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CONDENSED HETEROCYCLES.

42.* SYNTHESIS AND SOME PROPERTIES OF 3-HYDROSELENOBENZO[b]FURAN-2-CARBALDEHYDE AND 2-HYDROSELENOBENZO[b]FURAN-3-CARBALDEHYDE

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The reactions of 3-chlorobenzo[b]furan-2-carbaldehyde and 2-bromobenzo[b]furan-3-carbaldehyde with sodium hydrogen selenide have yielded isomeric hydroseleno aldehydes which, under the action of atmospheric oxygen, have oxidized to diselenides, while alkylation of the seleno aldehydes with methyl iodide leads to the formation of the corresponding methylseleno derivatives.

Ortho-bifunctionally substituted heterocycles are attracting attention as intermediates in the synthesis of various condensed heterocyclic systems, and also of different substances with properties of practical use [2, 3]. Continuing the search for methods of synthesizing and of studying the structure and properties of hydroxy, mercapto, and seleno aldehydes and aldimines of the heterocyclic series, we have made an attempt to synthesize previously unknown isomeric hydroselenobenzo[b]furancarbaldehydes.

One of the possible methods of obtaining ortho-hydroseleno aldehydes of the heterocyclic series is the nucleophilic replacement of hydrogen atoms in the corresponding ortho-halo aldehydes by a hydroseleno group. Thus, isomeric hydroselenobenzo[b]thiophenecarbaldehydes have previously been synthesized by this method [4]. The initial compounds for obtaining hydroselenobenzo[b]furancarbaldehydes — 3-chlorobenzo[b]furan-2-carbaldehyde (I) and

*For communication 41, see [1].

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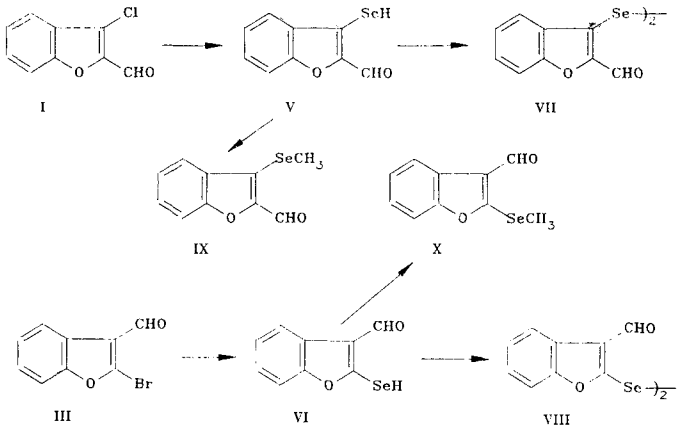

2-chlorobenzo[b]furan-3-carbaldehyde — can be obtained by the chloroformylation of coumarin-3-one [5] and coumaran-2-one [6]. However, while coumaran-3-one is readily formed from o-hydroxychloroacetophenone [7], coumaran-2-one can be obtained only by a multistage synthesis from difficultly accessible compounds and with low yield [8]. An attempt to synthesize coumaran-2-one by one of the simplest methods, in our opinion — the reduction of 2-nitrobenzo[b]furan [9] with tin in hydrochloric acid [10] — proved unsuccessful: it was impossible to isolate coumaran-2-one from the reaction mixture. We therefore decided to synthesize a 2-halobenzo[b]furan-3-carbaldehyde by another route. Thus, starting from 2-bromo-3-bromomethylbenzo[b]furan (II), 2-bromobenzo[b]furan-3-carbaldehyde (III) was obtained by the Sommelet reaction (method A), but its yield did not exceed 5%. In order to raise the yield of the bromo aldehyde (III) we changed the scheme of synthesis, and by hydrolyzing (II) we obtained 2-bromo-3-hydroxymethylbenzo[b]furan (IV), the oxidation of which with manganese dioxide led to (III) with a yield of 76% (method B).

The IR spectrum of compound (IV) contained a broad band in the 3150 cm^{-1} region, while that of the aldehyde (III) contained a band at 1660 cm^{-1} that is characteristic for a carbonyl group. In the PMR spectrum of compound (IV) there was a singlet of methylene protons at 4.58 ppm and a broadened singlet of the protons of an OH group at 2.16 ppm, while the spectrum of (III) contained the singlet of an aldehyde proton at 9.9 ppm.

The reaction of the halo aldehydes (I) and (III) with sodium hydrogen selenide led to 3-hydroselenobenzo[b]furan-2-carbaldehyde (V) and 2-hydroselenobenzo[b]furan-3-carbaldehyde (VI), which readily underwent oxidation in air and were therefore characterized in the form of the diselenides (VII) and (VIII). It must be mentioned that the isomeric hydroseleno aldehydes of benzo[b]thiophene are more stable to the action of atmospheric oxygen.

The reaction of methyl iodide with the hydroseleno aldehydes (V) and (VI) without their isolation from the reaction mixture led to the formation of the corresponding isomeric methylselenobenzo[b]furancarbaldehydes (IX) and (X) with high yields.

