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REGULARITIES AND FEATURES OF THE REACTION OF 2-AMINO-6-NITRO- AND 2,6-DIAMINOBENZOTHIAZOLES WITH ETHYLENE CHLOROHYDRIN

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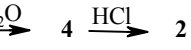
The alkylation of 2-amino-6-nitro- and 2,6-diaminobenzothiazoles by ethylene chlorohydrin has been studied. A comparative analysis has been made of the composition of these reaction mixtures and of those obtained from other 2-aminobenzothiazoles using this reaction. The structure of the synthesized compounds was confirmed using IR and ^{1}H NMR spectroscopy, mass spectrometry, and X-ray diffraction and via alternative syntheses.

Keywords: 2-aminobenzothiazoles, benzothiazoline-2-thiones, 2-iminobenzothiazoles, ethylene chlorohydrin, hydroxyalkylation, X-ray analysis.

Continuing our investigation of the unusual behavior of halohydrins when reacting with 2-aminobenzothiazoles we have studied the interactions of 2-amino-6-nitro- and 2,6-diaminobenzothiazoles (**1a** and **1b**) with ethylene chlorohydrin. It has been shown previously that the reaction both with the unsubstituted 2-aminobenzothiazole [1, 2] and also with its 6-methyl, -methoxy-, and chloro derivatives [3] gives a mixture of three products, i.e. 3-(β-hydroxyethyl)-2-imino-6-R-benzothiazoline, 3-(β-chloroethyl)-6-R-benzothiazolin-2-one, and bis[3-(β-hydroxyethyl)-6-R-benzothiazolyl-2-idene]ammonium chloride. The ratio of these reaction products depends basically on the conditions for carrying it out. It was of interest to us to study the effect of introducing an electron acceptor substituent or a reactive group in the position 6 of the benzothiazole system on the course of the reaction.

Refluxing the amine **1a** in ethylene chlorohydrin solution gave a complex reaction mixture from which four products were separated (see Scheme 1).

Formation of the main reaction product 3-(β-chloroethyl)-6-nitrobenzothiazolin-2-one (**2**) and of 3-(β-hydroxyethyl)-2-imino-6-nitrobenzothiazoline (**3**) confirms that the overall scheme of the reaction is also retained in this case. However, the introduction of a nitro group, besides accounting well for the lowering of the yield of the products, introduces significant changes in the given process. In the first place, the formation of compound **4** (analogs of which were not found in other reaction mixtures) points to the possible realization of an alternative to the previously proposed [3] mechanism for the synthesis of compounds of type **2** (water and hydrogen chloride being the products of degradation of ethylene chlorohydrin [4]).



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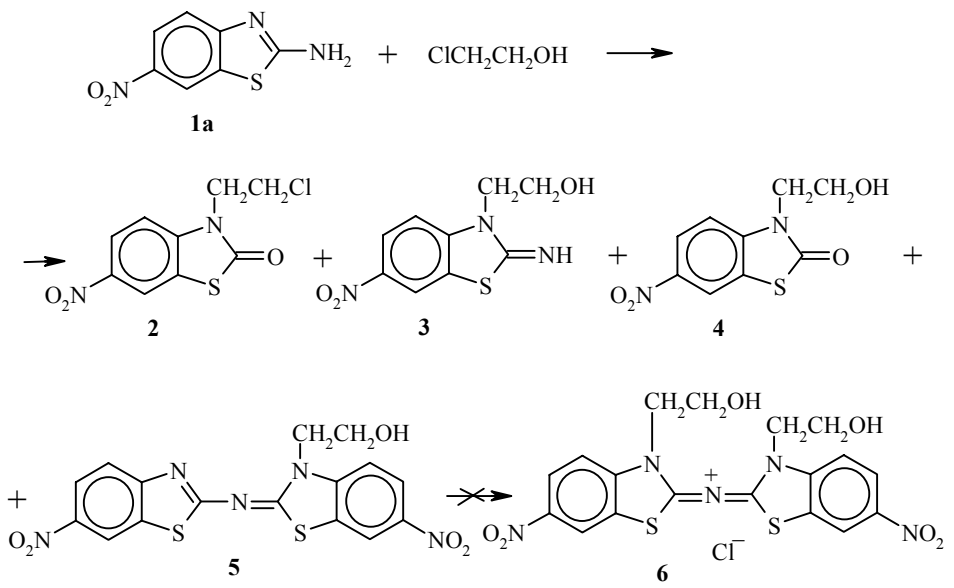
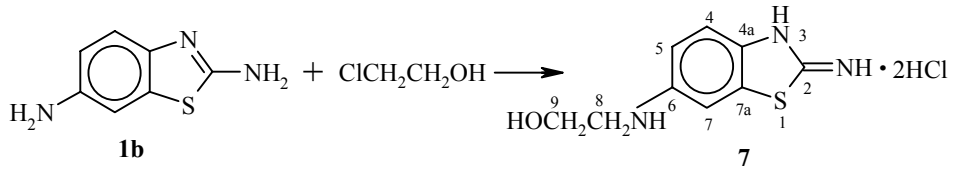
Scheme 1



