BENZOSELENAZOL-2-YLALKYL(ARYL) CARBINOLS

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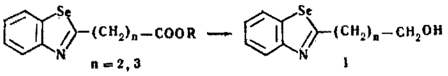
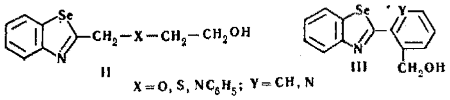
A method is described for the preparation of the previously unknown benzoselenazol-2-ylakyl(aryl) carbinols which involves reduction of the benzoselenazol-2-ylakane(arene)carboxylic esters with lithium aluminum hydride at low temperature.

Previously we have described a simple method for synthesizing benzoselenazol-2-ylalkane(arene)carboxylic acids which involves condensation of zinc o-aminoselenophenolate with the anhydrides of dibasic carboxylic acids [1].

In the present work it was found that by the reduction of esters of these acids with lithium aluminum hydride it was possible to prepare the benzoselenazol-2-ylalkyl carbinols in good yield:



The reaction also proceeded readily with esters in which one of the methylene groups of the saturated chain was replaced by O or S-atoms or a NC_6H_5 group, and yielded the alcohols II.



The benzoselenazol-2-ylaryl carbinols III are formed particularly smoothly from the corresponding esters and lithium aluminum hydride. It is necessary to carry out the lithium aluminum hydride reduction at a low temperature (–50, –60° C), in order to avoid the reaction of this reagent with the C═N bond in the selenazole nucleus.

Table 1. Benzoselenazol-2-ylalkyl(aryl) Carbinols

Compound	Name	Mp, °C	Bp, °C (mm)	Empirical formula	Se, % found	Se, % calculated	Yield, %
I, $n=2$	3-(Benzoselenazol-2'-yl)-propanol-1	36	173—175 (0.5)	$C_{10}H_{11}NOSe$	33.02	32.91	71
I, $n=3$	2-(Benzoselenazol-2'-yl)-butan-1-ol	27	104 (0.01)	$C_{11}H_{13}NOSe$	31.11	31.10	84
II, X=O	2-[(Benzoselenazol-2'-yl)-methoxy]ethan-1-ol	45	122 (0.01)	$C_{10}H_{11}NO_2Se$	30.95	30.85	58
II, X=S	2-[(Benzoselenazol-2'-yl)-methylthio]ethan-1-ol	—	138 (0;01)	$C_{10}H_{11}NOSSe$	29.21	29.04	81
II, $X=NC_6H_5$	2-(N-Phenyl-N-benzoselenazol-2'-amino)ethan-1-ol	84*	—	$C_{16}H_{16}N_2OSe$	24.10	23.86	89
III, Y=CH	2-(Benzoselenazol-2'-yl)-benzyl alcohol	78*	—	$C_{14}H_{11}NOSe$	27.33	27.43	94
III, Y=N	2-(Benzoselenaz ol-2'-yl)-pyrid-3-yl carbinol	99**	—	$C_{13}H_{10}N_2OSe$	27.40	27.33	85

*From light petroleum

**From a water-alcohol mixture

Details of the carbinols synthesized are given in Table 1. In order to characterize the new alcohols derivatives with respect to the hydroxyl group were prepared—the urethanes and the 3, 5-dinitrobenzoates (Table 2).

With dimethyl sulfate or with methyl iodide the carbinols form quaternary salts. Preliminary experiments showed that the carbinols of types I, II, III on treatment with phosphorus tribromide were converted into bromides

