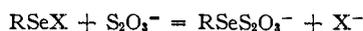


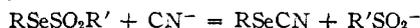
Some reactions of the tabulated compounds are mentioned below. The reactions are rapid and quantitative, and serve to characterize the compounds as derivatives of  $RSe^+$ .

In ethyl acetate-ethanol solutions *o*-nitrobenzeneselenenyl thiocyanate, di-*O*-alkyl monothio-phosphates and thiosulfonates react with aqueous sodium thiosulfate as follows



This is analogous to the behavior of the corresponding sulfonyl compounds.<sup>4</sup>

*o*-Nitrobenzeneselenenyl sulfinates, in ethyl acetate-ethanol or ethanol solutions, react with aqueous potassium cyanide to give *o*-nitrophenyl selenocyanate



*o*-Nitrobenzeneselenenyl thiosulfate reacts with sodium cyclohexamethylenedithiocarbamate thus  $RSeS_2O_4^- + C_6H_{10}NCS_2^- = RSe(S)CNC_6H_{10} + S_2O_4^{2-}$ . The product has previously been prepared<sup>1</sup> from the bromide.

(4) Foss, *ibid.*, in press.

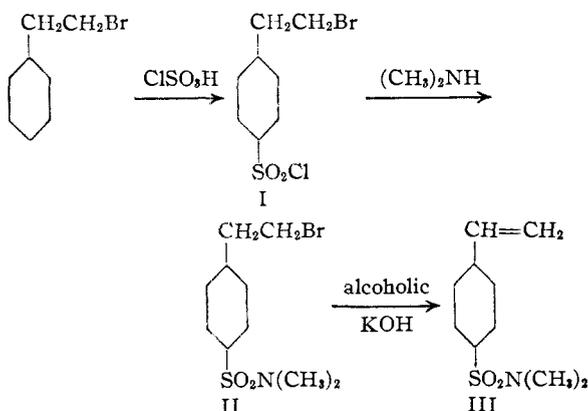
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RECEIVED APRIL 19, 1947

## Preparation and Polymerization of *p*-*N,N*-Dimethylsulfonamidostyrene<sup>1</sup>

BY G. ESLER INSKEEP AND RUDOLPH DEANIN

As a part of the general program for the study of substituted styrenes as replacements for styrene in GR-S, *p*-*N,N*-dimethylsulfonamidostyrene (III) has been prepared, polymerized and copolymerized with butadiene. The new styrene derivative was prepared by the following series of reactions.



*p*-*N,N*-Dimethylsulfonamidostyrene polymerizes very readily at its melting point to give a high melting polymer which dissolves slowly in nitromethane and is insoluble in acetone, amyl acetate,

(1) This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

benzene and chloroform. It copolymerizes readily with butadiene in soap emulsion in the presence of potassium persulfate and dodecyl mercaptan. The substituted styrene enters the growing copolymer more rapidly than does butadiene.

### Experimental

**$\beta$ -(*p*-Chlorosulfonylphenyl)-ethyl Bromide (I).**—To 1 kg. (8.5 moles) of chlorosulfonic acid in a 2-liter three-necked flask equipped with stirrer, dropping funnel, and outlet to a vapor trap was added 315 g. (1.7 moles) of  $\beta$ -phenylethyl bromide over a period of two hours; the temperature was held below 27° by external cooling with water. After another hour the contents were poured over a large quantity of ice, the aqueous layer was decanted, and the semi-solid product was triturated in ice-water. Attempts to recrystallize the sulfonyl chloride or to distill it at a pressure of 7 mm. were unsuccessful. The yield of crude product was 431 g. or 89%.

In some runs a small amount of crystalline by-product m. p. 159–160° (cor.), was separated from the sulfonyl chloride (e. g., by its relative insolubility in alcohol). Analysis and rough determination of molecular weight by boiling point rise of chloroform showed this to be the corresponding sulfone.

*Anal.* Calcd. for  $C_{10}H_{10}O_2SBr_2$ : C, 44.46; H, 3.73; mol. wt., 432. Found: C, 45.41; H, 4.04; mol. wt., 408; S and halogen present.

**$\beta$ -(*p*-Sulfonamidophenyl)-ethyl Bromide.**—A small portion of the sulfonyl chloride was heated with ammonium hydroxide and the sulfonamide was recrystallized repeatedly from alcohol, m. p. 185.5–186° (cor.).

*Anal.* Calcd. for  $C_8H_{10}O_2SNBr$ : N, 5.30. Found: N, 5.30.

**$\beta$ -(*p*-*N,N*-Dimethylsulfonamidophenyl)-ethyl Bromide (II).**—To 920 g. (5.1 moles) of 25% aqueous dimethylamine was added in portions 431 g. (1.5 moles) of crude  $\beta$ -(*p*-chlorosulfonylphenyl)-ethyl bromide. The mixture was stirred frequently during an interval of two hours; its maximum temperature was approximately 60°. An equal volume of water was added and the aqueous layer was decanted. Benzene (500 ml.) was added and the solution was washed with water and dried overnight with calcium chloride. The solvent was removed at reduced pressure; the residual brown oil became partly solid upon standing. The solid portion was separated on a Buchner funnel; it weighed 113 g., or 25% of theoretical. Four recrystallizations from alcohol followed by thorough drying gave a product, m. p. 99–100° (cor.).

