added 0.5 mmole of triethylamine. The mixture was heated at 100°C for 15 min, and the dye was precipitated with water.

2-Phenyl-5-methylthiazolo[3,2-a]pyridinio-3-oxide (VIIIb). A 0.52-g sample (2 mmole) of α-(6-methyl-2-pyridylthiophenyl)acetic acid [obtained by analogy with α-(2-pyridylthiophenyl)acetic acid [10]] was boiled in 2 ml of acetic anhydride for 2 min. After cooling, the precipitate was filtered off. PMR spectrum, δ (in trifluoroacetic acid): 3.12 (s, CH_3), 7.15-8.1 ppm (m, aromatic —H). Found: Mol.wt. 240. Calculated: Mol.wt. 241.

2-Phenyl-3-methoxythiazolo[3,2-a]pyridinium Perchlorate (IXa). Compound (IXa) was obtained by heating (VIIIa) and dimethyl sulfate in a molar ratio of 1:2 to 80°C. The product was rubbed with ether and converted into the perchlorate from an alcohol solution. PMR spectrum, δ (in trifluoroacetic acid): 3.9 (s, OCH_3), 7.26-8.9 ppm (m, aromatic —H).

2-Phenyl-3-methoxy-5-methylthiazolo[3,2-a]pyridinium Perchlorate (IXb). Compound (IXb) was obtained similarly to (IXa). PMR spectrum, δ (in trifluoroacetic acid): 3.78 (s, OCH_3), 3.0 (s, CH_3), 7.27-8.07 ppm (m, aromatic —H).

Dealkylation of the Salts (IXa, b). A 1-mmole sample of the salt (IXa) or (IXb) was heated in 15 ml of absolute alcohol with 1 mmole of triethylamine for 1 h at 75°C. The precipitated ammonium salt was filtered off, and the mesoionic compounds (VIIIa, b) were precipitated from the filtrate with water.

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PRODUCTION OF 3-BROMOSELENOPHENO[2,3-b]SELENOPHENE

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β-Monobromo-substituted condensed five-membered heterocycles are of considerable interest for the synthesis of various derivatives of this series. However, their production by traditional direct bromination involves a series of difficulties (bromination of the initial compound to the tribromide, debromination, purification) [1]. The synthesis of β-bromoselenophenoselenophenes in this way is also complicated by the absence of developed methods for the production of the starting compounds. The selenophenoselenophene system was first reported in 1928, when English investigators [2], in the reaction of acetylene and selenium, isolated in addition to other compounds, a compound boiling at 240-250°C and containing ∿ 20% of selenium, which in their opinion represented contaminated selenopheno[2,3-b]selenophene. More recently Umezawa et al. [3, 4] investigated the residue formed during the production of

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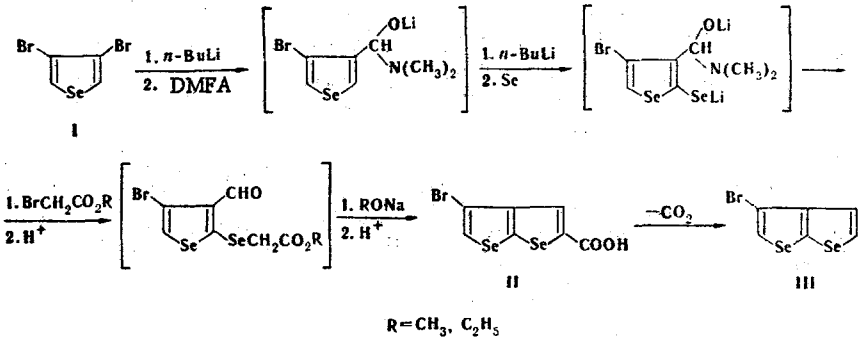
selenophene from selenium and acetylene and by complex treatment isolated small yields of three substances melting at 123-124.5°C and 51-51.5°C and boiling at 90-93°C (14 mm Hg). On the basis of dipole moment measurements they were assigned the structures of selenopheno-[3,4-b]-, selenopheno[3,2-b]-, and selenopheno[2,3-b]selenophene, respectively. However, during investigation of the ^{77}Se and ^{13}C NMR spectra of the high-melting compound, Gronowitz et al. [5] showed that it is in fact selenopheno[3,2-b]selenophene. Unfortunately, the work completed somewhat earlier by Italian investigators [6] on the x-ray diffraction analysis of the isomer does not contain information about the melting point of the sample which they investigated; it is only stated that the sample was prepared by crystallization from ethanol. Recently, French investigators reported [7] the possibility of obtaining (without a description of the experimental details) tetrachlorosubstituted selenopheno[2,3-b]- and selenopheno[3,2-b]-selenophenes by the reaction of β-(3-selenienyl)- and β-(2-selenienyl)acrylic acids with selenoxyl chloride in the presence of pyridine in chlorobenzene, i.e., under conditions analogous to those used by Wright [8] for the production of chlorinated thieno[3,2-b]thiophenes and by Gronowitz and Maltesson [9] for the synthesis of 3,5-dichloroselenopheno[2,3-b]thiophene-2-carbonyl chloride. The above-mentioned papers and an investigation into the magnetic susceptibility of selenophenoselenophenes [10] complete the data on their investigation.

