When petroleum ether (Skellysolve B) was added to this clear ether solution, an oily product separated. After the mixture had been allowed to stand overnight, the oil had not crystallized but crystalline material was present throughout the solution. This crystalline material, when carefully separated from the oil, gave a negative Legal (nitroprusside) test. The oil was crystallized from a mixture of alcohol and water. After two recrystallizations, 350 mg. (19%) of product was obtained. The compound crystallizes as needles, which contain 1.5 moles of water of crystallization. The melting point depends upon the rate of heating, but ordinarily the compound melts at 145–150° after preliminary sintering. For analysis it was dried over calcium chloride at 75° and 10 mm.

Anal. Calcd. for $C_{37}H_{52}O_{14}\cdot1.5H_2O$: C, 59.4; H, 7.4. Found: C, 59.4; H, 7.4.

Periplogenin-(3)-β-*d*-glucoside.—The viscous oil obtained on deacetylation was crystallized initially from ethyl acetate saturated with water, and recrystallized from 95% alcohol–ether. It crystallized as fine needles containing two waters of crystallization and melted at 195–200° (dec.). For analysis it was dried over calcium chloride at 75° and 10 mm.

Anal. Calcd. for $C_{29}H_{44}O_{10}\cdot2H_2O$: C, 59.2; H, 8.2. Found: C, 59.5; H, 8.0.

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Pyrolysis of Diketene

By J. T. FITZPATRICK

There is considerable evidence in favor of the Boese–Wilson[1] vinylaceto-β-lactone structure for diketene.[1–5] However, on pyrolysis this structure would be expected to give allene and carbon dioxide as well as the previously observed product, ketene.[1,3] It has now been found that significant amounts of these by-products are present in ketene made in a "ketene lamp"[1] with a Nichrome filament. The amount of impurities depends on both the temperature and the condition of the filament. A filament which had been used for some time gave a product containing 13% allene and carbon dioxide in approximately equal amounts; after thorough cleaning with nitric acid the filament gave only 8% by-products. When a used filament was operated at a voltage lower than usual, the by-products accounted for more than 18% of the reacted diketene.

The diketene used was commercial material which had been redistilled in the laboratory; it boiled at 62° at 75 mm., and froze at −6.5 to −7.0°; its purity was estimated to be well over 99%. It was cracked in a ketene lamp with a filament made of approximately 14 ft. of no. 22 B. and S. gage Nichrome wire. The rate of cracking was 320–350 g./hour with 75 volts, or 50–55 g./hour with 55 volts on the filament. After passing through a partial condenser to remove unreacted diketene, the products were condensed and weighed in tared traps cooled with liquid air. The material was vaporized from these traps and passed through 0.25% aqueous sulfuric acid at 50–55° to remove the ketene. The small amount of residue which did not vaporize at room temperature was considered to be unreacted diketene. The blow-off gas from the absorber was again collected in tared traps and weighed. Samples of this condensate were analyzed in the mass spectrograph by the South Charleston Works Laboratory of this Company. A typical analysis was: carbon dioxide, 53.9%; allene, 45.1%; acetone, 0.4%; and trifling amounts of other compounds, including 0.1% ketene. Lack of a reaction with silver nitrate solution showed the absence of methylacetylene, which is nearly indistinguishable from allene in the mass spectrograph.

RESEARCH AND DEVELOPMENT DEPARTMENT
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RECEIVED JUNE 16, 1947

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[1] Boese, *Ind. Eng. Chem.*, **32**, 16 (1940).

[2] Hurdis and Smyth, THIS JOURNAL, **65**, 89 (1943).

[3] Rice and Roberts, *ibid.*, **65**, 1677 (1943).

[4] Taufen and Murray, *ibid.*, **67**, 754 (1945).

[5] Bauer, Bregman and Wrightson, paper presented before the Division of Physical Chemistry of the American Chemical Society at the Atlantic City meeting, April, 1946.

