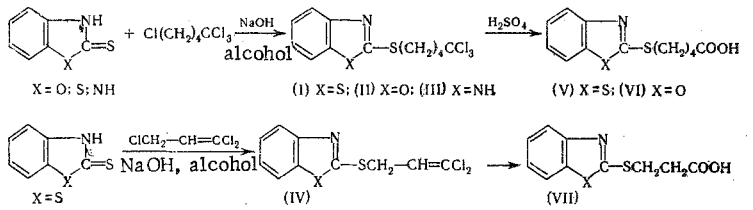
ALKYLATION OF 2-MERCAPTOBENZOTHIAZOLE, 2-MERCAPTOBENZOXAZOLE, AND 2-MERCAPTOBENZIMIDAZOLE BY POLYCHLOROALKANES AND ALKENES

E. N. Prilezhaeva and L. I. Shmonina

UDC 542.91+547.789+547.787+547.781

In our overall plan of synthesis of benzothiazoles, benzoxazoles, and benzimidazoles containing in the 2 position side chains with polar groups [1, 2], we alkylated these compounds with trichloropropene and tetrachloropentane [3] in an alkaline medium. The chlorides thus obtained were hydrolyzed to the corresponding carboxylic acids

Scheme 1



Alkylation of these heterocyclic thiones with trichloropropene and tetrachloropentane took place readily, giving chlorides (I)-(IV) (with 75.80% yields) in the form of low-melting slightly yellow crystalline substances.

Polyhalide compounds (I)-(IV) were hydrolyzed with concentrated H_2SO_4 to crystalline carboxylic acids (V)-(VII) with 50-60% yields. Hydrolysis with fuming nitric acid [4] led to formation of yellow complex mixtures of nitration products, which were not subjected to further investigation. Table 1 gives the properties and yields of the compounds obtained.

TABLE 1

Compound No.	bp, °C (p, mm Hg) or mp, °C (solvent)	Found, %			Empirical formula	Calculated, %			Yield, %
		C	H	S		C	H	S	
I	38–40 (hexane)	42,15	3,36	19,30	$C_{12}H_{12}NS_2Cl_3$	42,29	3,52	18,79	80
II	34–35 (hexane)	44,88	3,65	10,24	$C_{12}H_{12}NOSCl_3$	44,38	3,72	9,88	80
III	169–170 (alcohol)	44,07	4,07	9,92	$C_{12}H_{13}N_2SCl_3$	44,52	4,05	9,90	80,5
IV	97 — 99 (0,02)	43,43	2, 79	23,51	$C_{10}H_7NS_2Cl_2$	43,49	2,68	23, 22	75
V*	76,5–77,3 (hexane)	53,52	4,95	23,52	$C_{12}H_{13}NO_2S_2$	53,89	4,90	23,99	50
VI*	68 –69 (hexane – alcohol)	57,27	5,16	13,08	$C_{12}H_{13}NO_3S$	57,34	5,21	12,76	56
VII	149,8–150,5 (alcohol)	50,55	4,05	26,78	$C_{10}H_9NO_2S_2$	50, 19	3,79	26,79	61

*The infrared spectra exhibited bands at 1700-1730 cm^{-1} characteristic of the C = O group.

N. D. Zelinskii Institute of Organic Chemistry of the Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No.3, pp. 693-694, March, 1969. Original article submitted April 11, 1968.

EXPERIMENTAL SECTION

The melting points of the crystalline compounds were determined in a Koppler apparatus (uncorrected). The infrared spectra were obtained in a UR-10 spectrophotometer in a chloroform solution.

1,1,1-Trichloro-5-(2)-thiobenzotriazolylpentane (I), 1,1,1-trichlorothiobenzoxazolylpentane (II), 1,1,1-trichloro-5-(2)-thiobenzimidazolylpentane (III), and 1,1-dichloro-3-(2)-thiobenzothiazolylpropene (IV) was obtained by mixing an alcoholic solution of the corresponding chloride (0.1-0.05 M) with an equivalent amount of 2-mercaptobenzothiazole, 2-mercaptobenzoxazole, and 2-mercaptobenzimidazole, respectively in a solution of an equivalent amount of alcoholic solution of NaOH.

Hydrolysis to carboxylic acids was affected by gradual addition of chlorides (I), (II), and (IV) in concentrated H_2SO_4 with constant stirring. After addition of the chloride, the reaction mass was heated at 60-68°C for 5 h, poured into icewater, extracted with ether and dried over $CaCl_2$.

CONCLUSIONS

By alkylating 2-mercaptobenzothiazole, 2-mercaptobenzoxazole, and 2-mercaptobenzimidazole with 1,1,3-trichloropropene and 1,1,1,5-tetrachloropentane, the authors obtained the corresponding chlorides, which were then hydrolyzed to carboxylic acids.

LITERATURE CITED

1. E. N. Prilezhaeva and L. I. Shmonina, Zh. Organ. Khim., 2, 1883 (1966).
2. E. N. Prilezhaeva and L. I. Shmonina, Izv. Akad. Nauk SSSR, Ser. Khim., 670 (1969).
3. R. M. Joyce, W. F. Hanford, and J. Harman, J. Amer. Chem. Soc., 70, 2529 (1948).
4. R. Zh. Freidlina and E. N. Vasil'eva, Dokl. Akad. Nauk SSSR, 100, 85 (1955).