[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF SWARTHMORE COLLEGE]

Organic Selenium Compounds. The Nitration of Phenyl Alkyl Selenides and their Reduction to Amines[1]

BY DUNCAN G. FOSTER

This paper describes the preparation of a series of alkyl aryl selenonium nitrates, in which the alkyl group is methyl to heptyl, always normal, and their nitration in the meta position, the products, except in the first two instances, being isolated as the dichlorides, $O_2NC_6H_4SeCl_2R$. These dichlorides can be neutralized with sodium hydroxide and the solution so obtained reduced catalytically to the amines, $H_2NC_6H_4SeR$.

The paper also describes the preparation of *m*-aminoselenophenol, by a different procedure.

The starting material was selenophenol, C_6H_5SeH, prepared by the Grignard reaction from bromobenzene and selenium.[2] Phenyl alkyl selenides were prepared from this by treating its sodium salt with alkyl halide in alcohol solution.[3]

Nitration of organic selenides offers the difficulty that the selenium atom is oxidized and then combines with the nitric acid to form selenonium nitrates, $C_6H_5SeO(HNO_3)R$,[3] so depleting the nitric acid that nitration does not occur. The selenides were therefore dissolved in concentrated nitric acid,[4] after which the nitric acid was distilled off in an all-glass apparatus at 50° at the water pump.

The crude products thus obtained were nitrated directly—50 ml. of fuming nitric acid was added, then 70 ml. of concentrated sulfuric acid dropwise over a period of one hour with frequent shaking. The reaction mixture was heated on the water-bath for one hour, then poured onto an equal weight of cracked ice. The methyl and ethyl derivatives gave solid nitrates, which were filtered off and recrystallized from dilute nitric acid. All the others gave non-crystallizable oils.

All of the reaction mixtures, including additional runs of the methyl and ethyl compounds, were converted to the selenonium dichlorides by adding 200 ml. of concentrated hydrochloric acid to the rapidly stirred cold mixture. A drop of the oil which first appeared was removed on a glass rod and rubbed, causing it to solidify. This was used as seed for the main batch. The dichlorides were recrystallized from benzene–petroleum ether mixtures, giving slightly yellow crystalline solids.

Both nitrates and dichlorides were analyzed simply by dissolving in an excess of 0.02 *N* sodium hydroxide and titrating the excess with 0.02 *N* hydrochloric acid, using methyl red–methylene blue indicator.

***m*-Nitro-phenyl Methyl Selenonium Dihydroxide,** $O_2NC_6H_4Se(OH)_2CH_3$.—12.7 g. of the methyl nitrate was added slowly with mechanical stirring to a solution of 3 g. of potassium carbonate in 35 ml. of water. The water was removed completely at the pump and the residue extracted with absolute alcohol, filtered and allowed to evaporate; recrystallized from benzene it gave yellow needles, m. p. 118°; yield, 9.5 g. or 95%.

Anal. (Semi-micro Kjeldahl). Calcd. for $C_7H_9O_4NSe$: N, 5.60. Found: N, 5.56.

Only the methyl derivative would give a stable dihydroxide.

Orientation of the Nitro Group.—19 g. of $O_2NC_6H_4SeBr_2CH_3$ was heated in a distilling flask to 120–130° until effervescence ceased, giving the monobromide, $O_2NC_6H_4SeBr$;[5] yield, 14 g., 98%. The product was boiled with water, cooled, and the solid, a mixture of $O_2NC_6H_4SeO_2H$ and $(O_2NC_6H_4Se-)_2$,[6] filtered off. The crude solid was then dissolved in concentrated nitric acid, oxidizing the diselenide in it to the seleninic acid.[4] The white product was recrystallized from hot water, dried and had m. p. 156°, alone or mixed with a sample of *m*-nitrobenzene seleninic acid prepared as described below. This compound is known (literature m. p. 156°) and the fact was therefore established that the nitration had occurred in the meta position.

Reduction to the Amines.—The methyl selenonium dihydroxide was reduced directly in alcohol with Raney nickel at 30–40 lb. Its dichloride also and all the other dichlorides were reduced by the following procedure.

One-half mole of dichloride was dissolved in 50 ml. of alcohol and a slight excess of 2 *N* sodium hydroxide added. The mixture was titrated with 2 *N* hydrochloric acid until it had a *p*H of 8 to Alkacid paper. About 3 g. of Raney nickel was added and the whole subjected to reduction at 30–40 lb. pressure in a standard low-pressure hydrogenator. Hydrogenation took four to six hours and consumed 4 moles of hydrogen per mole of compound, reducing both nitro group and selenoxide group. The catalyst was filtered off and the alcohol evaporated. The methyl and ethyl derivatives were taken up with benzene and the hydrochlorides precipitated with dry hydrogen chloride. The other

---

[1] The previous (fourth) paper in this series was published in *Rec. trav. chim.*, **54**, 447 (1935).