Selenenyl Sulfur Compounds

By OLAV FOSS

Twiss, Jones and Hadley[1] reported the reactions of *o*-nitrobenzeneselenenyl bromide[2] with mercaptobenzthiazole and thiocarbonyl salts. We have found that *o*-nitrobenzeneselenenyl bromide reacts rapidly with sodium or potassium thiocyanate, di-O-alkylmonothiophosphates,[3] thiosulfonates, and sulfinates, to give *o*-nitrobenzeneselenenyl thiocyanate, di-O-alkylmonothiophosphates, thiosulfonates and sulfinates, respectively. The general procedure consists in dissolving 1 g. of the bromide in 3–4 ml. of ethyl acetate and 5 ml. of methanol, and adding a slight excess of the thio salt or sulfinate, dissolved in 10 ml. of methanol. The product thereon crystallizes out rapidly (in the case of di-O-alkylmonothiophosphates after addition of some water). Potassium *o*-nitrobenzeneselenenyl thiosulfate was obtained by reaction of the bromide, dissolved in benzene, with a slight excess of potassium thiosulfate in the double amount of water. The crystals are stable, and have a yellowish green color. The di-O-ethylmonothiophosphate was obtained as a yellowish green oil. Among the compounds prepared are these in Table I.

TABLE I

Compound (R = *o*-nitrophenyl)	M. p., °C. (uncor.)	Selenium, % Calcd.	Selenium, % Found
$RSeSCN$	107[a]	30.5	30.4
$RSeSPO(OCH_3)_2$	79[b]	23.1	23.1
$RSeSPO(OC_2H_5)_2$	Oil	21.3	21.5
$RSeS_2O_2CH_3$	96[b]	25.3	25.3
$RSeS_2O_2C_2H_5$	90[b]	24.2	24.0
$RSeS_2O_2C_6H_5$	147[c]	21.1	21.3
$RSeS_2O_2C_6H_4CH_3$-*p*	148[c]	20.3	20.2
$RSeS_2O_2C_6H_4Br$-*p*	169[c]	17.4	17.1
$RSeSO_2C_6H_5$	109[d]	23.1	23.1
$RSeSO_2C_6H_4CH_3$-*p*	118[d]	22.2	22.0
$RSeSO_2C_6H_4CH_3$-*o*	95[e]	22.2	22.2
$RSeSO_2C_6H_4Br$-*p*	126[e]	18.8	18.7
$RSeS_2O_3K$	*ca.* 190[d], dec.	22.4	22.4

[a] Crystallized from carbon tetrachloride. [b] Crystallized from carbon disulfide. [c] Crystallized from benzene. [d] Crystallized from ethanol. [e] Crystallized from methanol.

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[1] Twiss, Jones and Hadley, British Patent 441,653 (1936).

[2] Behaghel and Seibert, *Ber.*, **66**, 708 (1933).

[3] Foss, *Acta Chemica Scandinavica*, **1**, 8 (1947).

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 monothiophosphates and thiosulfonates react with aqueous sodium thiosulfate as follows

$$RSeX + S_2O_3^= = RSeS_2O_3^- + X^-$$

This is analogous to the behavior of the corresponding sulfenyl compounds.[4]

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

$$RSeSO_2R' + CN^- = RSeCN + R'SO_2^-$$

o-Nitrobenzeneselenenyl thiosulfate reacts with sodium cyclopentamethylenedithiocarbamate thus

$$RSeS_2O_3^- + C_5H_{10}NCS_2^- = RSeS(S)CNC_5H_{10} + S_2O_3^=$$

The product has previously been prepared[1] from the bromide.

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

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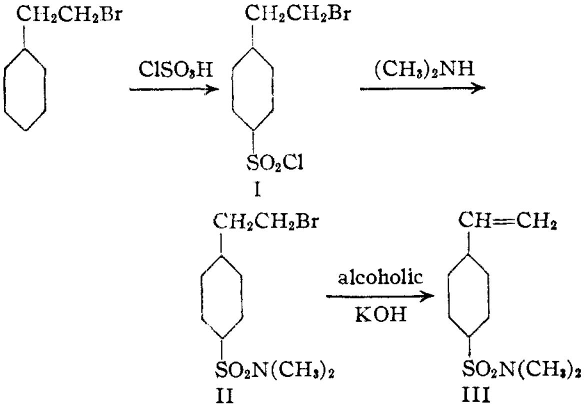
RECEIVED APRIL 19, 1947

Preparation and Polymerization of *p*-N,N-Dimethylsulfonamidostyrene[1]

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, 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

β-(*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 β-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 distil 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 $C_{16}H_{16}O_2SBr_2$: C, 44.46; H, 3.73; mol. wt., 432. Found: C, 45.41; H, 4.04; mol. wt., 408; S and halogen present.

β-(*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.

β-(*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 β-(*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

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(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.