*Anal.* Calcd. for  $C_{10}H_{14}O_2SNBr$ : C, 41.05; H, 4.80. Found: C, 41.45; H, 4.82.

***p*-*N,N*-Dimethylsulfonamidostyrene (III).**—A solution of 34 g. (0.6 mole) of potassium hydroxide in 400 ml. of 95% alcohol was heated to 50° and a slurry of 113 g. (0.4 mole) of crude dimethylsulfonamidophenylethyl bromide in 300 ml. of alcohol, also at 50°, was added rapidly; the temperature rose 10°. The mixture was allowed to stand fifteen minutes, and the precipitated potassium bromide was removed by filtration. The cooled solution was made neutral to litmus with dilute hydrochloric acid and diluted to 4 liters with water. The yellow liquid which separated was removed and the aqueous layer was extracted three times with 200-ml. portions of chloroform. The solvent was removed at reduced pressure and the residue was added to the main portion of the product. The liquid readily recrystallized in the ice box; its weight was 77 g. or 94% of the theoretical amount. Two recrystallizations from alcohol gave 55 g. (67%) of colorless product melting at 60–61° (cor.); two further recrystallizations from a large volume of high-boiling petroleum ether brought the m. p. to 63–63.5° (cor.).

*Anal.* Calcd. for  $C_{10}H_{12}O_2SN$ : C, 56.84; H, 6.20. Found: C, 57.01; H, 6.22.

Oxidation of this material with potassium permanganate gave the known *p*-*N,N*-dimethylsulfonamidobenzoic

acid,<sup>2</sup> m. p. 249–251° (reported melting point 255–256°). This establishes the para relationship of the vinyl and sulfonamide groups, as well as the relationships of the corresponding groups in its two parent compounds, although there is no reason to believe that the crude sulfonyl chloride does not contain appreciable amounts of the other isomers.

**Polymerization.**—A benzene solution of the monomer after a week in the ice box had deposited a white, powdery polymer which was not appreciably soluble in any of a wide range of solvents such as chloroform, water, alcohol and ethanolamine. When the decanted benzene was evaporated on the steam cone, the residue was found to consist principally of a similarly insoluble polymer from which smaller amounts of soluble polymer were separated by successive extractions with hot dioxane and hot benzene; these soluble portions were left as glassy solids upon evaporation of the solvents. The density of the insoluble polymer was approximately 1.25.

When the solid monomer was heated to 70° for five minutes, it first melted and then polymerized to a yellow, vitreous solid. This polymer had a softening point of 190–210°. It was insoluble in acetone, amyl acetate or benzene swelled in chloroform; and dissolved slowly in nitromethane. The molecular weight of the polymer, calculated from the relative viscosity of the nitromethane solution by means of the Kemp–Peters–Staudinger equation,<sup>3</sup> was 20,900.

*Anal.* Calcd. for C<sub>10</sub>H<sub>13</sub>O<sub>2</sub>SN: C, 56.8; H, 6.2; N, 6.6; S, 15.2. Found: C, 55.8; H, 6.0; N, 6.2; S, 15.4.

**Copolymerization with Butadiene.**—The monomer copolymerized readily with butadiene in the following formula.

Butadiene	15.0 g.
<i>p</i> -N,N-Dimethylsulfonamidostyrene	5.0
Water	36.0
Soap <sup>a</sup>	1.0
Potassium persulfate	0.06
OEt <sup>b</sup>	0.10

<sup>a</sup> Procter and Gamble Soap Flakes (silica free). <sup>b</sup> A commercial product containing a mixture of straight chain mercaptans of 10–16 carbon atoms.

When this emulsion recipe was placed in a four-ounce polymerization bottle and rotated end over end for six hours at 50°, a 76% conversion of copolymer was obtained. This copolymer was 84% soluble in benzene, and its dilute benzene solution had an intrinsic viscosity of 1.59. Elementary analysis of the copolymer indicated that it contained 29.4% by weight of *p*-N,N-dimethylsulfonamidostyrene. The calculated *alpha*-value<sup>4</sup> of 2.96 indicates that the substituted styrene entered the copolymer much more rapidly than did butadiene.

*Anal.* Calcd. for 29.4% substituted styrene in copolymer: C, 79.5; H, 9.7; N, 2.0; S, 4.5. Found: C, 79.6; H, 9.4; N, 2.0; S, 4.5.

(2) de Jong, *Verslag Akad. Wetenschappen Amsterdam*, **32**, 14 (1923).

(3) A. R. Kemp and H. Peters, *Ind. Eng. Chem.*, **34**, 1697 (1942).

(4) F. T. Wall, *This Journal*, **63**, 1862 (1941).

