ELECTROPHILIC REACTIONS OF HALIDES OF GROUP VI ELEMENTS.

7.* REACTIONS OF ALLYLBENZENE AND ALLYL PHENYL ETHER WITH SELENIUM TETRAHALIDES

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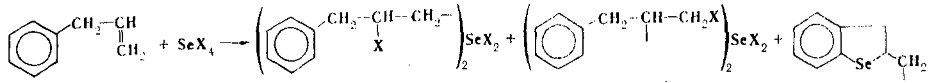
The reaction of selenium tetrachloride with allylbenzene and allyl phenyl ether proceeds in accordance with the Markownikoff rule to give 1:2 adducts. The use of selenium tetrabromide changes the course of the reaction and leads to the production of a mixture of adducts in accordance with and counter to the Markownikoff rule, as well as products of cyclization of the intermediate monoadducts to 2-bromomethyl-2,3-dihydrobenzo[b]selenophene or 2-bromomethyl-benzo-1,4-selenoxane derivatives.

We have previously developed a new general method for carrying out reactions involving the addition of selenium tetrahalides to olefins that ensures high yields of the desired products and is distinguished by its simplicity [1-5]. In the present research we extended this reaction to allylbenzene and allyl phenyl ether. As we will demonstrate below, these reactions proceed in part to give selenium-containing heterocycles.

We found that selenium tetrachloride reacts with allylbenzene to give only one product in accordance with the Markownikoff rule (Ia), regardless of the presence or absence of a solvent (see the data in [6]). The following signals are present in the PMR spectrum of adduct Ia: a doublet at 3.2 ppm (4H, CH_2Ph, J = 7 Hz), a multiplet of diastereotopic protons of CH_2SeCl_2 groups at 3.95-4.35 ppm (4H), and a multiplet of methylidyne protons at 5.05 ppm. The signals were assigned on the basis of the data in [7], which show that the halogen atoms have a greater deshielding effect than the SeX_2 group.

Once again, only a product of addition in accordance with the Markownikoff rule (Ib) was isolated in 70% yield in the reaction of selenium tetrabromide with allylbenzene. However, the action of selenium tetrabromide on an ether solution of allylbenzene gives another adduct with a 1:2 composition (IIb), as well as a product of further substitution in the benzene ring, viz. a 2-bromomethyl-2,3-dihydrobenzo[b]selenophene derivative (IIIb). The mixture of IIb and IIIb was separated with a chromatographic column filled with silica gel by elution with hexane—ether (5:1).



Ia,b IIb IIIb

Ia X=Cl; I-IIIb X=Br

The structure of adduct Ib was proved by the PMR spectrum, which contains signals (in $CDCl_3$) at 3.33 ppm (d, J = 7 Hz, 4H, CH_2Ph), four signals of diastereotopic protons of $CH_2SeBr_2CH_2$ equivalent methylene groups at 4.34, 4.30, 4.22, and 4.18 ppm, and a quartet at 5.15 ppm (2H, CHBr), which constitutes evidence for addition in accordance with the Markownikoff rule, although it does not make it possible to form a judgment regarding the diastereomeric composition (compare with [8]). The PMR spectrum of IIb is in agreement with the spectrum expected for a 1:2 adduct. However, it is impossible to solve the following alternative on the basis of the PMR spectrum: Is IIb an anti-Markownikoff addition product or a stereoisomer (diastereomer) of adduct Ib (compare with the data in [8])? On the basis of general consider-

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*See [1-6] for previous communications.

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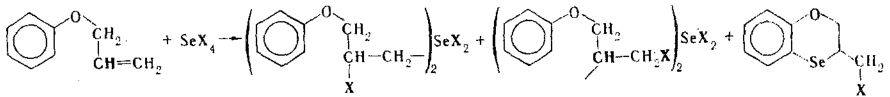
ations regarding the regioselectivity of the addition and its dependence on the solvent, we are inclined to favor the first possibility and assign the structure of an anti-Markownikoff adduct to IIb. Let us note that the addition of selenium tetrachloride proceeds more specifically than the addition of the tetrabromide in conformity with the data for the addition of these reagents to allyl halides [6].

