SYNTHESIS OF 1,3-DIHYDROBENZO[c]SELENOPHENE

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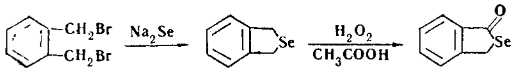
1,3-Dihydrobenzo[c]selenophene was synthesized from ω, ω'-dibromo-o-xylene and sodium selenide.

We have accomplished the synthesis of 1,3-dihydrobenzo[c]selenophene (I) from ω, ω'-dibromo-o-xylene and sodium selenide:



I II

Compound I was recovered unchanged when attempts were made to dehydrogenate it over palladium on carbon at 350°C under nitrogen. The oxidation of I by paracetic acid does not proceed at the heteroatom as in the case of the sulfur isolog [1], but at the methylene group to form 2-selenophthalide (II). The reaction of I with an equimolecular amount of bromine in carbon tetrachloride gives an addition product, from which starting I is formed by the action of alcoholic alkali.

EXPERIMENTAL

1,3-Dihydrobenzo[c]selenophene (I). A mixture of 47.5 g (20.31 mole) of Rongalite (sodium formaldehyde sulfoxylate), 29.2 g (0.73 mole) of sodium hydroxide, and 10.5 g (0.13 mole) of powdered selenium in 300 ml of water was stirred under nitrogen for 30 min. After the selenium had completely dissolved, a saturated solution of 35 g (0.13 mole) of ω, ω'-dibromo-o-xylene in dioxane was added dropwise, and the mixture was refluxed for 1 h. It was then poured into ice water, and the precipitate was filtered by suction and steam distilled. The distillate was cooled to 0°, and the precipitate was removed by filtration, dried over phosphorus pentoxide, and vacuum sublimed to give 11.2 g (47%) of I with bp 110-111° (2 mm) and mp 34-35°. Found: C 52.4; H 4.3%. C_8H_8Se. Calculated: C 52.4; H 4.4%. The compound had R_f 0.88 when chromatographed on a thin layer of activity II Al_2O_3 with elution by benzene and development by iodine. PMR spectrum, δ, ppm: 4.17 (singlet, CH_2); 7.02 (singlet, CH).

1,3-Dihydrobenzo[c]selenophene Bromide. A solution of 3.20 g (0.02 mole) of bromine in 20 ml of carbon tetrachloride was added dropwise with stirring in the course of 30 min to a solution of 3.66 g (0.02 mole) of I in 50 ml of carbon tetrachloride. The resulting precipitate was filtered by suction to give 6.65 g (97%) of 1,3-dihydrobenzo[c]selenophene bromide with mp 167° (from chloroform). Found: C 28.4; H 2.5%. $C_8H_8Br_2Se$. Calculated: C 28.0; H 2.3%.

2-Selenophthalide (II). A total of 11.5 ml of 22% hydrogen peroxide (0.08 mole) was added in the course of 30 min at 0° to a solution of 10 g (0.055 mole) of I in 100 ml of glacial acetic acid. Steam distillation of the reaction mixture gave 2 g of starting I. The residual oil was crystallized from ether to give 2.93 g of II (34% based on the I consumed in the reaction) with mp 71-72°. Found: C 48.6; H 3.5%. C_8H_6OSe. Calculated: C 48.7; H 3.1%. The product had R_f 0.45 when it was chromatographed on a thin layer of activity II Al_2O_3 with elution by benzene and development of iodine. IR spectrum: 1695 cm^{-1} (C = O). PMR spectrum, δ, ppm: 4.28 (singlet, CH_2); 7.50 (multiplet, CH); the intensity ratio was 1 : 2.

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The PMR spectra of 10% CCl_4 solutions were recorded with an RS-60 spectrometer with hexamethyldisiloxane (HMDS) as the internal standard. The IR spectra were recorded with a UR-20 spectrometer.

LITERATURE CITED

1. S. F. Birch, R. A. Dean, and E. V. Whitehead, J. Inst. Petrol., 40, 76 (1954).