CYCLIZATION OF α- AND β-(ARYLSELENO)ALKYLCARBOXYLIC ACIDS AND THEIR DERIVATIVES

E. G. Kataev, G. A. Chmutova,
and Yu. M. Mareev

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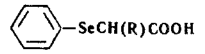
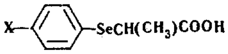
The cyclization of α- and β-(arylseleno)alkylcarboxylic acids in polyphosphoric acid was studied. It was found that α-(arylseleno)alkylcarboxylic acids do not cyclize under those conditions in which cyclization of the analogous β-(arylseleno)alkylcarboxylic acids does occur. A convenient method for the preparation of 2-methylselenonapthanone by the cyclization of α-phenylselenopropionyl chloride is proposed.

The cyclization of organoselenium compounds has not yet received sufficient study. Thus, there are only individual isolated data on the synthesis of condensed systems of the selenochroman and selenonaphthene series [1-6]. The latter were obtained chiefly from the rather inaccessible ortho-disubstituted benzenes [1-3]. We have noted [4, 5] that dihydroselenonaphthene derivatives can be obtained from aryl allyl selenides by refluxing them in quinoline, but the yields of the cyclization products are low. A convenient method for the preparation of selenochromanone is the cyclization of β-phenylselenopropionic acid in polyphosphoric acid (PPA), which was recently proposed by Renson [6].

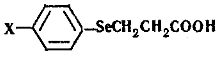
As an extension of earlier investigations [4, 5], we have studied the tendency for cyclization of a number of α- and β-(arylseleno)alkylcarboxylic acids (I-XI) and of α-phenylselenopropionyl chloride (XII).



I-III



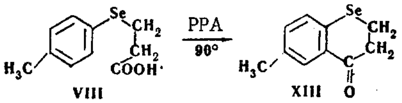
IV-VII



VIII-XI

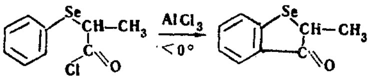
I R = CH_3, II R = C_2H_5, III R = H, IV X = CH_3, V X = CH_3O, VI X = Br, VII X = Cl, VIII X = CH_3, IX X = CH_3O, X X = Br, XI X = Cl

We have found that VIII, like β-phenylselenopropionic acid [6], is cyclized to 6-methylseleno-4-chromanone (XIII) by heating in PPA. Under the same conditions, IX is partially decomposed, and part of it is recovered unchanged; X and XI are recovered almost quantitatively from the reaction mixtures. Compound I is not cyclized to 2-methylselenonaphthanone (XIV) by heating in PPA but decomposes almost completely to diphenyl diselenide. Positive results were not achieved by varying the temperature and heating time. Acids II-VII also decompose rather than cyclizing.



VIII XIII

As expected, acid chloride XII turned out to be more active in intramolecular acylation than acid I and was readily cyclized to XIV under mild conditions:



XII XIV

V. I. Ul'yanov-Lenin Kazan' State University. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 333-334, March, 1971. Original article submitted September 29, 1969.

TABLE 1. α- and β-(Arylseleno)alkylcarboxylic Acids

Compound	mp, °C	Empirical formula	Found, %		Calc., %		Yield, %
			C	H	C	H	
I	47—48	$C_9H_{10}O_2Se$	47,1	4,2	47,2	4,4	81
II	53—54	$C_{10}H_{12}O_2Se$	49,7	5,0	49,4	5,0	62
IV	94—95	$C_{10}H_{12}O_2Se$	49,2	5,0	49,4	5,0	90
V	55—56	$C_{10}H_{12}O_3Se$	46,4	4,5	46,3	4,7	88
VI	126—127	$C_9H_9BrO_2Se$	35,1	2,9	35,1	2,9	80
VII	114—115	$C_9H_9ClO_2Se$	40,9	3,4	41,0	3,4	85
VIII	72—73	$C_{10}H_{12}O_2Se$	49,3	4,7	49,4	5,0	88
IX	76—77	$C_{10}H_{12}O_3Se$	46,4	4,7	46,3	4,7	87
X	119—120	$C_9H_9BrO_2Se$	35,1	3,0	35,1	2,9	76
XI	96—97	$C_9H_9ClO_2Se$	41,0	3,4	41,0	3,4	88

This method for obtaining selenonaphthanones is considerably more convenient than all of those hitherto proposed [1-3].

EXPERIMENTAL

The arylselenols were obtained according to the method in [7]. The α- and β-(arylseleno)alkylcarboxylic acids (I-XI) were obtained via the general method in [6] from the appropriate arylselenol and halogen-substituted carboxylic acid. The constants for I, II, and IV-XI (obtained for the first time) are presented in Table 1. The IR spectra of each of compounds I-XI contain a band at ~1720 cm^{-1} (C = O) and a high-intensity, diffuse band at ~2900 cm^{-1} (carboxylic acid OH) [8, 9].

Cyclization of α- and β-(Arylseleno)alkylcarboxylic Acids (I-XI). This was accomplished in PPA via the method in [6]. A total of 12.9 g (32.1%) of 6-methylseleno-4-chromanone (XIII) with bp 120-125° (0.5 mm) and mp 35-36° (from petroleum ether) was isolated from 43.4 g (0.17 mole) of VIII. Found %: C 53.4; H 4.5. $C_9H_{10}OSe$. Calculated %: C 53.4; H 4.5.

α-Phenylselenopropionyl Chloride (XII). Compound I [22 g (0.1 mole)] was stirred at room temperature with 55 g (0.5 mole) of $SOCl_2$ until HCl evolution ceased (12-20 h). Vacuum distillation of the $SOCl_2$ gave 14.1 g (56.2%) of XII with bp 100-102° (0.1-0.2 mm) and n_D^{25} 1.5890. Found %: C 43.7; H 3.5. C_9H_9OSeCl. Calculated %: C 43.6; H 3.7. The IR spectrum of XII contains an intense band at about 1780 cm^{-1} (acid chloride C = O). About 4 g of diphenyl diselenide with mp 61° was also isolated during distillation.

Cyclization of α-Phenylselenopropionyl Chloride (XII). A total of 11 g of anhydrous $AlCl_3$ was added in several portions to 11 g (0.04 mole) of XII dissolved in 100 ml of dry petroleum ether with cooling from −5 to −10°. The reaction mixture was stirred with cooling for 3 h, allowed to stand overnight, and then diluted to five times its original volume with ice water. The organic layer was extracted with ether. The ether extract was dried over $CaCl_2$, and the ether was removed by vacuum distillation to give 56.7% of 2-methylselenonaphthanone (XIV) with bp 89-91° (0.1-0.2 mm), d_4^{25} 1.5110, and n_D^{25} 1.6408. Found %: C 51.2; H 3.8. C_9H_8OSe. Calculated %: C 51.2; H 3.8. The product was a light-yellow, mobile liquid which began to vitrify after several hours. The IR spectrum of freshly distilled XIV contains a band at 1700 cm^{-1} (aliphatic aromatic ketones [9, 10]). Muth and Kiss [3], who first reported the synthesis of XIV, did not give its constants.

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