Secondly, the quaternary salt **6** is absent in the reaction mixture but 3-(β-hydroxyethyl)-6-nitro-2-[(6'-nitrobenzothiazol-2'-yl)-imino]benzothiazoline [5] is formed. In the previously reported reactions the synthesis of the analogs of compound **6** can take place *via* the intermediate formation of a compound of type **5** but, in our view, the lowering of the reactivity of the amine **1** hinders alkylation of the second endocyclic nitrogen atom in the compound **5** molecule.

With a lowering of the reaction temperature for the amine **1a** with ethylene chlorohydrin to 90-95°C there were recorded only traces of the products **2-5**, even after 20 h.

The reaction of amine **1b** with ethylene chlorohydrin occurs quite differently. Upon refluxing the reaction mixture, an alkylation of the amino group at position 6 of the benzothiazole system occurs to give compound **7**.



Such a behavior is a characteristic of the polydentate amine **1b** and also in other nucleophilic substitution reactions since the N=C–NH_2 system of atoms in this compound is much more inert than the amino group in position 6 [5, 6]. Hence amine **1a** and ethylene chlorohydrin give a mixture of products whereas in the case of amine **1b** the reaction takes place regioselectively.

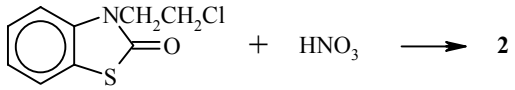
The identification of compounds **2-5** is based on the results of elemental analysis (Table 1), spectroscopic data (Table 2), and alternative syntheses. The IR spectra clearly show the presence of a carbonyl group in compounds **2** and **4** and an exocyclic C=N group in compounds **3** and **5** (in compound **5** this bands undergoes a marked bathochromic shift due to conjugation with the endocyclic C=N bond). In the mass spectra of compounds **3** and **5** the ratio of peak intensities due to the results of α- and β- fission in the alkyl chains [7] points to an imine structure for the heterocyclic fragment. The ^{1}H NMR spectra also correspond to the proposed structure. It should also be mentioned that one of the mobile hydrogen atoms (most likely the OH) does not exchange with trifluoroacetic acid and appears at 8.42 ppm, apparently because of the formation of hydrogen bonds.

TABLE 1. Characteristics of Compounds **2-5**

Compound	Empirical formula	Found, % / Calculated, %			mp, °C	R_f*
		C	H	N		
2	$C_9H_7ClN_2O_3S$	41.6 / 41.8	2.4 / 2.7	10.9 / 10.8	172-173.5	0.86
3	$C_9H_9N_3O_3S$	45.0 / 45.2	3.9 / 3.8	17.5 / 17.6	201-203	0.14
4	$C_9H_8N_2O_4S$	45.1 / 45.0	3.3 / 3.4	11.9 / 11.7	152-153	0.33
5	$C_{16}H_{11}N_5O_5S_2$	46.3 / 46.0	2.5 / 2.7	16.5 / 16.8	285-287	0.64

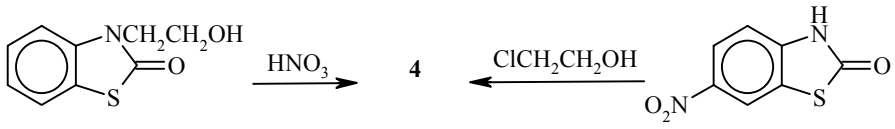
* In the system acetone–benzene–chloroform, 1:2:2 for compounds **2**, **4**, and **5** and 1:1:1 for compound **3**.

