PREPARATION OF KETONES OF THE SELENOPHENE SERIES

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A number of 2-acyl derivatives of selenophene were synthesized in high yields by treatment of selenophene and its homologs with carboxylic acid anhydrides in the presence of perchloric acid.

Acyl derivatives have found broad application in selenophene chemistry. 2-Acylselenophenes are obtained by the Friedel-Crafts reaction. Umezawa [1] first acylated the selenophene ring using acetyl and propionyl chlorides and stannic chloride as the catalyst. Kataev and Palkina [2] acylated selenophene and its homologs with acid anhydrides in the presence of phosphoric acid. Many acylselenophenes, including unsaturated ketones and ketocarboxylic acids, were synthesized by Yur'ev and co-workers [3-5], who used silicoanhydrides of carboxylic acids as acylating agents.

We have studied the acylation of selenophene and its homologs with acid anhydrides in the presence of perchloric acid, which, as was shown in [6-9], is an effective catalyst for the acylation of furan, thiophene, and pyrrole.

It is well known that, on reaction with carboxylic acid anhydrides, perchloric acid forms reactive acyl perchlorates [10, 11] which are also acylating agents.

$$(RCO)_2O + HClO_4 \rightleftharpoons RCO^+ ClO_4^- + RCOOH$$

TABLE 1. 2-Acylselenophenes

Compound	Bp (mm)	Semicarbazone				Yield, %
		mp	Empirical, formula	N, % found	N, % calculated	
2-Acetylselenophene	96—97 (8)	197—198	$C_7H_9N_3OSe$	18,57	18,26	77,4
2-Propionylselenophene	122—124 (12)	171—171,5*	$C_8H_{11}N_3OSe$	17,76	17,23	74,5
2-Butyrylselenophene	135 (12)	167	$C_9H_{13}N_3OSe$	16,5	16,27	82
2-Isobutyrylselenophene	110—112 (8)	157—158†	$C_{14}H_{14}N_4O_4Se$	15,11	14,7	75,2
2-Valerylselenophene	130—131 (8)	172,5—173	$C_{10}H_{15}N_3OSe$	15,32	15,45	80,5
2-Isovalerylselenophene	122—124 (10)	166—166,5	$C_{10}H_{15}N_3OSe$	15,84	15,45	78
2-Diethylacetylselenophene	129—131 (8)	159—160†	$C_{16}H_{18}N_4O_4Se$	—	—	78
3-Methyl-2-acetylselenophene	107—108 (10)	207—209	$C_8H_{11}N_3OSe$	18,53	17,23	78,5
5-Methyl-2-acetylselenophene	111—112 (10)	219—221	$C_8H_{11}N_3OSe$	17,32	17,23	79

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*mp 175-176° [1].

†The melting point and analytical results for the 2,4-dinitrophenylhydrazone are presented.

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The acylation of selenophene with carboxylic acid anhydrides in the presence of small, catalytic amounts of perchloric acid proceeds readily and rapidly and makes it possible to quickly obtain ketones of the selenophene series in yields from 75 to 82%.

EXPERIMENTAL

Selenophene and 3-methylselenophene were synthesized by the reaction of the appropriate olefins with selenium metal [12]. The side formation of toluene, which boils at the same temperature as selenophene, was observed during the preparation of selenophene; this complicated the purification of selenophene. In this study, selenophene containing 92% of pure compound in 8% toluene, which, in the presence of perchloric acid, is virtually unreactive with respect to acylation [13], was used in this work. 2-Methylselenophene was obtained by Kishner reduction [15] of selenophene-2-aldehyde [14]. Selenophene and its homologs were analyzed by gas-liquid chromatography.

2-Acetylselenophene. A solution of 0.65 g (0.005 mole) of 72% perchloric acid in 17.3 g (0.17 mole) of acetic anhydride was added with stirring to a mixture of 48.4 g (0.34 mole) of selenophene (92% pure) and 34.7 g (0.34 mole) of acetic anhydride. The reaction mixture, which warmed up and darkened, was poured after 30 min into 250 ml of water. The organic product was extracted with ether, and the extract was washed with sodium carbonate solution and water and dried over calcined calcium chloride. The solvent was removed, and the residue was vacuum distilled to give 45.5 g (77.4%) of 2-acetylselenophene with bp 96-97° (8 mm) and n_D^{20} 1.6009 (bp 93.5 (7 mm), n_D^{20} 1.6011 [12]). The semicarbazone had mp 197-198° [from alcohol-benzene (1:1)]. Found %: N 18.57. $C_7H_9N_3OSe$. Calc. %: N 18.26. The phenylhydrazone had mp 112-114° (from dilute alcohol). Found %: N 10.59. $C_{12}H_{11}N_2Se$. Calc. %: N 10.64. According to [1] the phenylhydrazone has mp 114-116°.

The other 2-acyl derivatives of selenophene were similarly obtained (see Table 1). In the acylation with butyric, isobutyric, valeric, and isovaleric anhydrides the product was washed with 20% sodium hydroxide.

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