The structure of heterocycle IIIb follows from the results of elementary analysis and data from the PMR spectrum, which differs markedly from the spectra of adducts Ib and IIb and contains a broad multiplet consisting of 12 lines at 3.0-4.0 ppm (AB part of an ABX system; CH_2 group), which is overlapped by a doublet of the CH_2Br group at 3.8 ppm, and a one-proton multiplet at 4.18-4.65 ppm (CHSe group). Thus a distinctive feature of the addition of selenium tetrabromide to allylbenzene is electrophilic substitution in the intermediate monoadduct as a step that is competitive with the addition of a second molecule of the olefin.

The reaction of selenium tetrachloride and tetrabromide with allyl phenyl ether proceeds similarly. Selenium tetrachloride gives only one product (IVa), to which we assign the structure of a Markownikoff adduct on the basis of its PMR spectrum, which contains the following three groups of signals: signals of aromatic protons at 6.48-7.42 ppm, overlapped multiplets at 4.04-4.55 ppm (8H, CH_2O and CH_2Se), and a multiplet at 4.90-5.30 ppm (2H, CHCl). As in the preceding case, selenium tetrabromide gives a mixture of three compounds, two of which (IVb and Vb) are adducts in accordance with and counter to the Markownikoff rule. Once again, the assignment of the structures was made hypothetically on the basis of data on the relative electronegativities of the functional groups. We assigned the cyclic structure of a benzoselenoxane derivative to the third compound (VIb).



IVa,b　　Vb　　VIb

IVa X = Cl; IV-VI b X = Br

Thus the addition of selenium tetrahalides to the investigated allyl compounds can be carried out with the formation of 1:2 adducts. At the same time, the specificity of the reaction with these olefins in the case of selenium tetrabromide can be altered markedly and directed to favor the formation of heterocyclic organoselenium compounds. It is obvious that the synthetic aspects of this cyclization are worthy of special study.

EXPERIMENTAL

The PMR spectra of solutions of the compounds in CCl_4 were recorded with Tesla BS-467 (60 MHz) and Tesla BS-487A (80 MHz) spectrometers with hexamethyldisiloxane as the internal standard; the chemical shifts are presented relative to tetramethylsilane. The course of the reactions and the individuality of the substances were monitored by means of thin-layer chromatography (TLC) on Silufol UV-254 plates with elution by hexane—ether (5:1).

The reactions of allylbenzene and allyl phenyl ether with selenium tetrachloride and tetrabromide were carried out by the following methods.

A) A 5.5-g (0.05 mole) sample of selenium dioxide dissolved in 28 ml of hydrochloric acid (sp. gr. 1.19) was added with stirring and cooling to 0°C to 5.9 g (0.05 mole) of allylbenzene. The precipitated Ia was removed by filtration, dried, and recrystallized from CCl_4 to give 7.0 g (61.4%) of a product with mp 124°C. PMR spectrum ($CDCl_3$): 3.2 (d, 4H, CH_2Ph), 3.95-4.35 (m, 4H, CH_2SeCl_2), 5.05 (m, 2H, CHCl), and 7.10 ppm (m, 10H, aromatic). Found: C 47.7; H 4.3; Cl 31.2%. $C_{18}H_{20}Cl_4Se$. Calculated: C 47.3; H 4.4; Cl 31.1%.

A similar procedure was used to obtain 11.2 g (70%) of Ib with mp 106°C. PMR spectrum ($CDCl_3$): 3.33 (d, 4H, CH_2Ph), 4.10-4.42 (m, 4H, CH_2SeBr_2), 5.15 (m, 2H, CHBr), and 7.10 ppm (m, 10H, aromatic). Found: C 34.2; H 3.0; Br 50.8%. $C_{18}H_{20}Br_4Se$. Calculated: C 34.0; H 3.1; Br 50.4%.

This procedure also gave 7.3 g (60%) of IVa with mp 125°C (acetonitrile). PMR spectrum: 4.04-4.55 (m, 8H, CH_2, CH_2Se), 4.90-5.30 (m, 2H, CHCl), and 6.78-7.42 ppm (m, 10H, aromatic). Found: C 44.7; H 3.8; Cl 28.3%. $C_{18}H_{20}Cl_4O_2Se$. Calculated: C 44.2; H 4.1; Cl 28.0%.