The alternative syntheses of compounds **2-4** were carried out in the following manner. Compound **2** was prepared by the nitration of 3-(β-chloroethyl)benzothiazolin-2-one:



The amino alcohol **3** was synthesized by alkylation of amine **1a** using ethylene oxide in acetic acid;

Compound **4** was prepared by two routes i.e. the nitration of 3-(β-hydroxyethyl)benzothiazolin-2-one and the reaction of 6-nitrobenzothiazolin-2-one with ethylene chlorohydrin.



The identification of compound **7** solely on the basis of the ^{1}H NMR, IR, UV, and mass spectra was difficult because it was not possible to determine uniquely the position of the hydroxyalkyl substituent. For this purpose we have used X-ray analysis of this material.

Solving the structure of compound **7** has shown that the amino alcohol formed crystallizes as the dihydrochloride with two molecules of HCl to one molecule of the amino alcohol. The packing of the molecule in the crystal is shown in Figure 1. In the independent part of the unit cell each crystal contains two molecules of the protonated amino alcohol and four chlorine anions. Because of this there is observed a series of shortened intermolecular contacts of the chlorine anions with the atoms of nitrogen, oxygen, and sulfur causing donor-acceptor interactions. These contacts are presented in Table 3 and are shortened when compared with the sum of the van der Waal radii [8] of the corresponding atoms thus indicating the proposed interaction. As evident from Table 3 the chlorine anions occupy two types of environment in the crystal packing. In one the chlorine ions [Cl(1) and Cl(2)] are close to the two apparently protonated endocyclic atoms N(3) and N(3'). In the other the chlorine ions [Cl(3) and Cl(4)] interact with the atoms N(2), N(2'), N(6), N(6'), O, O', and S(1), S(1') but this

TABLE 2. Spectroscopic Characteristics of the Synthesized Compounds

Compound	IR spectrum, ν, cm^{-1}	UV spectrum, λ_{max}, nm	^1H NMR spectrum, ppm	Mass spectrum, *m/z* (*I*, % from I_{max})*			
				$[M]^+$	$[M-CHOH]^+$	$[M-C_2H_3OH]^+$	Other ions
2	1685, 1603, 1585, 1530, 1335	220 (sh), 252, 320	3.83 (2H, t, CH_2Cl); 4.30 (2H, t, CH_2N); 7.25 (1H, d, H arom.); 8.15-8.40 (2H, m, H arom.)	258/260 (49)			181 (24), 150, (15), 149 (14), 138 (14), 135 (100), 121 (22)
3	3332, 3211, 1604, 1578	226, 247 (sh), 270, 367	3.97 (2H, t, CH_2O); 4.26 (2H, t, CH_2N); 7.38 (1H, d, H arom.); 8.15 (1H, dd, H arom.); 8.30 (1H, d, H arom.); 8.42 (1H, br. s, OH)	239 (15)	209 (12)	195 (100)	165 (26), 149 (29), 135 (22)
4	3549, 3070, 1674, 1597, 1583	229.5 (sh), 250 (sh), 272	4.09 (2H, t, CH_2O); 4.22 (2H, t, CH_2N); 7.14 (1H, d, H arom.); 8.13 (1H, dd, H arom.); 8.48 (1H, d, H arom.)	240 (52)	210 (34)	196 (65)	197 (80), 181 (33), 151 (37), 135 (100), 108 (20), 107 (22)
5	3460, 1508, 1471, 1444	221, 249 (sh), 347	3.82 (2H, q, CH_2O); 4.48 (2H, t, CH_2N); 7.80 (1H, d, H arom.); 7.85 (1H, d, H arom.); 8.23 (1H, dd, H arom.); 8.30 (1H, dd, H arom.); 8.89 (1H, d, H arom.); 8.90 (1H, d, H arom.)	417 (12)	387 (46)	373 (100)	374 (46), 343 (81), 327 (42), 297 (80), 294 (35), 281 (24), 280 (21), 206 (32), 122 (97), 121 (86), 108 (98), 107 (98)
7	3388, 3287, 3175, 3041, 1645, 1616, 1603, 1587	223, 282, 396	3.26 (2H, t, CH_2O); 3.63 (2H, t, CH_2N); 7.32 (1H, dd, H arom.); 7.48 (1H, d, H arom.); 7.75 (1H, d, H arom.)	209 (67)		165 (20)	191 (100), 150 (29), 137 (6), 122 (13)

*Compound **2**: 209 (25) $[M-CH_2Cl]^+$; 196 (82) $[M-C_2H_3Cl]^+$; compound **7**: 178 (100) $[M-CH_2OH]^+$.