Table 2. Derivatives of Benzoselenazol-2-ylakyl(aryl) Carbinols

Carbinol	3,5-Dinitrobenzoates						Urethanes						
	Mp, °C	*empirical formula*	found, %		calculated, %		Mp, °C	empirical formula	found, %		calculated, %		yield %
			N	Se	N	Se			N	Se	N	Se	
I, *n*=2	114	$C_{17}H_{13}N_3O_6Se$	9.65	—	9.68	—	98	$C_{17}H_{16}N_2O_2Se$	7.83	—	7.79	—	71
I, *n*=3	117	$C_{18}H_{15}N_3O_6Se$	—	17.97	—	17.63	171	$C_{18}H_{18}N_2O_2Se$	—	21.62	—	21.17	64
II, X=O	115	$C_{17}H_{13}N_3O_7Se$	—	17.56	—	17.55	215	$C_{17}H_{16}N_2O_3Se$	—	21.90	—	21.64	56
II, X=S	105*	$C_{17}H_{13}N_3O_6SSe$	—	16.82	—	16.95	236	$C_{17}H_{16}N_2O_2SSe$	—	18.16	—	17.99	38
II, X=NC_6H_5	100	$C_{23}H_{18}N_4O_6Se$	—	15.32	—	15.04	204	$C_{23}H_{21}N_3O_2Se$	—	17.85	—	17.55	78
III, Y=CH	80	$C_{21}H_{13}N_3O_6Se$	8.80	—	8.71	—	83*	$C_{21}H_{16}N_2O_2Se$	6.47	—	6.87	—	76
III, Y=N	196	$C_{20}H_{12}N_4O_6Se$	11.78	—	11.59	—	180	$C_{20}H_{15}N_3O_2Se$	—	19.53	—	19.36	43

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*From a water-alcohol mixture.

which on heating gave the corresponding benzoselenazolium salts.

Carbinols of types I, II, and III have not been previously described in the literature.

EXPERIMENTAL

Benzoselenazol-2-ylalkane(arene)carboxylic esters were prepared by a published method [1].

3-(Benzoselenazol-2'-yl)propan-1-ol (I, n = 2). To a solution of 2.22 g (0.058 mole) of lithium aluminum hydride in 100 ml of absolute ether cooled to –50° C was added dropwise with stirring over 1 hr 9.30 g (0.03 mole) of ethyl 3-(benzoselenazol-2-yl)propionate in 100 ml of absolute ether, and the mixture was stirred at the same temperature for a further 1 hr. Reduction was carried out in a current of dry hydrogen freed from oxygen. To decompose the excess of lithium aluminum hydride, 90 ml of ether saturated with water was added dropwise to the mixture, warmed to –30° C, and then at –20° C a solution of 3.7 g of sodium hydroxide in water. When the mixture had warmed to room temperature the precipitate was filtered off and washed with 100 ml of ether. The combined ether solutions were washed with water three times and dried with sodium sulfate, and the residue, after the ether had been driven off, was distilled under vacuum.

The other compounds given in Table 1 were obtained analogously.

Methyl perchlorate derivative of 2-(benzoselenazol-2'-yl)benzyl alcohol. 0.6 g of the alcohol was heated with 0.5 ml of methyl iodide in a sealed tube 2 hr at 100° C. The product was washed with acetone, dissolved in water, and treated with sodium perchlorate. 0.46 g of the perchlorate was obtained, mp 207° C (from alcohol). Found, %: Cl 8.91. Calculated for $C_{15}H_{14}ClNO_5Se$, %: Cl 8.81.

Urethane from the Alcohol I (n = 1). 0.4 g (1 mM) of the alcohol and 0.19 g (1 mM) of phenyl isocyanate in 3 ml of dry benzene was heated 20 min at 60–70° C and then the benzene was distilled off and the residue was crystallized.

3, 5-Dinitrobenzoate of 3-(benzoselenazol-2'-yl)propan-1-ol). 0.5 g of alcohol and 0.48 g of 3, 5-dinitrobenzoyl chloride were heated for 20 min at 60–70° C. The solidified product was pulverized, washed with sodium carbonate solution and water, and crystallized from alcohol.

REFERENCE

1. F. S. Babichev and V. S. Likhitskaya, KhGS [Chemistry of Heterocyclic Compounds], 5, 508, 1969.

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