d^{25}_4 1.0384, yield 29 g. (54%).

Anal. Calcd. for $C_9H_{10}S$: C, 72.0; H, 6.71. Found[6]: C, 72.0; H, 6.95.

***p*-Methylsulfonylacetophenone.**—A solution of 20 g. (0.12 mole) of *p*-methylmercaptoacetophenone in 50 ml. of glacial acetic acid was heated to 40°. A solution of potassium permanganate, 26 g., in 600 ml. of water was added and the temperature rose to 60–70°. Four hundred ml. of water was added, and the solution was allowed to stand until it reached room temperature. Small portions of a saturated solution of sodium sulfite were added to remove the excess permanganate. The solution was cooled to 10° and filtered; yield 22.8 g. (95%) of white crystals, m.p. 127–128°, from 95% ethanol.

Anal. Calcd. for $C_9H_{10}O_3S$: C, 54.6; H, 5.21. Found[6]: C, 54.6; H, 5.05.

1-(*p*-Methylsulfonylphenyl)-ethanol.—A solution containing *p*-methylsulfonylacetophenone, 19.8 g. (0.1 mole), aluminum isopropoxide, 20 g. (0.1 mole), and 150 ml. of isopropyl alcohol was distilled at a rate of 10 drops per minute for two hours. The excess isopropyl alcohol was removed under reduced pressure, and the residual oil poured into dilute hydrochloric acid. Some resinous material was filtered, and the solution was extracted 4 to 6 times with 150-ml. portions of ether. Evaporation of the ether yielded 14 g. (71%) of white crystals, m.p. 95–96° (from 95% ethanol).

Anal. Calcd. for $C_9H_{12}O_3S$: C, 54.1; H, 6.00. Found[6]: C, 54.4; H, 5.94.

1-(*p*-Methylsulfonylphenyl)-ethyl Bromide.—The above alcohol, 25 g. (0.125 mole), was dissolved in a tenfold excess of 48% hydrobromic acid. The solution was allowed to stand for two days, during which time a white crystalline solid was formed. This solid was filtered, washed with water, and dried in a vacuum desiccator, m.p. 87–88° (from petroleum ether), yield 22 g. (66%).

Anal. Calcd. for $C_9H_{11}BrO_2S$: C, 41.1; H, 4.18. Found[6]: C, 41.4; H, 4.48.

***p*-Methylsulfonylstyrene.**—Twenty-two grams (0.084 mole) of the secondary bromide described above was dissolved in 200 ml. of absolute ethanol containing a twofold excess of potassium hydroxide. The solution was refluxed for one hour, cooled, and filtered. It was evaporated to a small volume and taken up in ether. The ether solution was filtered, dried, and distilled. A fraction was collected from 148–150° (4 mm.), m.p. 37–38°, yield 6 g. (40%).

Anal. Calcd. for $C_9H_{10}O_2S$: C, 59.4; H, 3.49. Found[6]: C, 59.2; H, 5.73.

Preparation of Polymers and Copolymers.—Polymers of *p*-(methylmercapto)-styrene and *p*-(methylsulfonyl)-styrene were prepared by heating a 10% solution of the monomers in benzene at 75–80° for several hours, using 1% benzoyl peroxide as catalyst. Copolymers of the four new monomers with butadiene were made at 40° in sealed Pyrex tubes, using the following formula, butadiene 7.5 parts, substituted styrene or methylstyrene 2.5 parts, water 20 parts, soap 0.5 parts, potassium persulfate 0.3 part and dodecyl mercaptan 0.06 part. *p*-(Methylsulfonyl)-styrene did not form a copolymer with butadiene since most of the monomer was recovered unchanged. The other three monomers copolymerized readily with butadiene.

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(6) Carbon and hydrogen analyses by Dr. H. Galbraith, Purdue University.

(7) Auwers and Berger, *Ber.*, **27**, 1738 (1894).