TABLE 3. Shortened Intermolecular Contacts (*d*) in the Crystal of Molecule **7**

Atoms	*d*, Å	Atoms	*d*, Å	Atoms	*d*, Å
Cl(1)–N(6)	3.14	Cl(3)–S(1)	3.36	Cl(4)–N(6)	3.22
Cl(1)–N(6')	3.09	Cl(3)–N(2')	3.15	Cl(4)–N(2)	3.16
Cl(1)–N(3')	3.02	Cl(3)–N(2)	3.23	Cl(4)–N(2')	3.21
Cl(2)–N(3)	3.03	Cl(3)–O'	3.11	Cl(4)–S(1')	3.40
Cl(2)–N(6)	3.16	Cl(3)–N(6')	3.26	Cl(4)–O	3.21
Cl(2)–N(6')	3.20				

interaction is clearly weaker than that described above. For this reason it was not possible to determine which of the nitrogen atoms is protonated as a result of salt formation. Establishing the position of the hydrogen atoms from the electron density difference synthesis was not successful because of poor experimental statistics.

The benzothiazole heterocycle in the cations is virtually planar. Analysis of the valence bond lengths (Table 4) shows that the formal C=N double bond in the five membered ring of the starting amine molecule **1b** is lengthened (C(2)–N(3) 1.364 and C(2')–N(3') 1.304 Å) and the C–N single bond shortened (C(2)–N(2) 1.295 and C(2')–N(2') 1.307 Å) when compared with standard values [9]. This fact points to a redistribution of electron density into the heterocycles and leads one to propose an imino structure for compound **7**. In fact, the imine structure of compound **7** explain the appearance in its IR spectrum of an absorption band at 1645 cm^{-1} due to the stretching vibration of the exocyclic C=N group. However the values of the bond lengths is overall an average and this points to a powerful conjugation of the π-electron system of the double bond with the nitrogen atom unshared electron pair. The apparent shortening of the C–OH bond (C(9)–O 1.24 and C(9')–O' 1.32 Å) in the cations is apparently due to strong thermal vibrations of the hydroxyalkyl groups (Table 5). Other hetero bonds and valence bonds in the benzothiazole ring within a 3σ range do not differ from well known standard values [9].

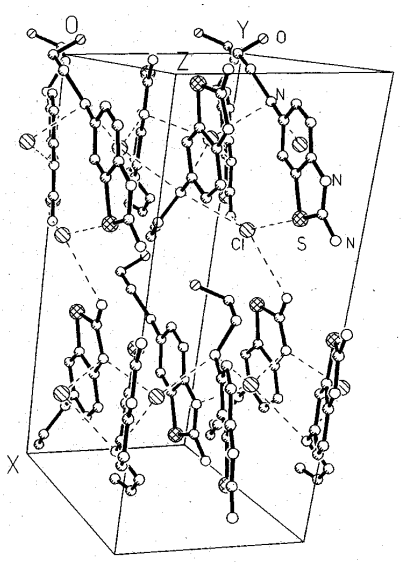


Fig. 1. Crystal packing in the molecule of compound **7**.

TABLE 4. Bond Lengths (*r*) and Valence Angles (ω) in the Molecule of Compound **7**