[2] Taboury, *Ann. chim. phys.*, **15**, 5 (1908).

[3] Foster and Brown, THIS JOURNAL, **50**, 1182 (1928), and many others.

[4] Pyman, *J. Chem. Soc.*, **115**, 166 (1919).

[5] Morgan and Porritt, *J. ibid.*, **127**, 1758 (1925).

[6] Foster, *Rec. trav. chim.*, **53**, 406 (1934).

TABLE I

PREPARATION AND PROPERTIES OF *m*-NITRO-PHENYL ALKYL SELENONIUM DICHLORIDES AND NITRATES, $O_2NC_6H_4SeCl_2R$

R	Yield, %	M. p., °C.[a]	Analyses Constituent detd.		
				Calcd.	Found
CH_3	(Nitrate) 75	111	Nitrate N	4.74	4.71
	(Dichloride) 17[b]	122	Cl	24.68	24.27
	Dibromide[c]	107	Br	42.50	42.18
C_2H_5	(Nitrate) 70	93- 94	Nitrate N	4.53	4.55
	(Dichloride) 88	92- 93	Cl	23.54	23.74 23.33
C_3H_7	66	103-104	Cl	22.46	22.47
C_4H_9	81	100	Cl	21.54	21.00
C_5H_{11}	70	71- 73	Cl	20.69	20.61
C_6H_{13}	52	57	Cl	19.87	19.71
C_7H_{15}	73	65	N[d]	3.76	3.74

[a] All melting points with decomposition. [b] By-product from preparation of the nitrate prepared by saturating reaction mixture from which the nitrate had been filtered with NH_4Cl. [c] Prepared from *m*-nitro phenyl methyl selenonium dihydroxide (see just below) by dissolving in water, saturating with NH_4Br and adding excess HBr. Yield, the theoretical. Golden yellow needles from $CHCl_3$. [d] Semi-micro Kjeldahl.

hydrochlorides were too soluble in benzene, and were prepared by adding excess hydrochloric acid to the free crude amine and evaporating. All were reconverted to the free amines by dissolving in water, adding an excess of sodium hydroxide, extracting with benzene, drying over anhydrous sodium sulfate, distilling off the benzene and distilling the amines *in vacuo*. The amines were all colorless liquids, turning dark on standing.

Analyses were performed by titrating the hydrochlorides with standard base in the case of the methyl and ethyl compounds, and by semi-micro Kjeldahl on the free amines for all the others.

Table II gives details of these reductions.

TABLE II

PREPARATION AND PROPERTIES OF *m*-AMINO-PHENYL ALKYL SELENIDES, $H_2NC_6H_4SeR$

R	Yield, %	B. p., °C.	Mm.	Analyses, % N Calcd.	Found
CH_3	96	128	4	6.28	6.38
C_2H_5	81	129	4	5.92	5.97
C_3H_7	80	137	3	6.54	6.52
C_4H_9	98	154	4	6.14	6.03
C_5H_{11}	58	176	7	5.78	5.79
C_6H_{13}	73	174	4	5.47	5.47
C_7H_{15}	30	173	4	5.18	5.18

***m*-Amino Selenophenol.**—Benzene seleninic acid was prepared[4] and nitrated as described above: 22 g. gave 21.7 g. or 81% of product; 19.5 g. of this was dissolved in 40 ml. of 6 *N* sodium hydroxide and 160 ml. of water, 16 g. of hydrazine sulfate added and the mixture stirred until no more nitrogen was evolved (one-half hour). The yellow precipitate of $(O_2NC_6H_4Se\text{-})_2$ was filtered off and recrystallized from methyl alcohol, m. p. 81°; yield, 16 g. or 95%.

Anal. (Parr bomb.) Calcd. for $C_{12}H_8O_4N_2Se_2$: Se, 39.3. Found: Se, 39.8.

Sixteen grams of the above product in 200 ml. of alcohol was reduced with 4 g. of Raney nickel at room temperature and 30–40 lb. pressure. The reduction took nine hours and required 7 moles of hydrogen per mole of compound. The catalyst was filtered off and excess concentrated hydrochloric acid added; pale yellow granular crystals, yield, 13 g. or 72%.

Ten and one-half grams of this hydrochloride was dissolved in 200 ml. of water and 50 ml. of *N* sodium hydroxide added. The product was an oil which solidified on rubbing to pale yellow needles from alcohol, m. p. 58°, yield, 8 g. or 92%.

Anal. (Hydrochloride.) Calcd. for C_6H_8NClSe: Cl, 17.0. Found: Cl, 17.2.

Summary

A method for the nitration of phenyl alkyl selenides in the meta position has been worked out. An homologous series of seven of these compounds has been prepared and reduced catalytically to the amines.

m-Amino-selenophenol also has been prepared by a different procedure.

SWARTHMORE, PENNSYLVANIA RECEIVED MARCH 3, 1941