The results of elementary analysis and the mass spectra of the diselenides (VII) and (VIII) did not contradict the proposed structure, and the IR spectra of these compounds contained absorption bands at 1676 and 1680 cm^{-1}, respectively, which are characteristic for a carbonyl group. The composition of the methylseleno derivative (IX) and (X) was confirmed by their mass spectra and elementary analyses. The IR spectra of (IX) and (X) contained bands that are characteristic for a carbonyl group at 1663 and 1656 cm^{-1}, respectively, and the PMR spectra contained the singlets of aldehydic protons at 10.06 and 10.07 ppm and the signals of the protons of methyl groups at 2.35 and 2.46 ppm with characteristic splitting from ^{77}Se.

EXPERIMENTAL

IR spectra were taken on a UR-20 spectrometer (in KBr tablets). PMR spectra were recorded on a Tesla BS-467 spectrometer (60 MHz) in $CDCl_3$, with HMDS as internal standard. UV spectra were obtained on a Specord UV-vis spectrometer. Mass spectra were taken on a Varian MAT CH-6 instrument with direct introduction of the sample into the ion source, at an energy of the ionizing electrons of 70 eV. The masses of the molecular ions in the mass spectra are given on the basis of the main isotopes ^{80}Se and ^{81}Br.

The bromination of 3-methylbenzo[b]furan, synthesized by a published method [12] (bp 195-197°C), yielded 2-bromo-3-methylbenzo[b]furan (bp 104-106°C at 8 mm; according to the literature [11]: bp 114-115°C at 11 mm), and the starting compound (II) was obtained by brominating the latter with N-bromosuccinimide (mp 61-63°C; according to the literature [11]: mp 61-63°C).

2-Bromo-3-hydroxymethylbenzo[b]furan (IV). A solution of 16 g (55 mmole) of the bromide (II) in 276 ml of dioxane was added to a solution of 4.64 g (55 mmole) of $NaHCO_3$ in 276 ml of water. The mixture was boiled for 45 min and extracted with $CHCl_3$, and the extract was dried with $MgSO_4$. The solvent was distilled off and the residue was recrystallized from $CHCl_3$, giving 10.9 g (87%) of the carbinol (IV), mp 94.5-95°C. IR spectrum: 3150 cm^{-1} (OH). UV spectrum (in ethanol), λ_{max}, nm (log ε): 214 (4.17), 251 (4.04), 278 (3.61), 285 (3.57). PMR spectrum, ppm: 7.6-7.04 (4H, m, Ar), 4.58 (2H, s, CH_2), 2.16 (1H, br.s, OH). Found, %: C 47.8, H 3.2, Br 35.7. M^+ 228. $C_9H_7BrO_2$. Calculated, %: C 47.6, H 3.1, Br 35.2. M 227.

2-Bromobenzo[b]furan-3-carbaldehyde (III). A. A solution of 2.08 g (7.2 mmole) of the bromide (II) in 20 ml of $CHCl_3$ was treated with 1.4 g (10 mmole) of hexamethylenediamine in 20 ml of $CHCl_3$ at 25°C, and the mixture was left for 12 h. The salt that had deposited was filtered off, washed with $CHCl_3$, dried in the air for 1 h, and dissolved in 60 ml of 50% CH_3COOH, and the solution was boiled for 1.5 h. Then it was cooled, diluted with 60 ml of water, and extracted with ether, and the extract was washed with 10% KOH solution and with water and was dried with $MgSO_4$. The solvent was distilled off, the residue was chromatographed (2 × 15 cm column of 40-100 mesh silica gel with benzene as the eluent), the solvent was driven off, and the residue was recrystallized from hexane. This gave 0.07 g (4%) of compounds (III), mp 107-108.5°C. IR spectrum: 1660 cm^{-1} (C=O). UV spectrum (in ethanol): λ_{max}, nm (log ε): 208 (4.33), 233 (4.28), 250 (3.87), 285 (3.93). PMR spectrum, ppm: 9.9 (1H, s, CHO), 8.2-7.87 (1H, 4-H), 7.58-7.03 (3H, m, Ar). Found, %: C 48.3, H 2.5, Br 36.2. M^+ 226. $C_9H_5BrO_2$. Calculated, %: C 48.0, H 2.2, Br 36.2; mol. wt. 225.

B. A solution of 17.9 g (79 mmole) of compound (IV) in 1 liter of $CHCl_3$ was treated with 160 g of active manganese dioxide. The suspension was stirred at 25°C for 10 h and it was then left for 15 h and filtered; the MnO_2 residue was carefully washed with $CHCl_3$, and the filtrate was evaporated and chromatographed (3.5 × 30 cm column with 40-100 mesh silica gel using $CHCl_3$ as the eluent). The solvent was distilled off and the residue was recrystallized from hexane, giving 13.48 g (76%) of compound (III) with mp 107-108.5°C. The UV, IR, and PMR spectra and the elementary analyses of the samples of compound (III) obtained by methods A and B were identical.