A similar procedure was used to obtain 12 g (72%) of IVb with mp 126°C (CCl_4). PMR spectrum (hexachloroacetone): 3.30-4.65 (m, 8H, CH_2, CH_2SeBr_2), 4.92-5.37 (m, 2H, CHBr), and 6.55-7.40 (m, 10H, aromatic). Found: C 32.7; H 3.2; Br 47.9%. $C_{18}H_{20}Br_4O_2Se$. Calculated: C 32.4; H 3.0; Br 47.9%.

B) A 3.3-g (0.03 mole) sample of selenium dioxide dissolved in 16.5 ml of hydrochloric acid (sp. gr. 1.19) was added with stirring and cooling to 0°C to 3.6 g (0.03 mole) of allylbenzene in 125 ml of diethyl ether. At the end of the reaction, the ether layer was separated and dried with anhydrous sodium sulfate. The solvent was removed with a vacuum evaporator, and the residual oil began to crystallize to give 3.65 g (53%) of a product with mp 124°C (from CCl_4). The PMR spectrum was identical to the spectrum of the product obtained by method A. Found: C 47.9; H 4.1; Cl 31.9%. $C_{18}H_{20}Cl_4Se$. Calculated: C 47.3; H 4.4; Cl 31.1%.

C) A solution of 5.5 g (0.05 mole) of selenium dioxide in 45 ml of hydrobromic acid (sp. gr. 1.48) was added dropwise with stirring at 0°C to 5.9 g (0.05 mole) of allylbenzene in 250 ml of diethyl ether. After 2 days, the ether layer was separated and dried with anhydrous sodium sulfate. The solvent was removed with a vacuum evaporator, and the residue was distilled in vacuo to give 12.2 g (77%) of a product with bp 121-126°C (1 mm). The fraction obtained contained two substances that could not be separated by fractionation. A 1.3-g sample of a mixture of IIb and IIIb was separated with a chromatographic column [on 100/250 silica gel by elution with hexane—ether (5:1)]. The yield of IIb, with bp 121-122°C (2 mm), n_D^{19} 1.614, and R_f 0.15, was 0.4 g (30.8%). PMR spectrum: 2.81 (d, 4H, CH_2Ph), 3.05-3.40 (m, 4H, CH_2Br), 3.45-4.05 (m, 2H, $CHSeBr_2$), and 7.12 ppm (m, 10H, aromatic). Found: C 34.2; H 3.4; Br 50.9%. $C_{18}H_{20}Br_4Se$. Calculated: C 34.0; H 3.1; Br 50.4%. The yield of IIIb, with bp 105-106°C (2 mm), n_D^{19} 1.317, and R_f 0.68, was 0.8 g (61.5%). PMR spectrum: 3.0-4.0 (m, 2H, CH_2), 3.80 (d, 2H, CH_2Br), and 4.18-4.65 ppm (m, 2H, CHSe). Found: C 39.1; H 3.4; Br 29.5%. C_9H_9BrSe. Calculated: C 39.1; H 3.3; Br 29.0%.

D) A solution of 5.5 g (0.05 mole) of selenium dioxide in 45 ml of hydrobromic acid (sp. gr. 1.48) was added with stirring and cooling to 0°C to 6.7 g (0.05 mole) of phenyl allyl ether in 400 ml of diethyl ether. After 2 days, the ether layer was separated and dried with anhydrous sodium sulfate. The solvent was removed, and the residue was separated with a chromatographic column [silica gel, hexane—ether (5:1)]. The yield of Vb, with bp 81-84°C (2 mm), n_D^{19} 1.463, and R_f 0.53, was 4.2 g (25%). PMR spectrum: 3.84 (d, 4H, CH_2Br), 4.10-4.65 (m, 6H, CH_2O, $CHSeBr_2$), and 6.42-7.55 ppm (m, 10H, aromatic). Found: C 32.8; H 3.0; Br 47.4%. $C_{18}H_{20}Br_4O_2Se$. Calculated: C 32.4; H 3.0; Br 47.9%. The yield of VIb, with n_D^{19} 1.663 and R_f 0.34, was 1.33 g (9%). PMR spectrum: 3.57 (d, 2H, CH_2Br), 3.80-4.42 (m, 3H, CH_2O, CHSe), and 6.40-7.50 ppm (m, 4H, aromatic). Found: C 36.7; H 3.0; Br 27.8%. C_9H_9BrOSe. Calculated: C 36.9; H 3.1; Br 27.4%.

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