Earlier [11] we developed a convenient method for the production of β-bromo-substituted thieno[2,3-b]- and selenopheno[2,3-b]thiophenes from o-bifunctional derivatives of the thiophene series. By applying this method to derivatives of the selenophene series, we synthesized 4-bromoselenopheno[2,3-b]selenophene-2-carboxylic acid (II) by the successive action of one equivalent of n-butyllithium at −70°C, DMFA, a second equivalent of N-butyllithium, elemental selenium, monobromoacetic ester, and sodium alkoxide on 3,4-dibromoselenophene (I) without isolation or purification of the intermediate products.

By decarboxylation of the acid (II) in quinoline in the presence of copper, we obtained 3-bromoselenopheno[2,3-b]selenophene (III).



EXPERIMENTAL

The PMR spectra were recorded on a Varian DA-60-JL instrument in acetone with HMDS as internal standard.

3-Bromoselenopheno[2,3-b]selenophene-5-carboxylic Acid (II). To a solution of 17.3 g of 3,4-dibromoselenophene (I) in 40 ml of absolute ether at −70°C we added 33 ml of 1.83 N ether solution of n-butyllithium. After 1 h 30 min at −70°C we added a solution of 4.4 g of DMFA in 15 ml of absolute ether. After stirring for 40 min we added a second equivalent of n-butyllithium (here the temperature rose to −40°C) and then 6 g of powdered selenium. When it had dissolved (2 h at −10, −15°C) we added a solution of 9.2 g of ethyl monobromoacetate in 20 ml of absolute ether. The reaction mass was stirred at 20°C for 2 h and left overnight in a stream of argon. It was then hydrolyzed at a temperature between −5 and 0°C with dilute (1:1) hydrochloric acid. The ether layer was separated, and the aqueous layer was extracted with ether. The ether extracts were combined, washed with water, and dried over magnesium sulfate. The ether was distilled. A solution of sodium alkoxide (from 5 g of sodium and 250 ml of ethanol) was added to the residue, and after stirring for 4 h at 20°C the main part of the alcohol was distilled. The precipitate was filtered off, washed with ether and with water (to colorless wash water), and dissolved by heating in acetic acid. The solution was cooled and diluted with water, and the precipitate was filtered off. We

obtained 5.5 g (26%) of 3-bromoselenopheno[2,3-b]selenophene-5-carboxylic acid (II); mp 254-255°C (in a unit with preliminary heating). Methyl ester, mp 169-171°C (vacuum sublimation). PMR spectrum: 8.08 (3-H), 8.16 (5-H), 3.85 ppm (OCH_3). Found, %: Br 21.0; OCH_3 8.8. $C_8H_5BrO_2Se_2$. Calculated, %: Br 21.5; OCH_3 8.4.

3-Bromoselenopheno[2,3-b]selenophene (III). A mixture of 30 ml of freshly distilled quinoline, 1.8 g of the acid (II), and 0.5 g of powdered copper was boiled until the release of carbon dioxide had ceased. It was then cooled, acidified with 10% hydrochloric acid, and extracted with ether. The extract was washed with 10% hydrochloric acid, water, sodium chloride solution, and water and dried over sodium chloride. We obtained 1.1 g (70%) of compound (III); mp 66-67°C (from aqueous alcohol). PMR spectrum: 7.96 (2-H), 7.44 (4-H), 8.08 ppm (5-H), J_{25} = 1.0; J_{45} = 5.9; $J_{^{77}Se-5-H}$ = 48.0; $J_{^{77}Se-2-H}$ = 45.2 Hz. Found, %: Se 50.6. $C_6H_3BrSe_2$. Calculated, %: Se 50.5.

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CARBOLINES 10.*

BASICITY CONSTANTS OF SOME 1H-PYRIDO[2,3-b]INDOLES (α-ISOCARBOLINES)

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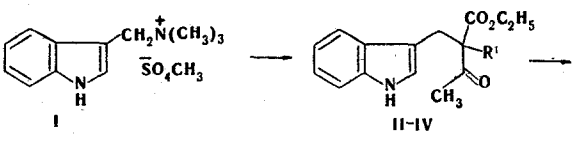
In connection with the fact that certain 2-chloro-α-isocarbolines possess fairly high cytotoxic activity [1], it seemed of interest to study their physicochemical characteristics for a subsequent structure—activity correlation in order to determine the factors which secure the maximum biological effect.

In the present work we studied the principal characteristics of a series of 2-chloro-α-isocarbolines containing alkyl substituents at positions 1 and 3.



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*For Communication 9, see [1].

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