Bond	*r*, Å	Angle	ω, deg.
S(1)–C(2)	1.734(8)	C(2)–S(1)–C(7a)	91.1(4)
S(1)–C(7a)	1.771(9)	C(6)–N(6)–C(8)	116.8(7)
O–C(9)	1.24(2)	C(2)–N(3)–C(4a)	114.7(7)
N(2)–C(2)	1.295(13)	N(2)–C(2)–N(3)	124.8(8)
N(6)–C(6)	1.470(12)	N(2)–C(2)–S(1)	123.6(7)
N(6)–C(8)	1.489(12)	N(3)–C(2)–S(1)	111.6(7)
N(3)–C(2)	1.364(12)	C(4a)–C(4)–C(5)	115.5(8)
N(3)–C(4a)	1.367(12)	N(3)–C(4a)–C(4)	125.7(8)
C(4)–C(4a)	1.381(14)	N(3)–C(4a)–C(7a)	113.6(8)
C(4)–C(5)	1.421(14)	C(4)–C(4a)–C(7a)	120.7(9)
C(4a)–C(7a)	1.413(12)	C(6)–C(5)–C(4)	122.2(8)
C(5)–C(6)	1.345(14)	C(5)–C(6)–C(7)	122.0(8)
C(6)–C(7)	1.405(12)	C(5)–C(6)–N(6)	119.6(8)
C(7)–C(7a)	1.342(12)	C(7)–C(6)–N(6)	118.5(8)
C(8)–C(9)	1.47(2)	C(7a)–C(7)–C(6)	116.4(8)
S(1')–C(2')	1.749(9)	C(7)–C(7a)–C(4a)	123.0(8)
S(1')–C(7a')	1.761(9)	C(7)–C(7a)–S(1)	128.1(6)
O'–C(9')	1.32(2)	C(4a)–C(7a)–S(1)	109.0(7)
N(2')–C(2')	1.307(12)	C(9)–C(8)–N(6)	113.2(9)
N(6')–C(6')	1.457(12)	O–C(9)–C(8)	121(2)
N(2')–C(8')	1.495(12)	C(2')–S(1')–C(7a')	90.2(4)
N(3')–C(2')	1.304(12)	C(6')–N(6')–C(8')	116.9(8)
N(3')–C(4a')	1.382(12)	C(2')–N(3')–C(4a')	114.9(8)
C(4')–C(4a')	1.372(14)	N(3')–C(2')–N(2')	123.6(9)
C(4')–C(5')	1.40(2)	N(3')–C(2')–S(1')	123.3(7)
C(4a')–C(7a')	1.418(12)	N(2')–C(2')–S(1')	116.8(10)
C(5')–C(6')	1.33(2)	C(4a')–C(4')–C(5')	113.0(7)
C(6')–C(7')	1.432(13)	C(4')–C(4a')–N(3')	126.9(9)
C(7')–C(7a')	1.336(13)	C(4')–C(4a')–C(7a')	120.2(9)
C(8')–C(9')	1.50(2)	N(3')–C(4a')–C(7a')	112.9(8)
		C(6')–C(5')–C(4')	122.8(9)
		C(5')–C(6')–C(7')	121.0(9)
		C(5')–C(6')–N(6')	122.1(8)
		C(7')–C(6')–N(6')	116.9(8)
		C(7a')–C(7')–C(6')	116.6(8)
		C(7')–C(7a')–C(4a')	122.5(8)
		C(7')–C(7a')–S(1')	128.5(6)
		C(4a')–C(7a')–S(1')	109.0(7)
		N(6')–C(8')–C(9')	111.0(10)
		O'–C(9')–C(8')	118.6(12)

EXPERIMENTAL

IR spectra were obtained on a Perkin-Elmer 2000 FT-IR spectrometer for KBr tablets. UV spectra were recorded on a Perkin-Elmer Lambda 16 spectrophotometer using ethanol solvent. The ^{1}H NMR spectra of solutions were recorded on a Jeol C-60 HL instrument for compound **2** in $CDCl_3$ and on a Varian Unity-400 plus (400 MHz) for compounds **3** (in CF_3COOH), **4** (in pyridine-d_5), and **5** and **7** (in DMSO-d_6). The internal standard was TMS.

TABLE 5. Atomic Coordinates ($\times 10^4$) and their Equivalent Thermal Parameters ($Å^2 \times 10^3$) in the Molecule of Compound **7**