Di(2-formyl-3-benzo[b]furyl)diselenide (VII). In a current of nitrogen, a solution of 5.7 g (32 mmole) of the aldehyde (I) (mp 78°C [5]) in 50 ml of methanol was added to a solution of 3.81 g (37 mmole) of NaSeH in 60 ml of methanol. The reaction mixture was boiled for 30 min, cooled to 10°C, and slowly acidified with 80 ml of 6% HCl. The precipitate that deposited was separated off, washed with water, dried over P_2O_5, dissolved in 100 ml of $CHCl_3$, and, after the solution had been filtered, it was reprecipitated in hexane. This gave the diselenide (VII) with a yield of 6.85 g (96%), mp 96-102°C (from hexane). IR spectrum: 1676 cm^{-1} (C=O). UV spectrum (in $CHCl_3$), λ_{max}, nm (log ε): 238 (3.78), 286 (3.69), 305 (3.71). Found, %: C 47.7, H 2.6, Se 35.2. M^+ 450. $C_{18}H_{10}O_4Se_2$. Calculated, %: C 48.2, H 2.2, Se 35.2; mol. wt. 448.

3-Methylselenobenzo[b]furan-2-carbaldehyde (IX). Under argon, 2 g (11 mmole) of the aldehyde (I) in 30 ml of methanol was added to a solution of 1.34 g (12.8 mmole) of NaSeH in 30 ml of methanol. The mixture was boiled for 30 min, 20 ml of water and 2 ml (32 mmole) of CH_3I were added, the mixture was stirred for 15 min, 50 ml of water was added, extraction was carried out with $CHCl_3$, the extract was dried with $MgSO_4$, the solvent was distilled off, and the residue was recrystallized twice from ether, giving compound (IX) with a yield of 1.27 g (48%), mp 61.5-63.5°C. IR spectrum: 1663 cm^{-1} (C=O). UV spectrum (in ethanol), λ_{max}, nm (log ε): 235 (3.88), 305 (4.23). PMR spectrum, ppm: 10.06 (1H, s, CHO), 7.82-7.10 (4H, m, Ar), 2.35 (3H, s, CH_3). Found, %: C 50.1, H 3.4, Se 33.4. M^+ 240. $C_{10}H_8O_2Se$. Calculated, %: C 50.2, H 3.4, Se 33.0; mol. wt. 239.

Di(3-formyl-2-benzo[b]furyl)diselenide (VIII) was obtained in a similar manner to compound (VII) with a yield of 87%, mp 133-138°C (from hexane). IR spectrum: 1680 cm^{-1} (C=O). UV spectrum (in $CHCl_3$), λ_{max}, nm (log ε): 236 (4.42), 306 (4.05). Found, %: C 48.0, H 2.1, Se 35.6. M^+ 450. $C_{18}H_{10}O_4Se_2$. Calculated, %: C 48.2, H 2.2, Se 35.2; mol. wt. 448.

2-Methylselenobenzo[b]furan-3-carbaldehyde (X) was obtained in a similar manner to (IX) with a yield of 67%, mp 38.7-40°C. IR spectrum: 1656 cm^{-1} (C=O). UV spectrum (in ethanol), λ_{max}, nm (log ε): 207 (4.39), 236 (4.19), 323 (3.95). PMR spectrum, ppm: 10.07 (1H, s, CHO), 7.98-7.75 (1H, m, 4-H), 7.47-7.07 (3H, m, Ar), 2.46 (3H, s, CH_4). Found, %: C 50.5, H 3.5, Se 33.5. M^+ 240. $C_{10}H_8O_2Se$. Calculated, %: C 50.2, H 3.4, Se 33.0; mol. wt. 239.

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A STUDY OF THE KINETICS OF THE INTERACTION OF BENZOXAZOLINE-2-THIONES WITH BUTYLAMINE

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The kinetics of the interaction of butylamine with 5- and 6-substituted benzoxazoline-2-thiones has shown the absence of a correlation between the rate of the reaction and the electronic properties of the substituents. Thus, the mechanism of the nucleophilic opening of the benzoxazoline-2-thione ring differs from those described previously.

It is known that the reaction of benzoxazoline-2-ones and benzoxazoline-2-thiones with nucleophilic agents such as metal hydroxides [1, 2], ammonia [3], or amines [2, 4-7] takes place with the opening of the heterocyclic ring and the formation, in the case of the nitrogenous nucleophiles of substituted o-aminophenols or o-hydroxyphenylureas or the corresponding thio compounds. That is, the nucleophilic attack on these heterocycles is directed to the carbonyl (thione) carbon atom.

In order to elucidate the mechanism of the interaction of benzoxazoline-2-thiones with aliphatic amines, we have studied the kinetics of the reaction of 5- and 6-substituted benzoxazoline-2-thiones (Ia-o) with butylamine. It is known that the reaction of the heterocycle (Ia) with amines takes place with high — frequently quantitative — yields and leads to the unsymmetrical disbustituted thioureas (IIa-o) and trisubstituted thioureas [5-7].

We performed the reaction of compounds (Ia-o) with butylamine at 65°C in butylamine solution, measuring the change in the concentration of the initial heterocycle from the decrease in the intensity of the absorption band in the 280-320 nm region. As can be seen from

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