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## Some *s*-Butyl- and 1,4-Di-*s*-butylbenzene Derivatives

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A number of new derivatives of *s*-butyl- and 1,4-di-*s*-butylbenzene have been prepared. 1,4-

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Di-*s*-butylbenzene-2-sulfonyl chloride, like the corresponding diisopropylbenzene derivative,<sup>2</sup> loses an alkyl group on nitration. There is evidence pointing to partial loss of a *s*-butyl group when 1,4-di-*s*-butylbenzene reacts with chlorosulfonic acid, since after hydrolysis of the resulting sulfonyl chloride, the second crop of sulfonic acid sodium salt contains a rather high per cent. of sodium.

### Experimental Part

Nitration of sulfonyl chlorides was performed with a large excess of 96% nitric acid, at 1 to 4° for thirty minutes, finally warming in the atmosphere to 25° and pouring immediately onto ice. Other derivatives were prepared by the methods already described.<sup>3</sup>

***s*-Butylbenzene-4-sulfonanilide.**<sup>4</sup>—The oily crude product (87%) was triturated with petroleum ether and recrystallized from the same solvent. It gave white crystals (25%), m. p. 65.0–66.0°.

*Anal.* Calcd. for C<sub>16</sub>H<sub>19</sub>O<sub>2</sub>NS: C, 66.4; H, 6.6. Found: C, 66.6; H, 6.5.

**2-Nitro-*s*-butylbenzene-4-sulfonamide.**—The pale yellow nitrosulfonyl chloride, an oil (61%), gave a slightly yellow sulfonamide (95%). This gave a red solution in 5% isopropyl alcohol from which it crystallized as silvery white flakes, m. p. 111.2–112.0°.

*Anal.* Calcd. for C<sub>10</sub>H<sub>14</sub>O<sub>4</sub>N<sub>2</sub>S: C, 46.5; H, 5.5. Found: C, 46.7; H, 5.4.

**1,4-Di-*s*-butylbenzene-2-sulfonic Acid Sodium Salt.**—The pale yellow liquid sulfonyl chloride (40 g.) was hydrolyzed with 100 ml. of 20% sodium hydroxide, some insoluble material, probably a sulfone, was filtered off, and the sodium salts were crystallized in two fractions; (a) 92%, (b) 8%.

*Anal.* Calcd. for C<sub>14</sub>H<sub>21</sub>O<sub>3</sub>SNa: Na, 7.8. Found: (a) Na, 7.8. Calcd. for C<sub>14</sub>H<sub>21</sub>O<sub>3</sub>SNa·4H<sub>2</sub>O: H<sub>2</sub>O, 19.7. Found: (a) H<sub>2</sub>O, 19.8.

Both (a) and (b) were reconverted to sulfonyl chlorides using phosphorus pentachloride, and other derivatives were prepared from (a).

*Anal.* Calcd. for C<sub>14</sub>H<sub>21</sub>O<sub>3</sub>SCl: Cl, 12.3. Found: Cl (by hydrolysis) (a), 12.3; (b), 12.6.

**Sulfonamide.**—The crude product (85%) from 16 g. of sulfonyl chloride crystallized slowly from the initially formed oil. Recrystallization from a large volume of 1% isopropyl alcohol gave flat, white plates (57%), m. p. 63.2–64.1°.

*Anal.* Calcd. for C<sub>14</sub>H<sub>23</sub>O<sub>2</sub>NS: C, 62.4; H, 8.5. Found: C, 62.5; H, 8.4.

**Sulfonanilide.**—The crude oily solid (91%) from 14 g. of sulfonyl chloride, gave 66% of white crystals, m. p. 105.4–106.3° when recrystallized from 90% isopropyl alcohol.

*Anal.* Calcd. for C<sub>20</sub>H<sub>27</sub>O<sub>2</sub>NS: C, 69.6; H, 7.9. Found: C, 69.5; H, 7.8.

**4-Nitro-*s*-butylbenzene-2-sulfonyl Chloride.**—Nitration of 1,4-di-*s*-butylbenzene-2-sulfonyl chloride gave 89% of white oily solid which turned yellow on standing. It crystallized from petroleum ether in buff colored plates (38%), m. p., 71.4–72.0°.

*Anal.* Calcd. for C<sub>10</sub>H<sub>12</sub>O<sub>4</sub>NSCl: Cl, 12.8. Found: Cl (by hydrolysis), 12.8.

**Sulfonamide.**—White flakes (91%) from isoöctane, m. p. 171.4–171.7°.

*Anal.* Calcd. for C<sub>10</sub>H<sub>14</sub>O<sub>4</sub>N<sub>2</sub>S: C, 46.6; H, 5.5. Found: C, 46.4; H, 5.3.

(2) Newton, *This Journal*, **65**, 2439 (1943).

(3) Legge, *ibid.*, **69**, 2078, 2086 (1947).

(4) For orientation, cf. Huntress and Autenrieth, *ibid.*, **63**, 3446 (1941).