Atom	*x*	*y*	*z*	U_{eq}
S(1)	456(1)	-5171(3)	4369(1)	37(1)
O	4073(22)	-4940(25)	3571(35)	392(33)
N(2)	111(5)	-4622(13)	5637(6)	55(2)
N(6)	2830(4)	-5057(10)	3973(5)	45(2)
N(3)	1316(4)	-4320(12)	5879(4)	44(2)
C(2)	609(5)	-4641(12)	5384(5)	39(2)
C(4)	2485(5)	-4280(14)	5857(6)	48(2)
C(4a)	1752(5)	-4526(13)	5490(5)	41(2)
C(5)	2825(5)	-4571(14)	5325(6)	45(2)
C(6)	2452(5)	-4919(11)	4504(6)	36(2)
C(7)	1705(5)	-5153(10)	4130(5)	32(2)
C(7a)	1379(4)	-4954(9)	4632(5)	29(2)
C(8)	3447(5)	-6322(15)	4255(7)	54(3)
C(9)	3809(7)	-6334(17)	3703(11)	77(4)
S(1')	3278(1)	268(3)	5807(1)	40(1)
O'	-285(14)	209(18)	1284(9)	195(11)
N(2')	3586(5)	906(16)	7424(6)	67(3)
N(6')	913(4)	-181(9)	3010(5)	43(2)
N(3')	2406(4)	720(12)	6456(5)	44(2)
C(2')	3091(5)	668(14)	6661(5)	44(2)
C(4')	1233(5)	459(16)	5233(7)	53(2)
C(4a')	1967(5)	443(14)	5616(6)	43(2)
C(5')	902(6)	169(14)	4369(7)	54(3)
C(6')	1267(4)	-40(9)	3919(6)	33(2)
C(7')	2033(5)	-69(10)	4310(6)	35(2)
C(7a')	2355(4)	153(9)	5140(5)	29(2)
C(8')	242(6)	-1274(15)	2637(8)	63(3)
C(9')	-60(7)	-1308(16)	1697(8)	72(4)
Cl(1)	1775(1)	-2786(3)	2440(1)	47(1)
Cl(2)	1943(1)	-7758(3)	2512(1)	46(1)
Cl(3)	82(1)	-3643(3)	7394(2)	49(1)
Cl(4)	3687(1)	1321(3)	9272(2)	51(1)

Mass spectra were taken on an MX-1310 double focussing instrument with direct introduction of the sample into the ion source and an ionizing intensity of 70 eV. Monitoring of the course of the reaction and the purity of the compounds was carried out using TLC on Silufol UV-254 plates. Column chromatography was carried out using L 100/160 micron silica gel.

The starting amines **1a,b** were obtained by a known method [10].

X-ray Analysis of Compound 7. Monocrystals of compound **7** are flesh colored and were obtained from methanol. The unit cell parameters and intensities of 1872 independent reflections were measured on a Nonius CAD-4 diffractometer (MoKα, graphite monochromator, θ/2θ scanning, $\theta < 25.1$). Crystals are monoclinic, a = 20.762 (12), b = 7.455 (3), c = 17.769 (11) Å; β = 115.90 (4) °; V = 2471 (2) $Å^3$; d_{calc} = 1.517 g/cm^3; Z = 8; ($C_9H_{13}Cl_2N_3O$); space group *Cc*. The structure was solved by a direct method with refinement using a full matrix least squares analysis in the anisotropic approximation for non hydrogen atoms. The coordinates of the hydrogen atoms were determined geometrically and located according to the "riding" model. In the calculations 2236 reflections with $I > 2\sigma(I)$ were used. The final difference factors were R = 0.0732 and R_w = 0.1758. The atomic coordinates are given in Table 5. All of the calculations were carried out on an IBM-486 PC using the SHELXTL and SHELXL-95 program package.

3-(β-Chloroethyl)-6-nitrobenzothiazolin-2-one (2), 3-(β-Hydroxyethyl)-2-imino-6-nitrobenzothiazoline (3), 3-(β-Hydroxyethyl)-6-nitrobenzothiazolin-2-one (4), and 3-(β-Hydroxyethyl)-6-nitro-2-[(6'-nitrobenzothiazol-2'-yl)imino]benzothiazoline (5). The amine **1a** (1.95 g, 10 mmol) was refluxed in ethylene chlorohydrin (5 ml) for 5 h. The reaction mixture was evaporated to dryness and then extracted with hot water (3 × 5 ml). The aqueous solution was cooled and neutralized with base to give compound **3** (0.07 g, 3%). The product insoluble in water was extracted with refluxing benzene (5 × 15 ml) and the benzene solution was evaporated and chromatographed on a column eluting successively with hexane, benzene, and chloroform to give products **2** (1.05 g, 41%), **5** (0.20 g, 10%), benzothiazolinone **4** (0.03 g, 1%), and unreacted amine **1a** (0.23 g, 12%). According to TLC, the residue after benzene extraction (0.33 g) was also the starting amine **1a** (17% based on that used in the reaction). The characteristics of compounds **2-5** are given in Table 1.

Alternative Synthesis of Compound 2. Sulfuric acid (98%, 2 ml) was added carefully with stirring to 3-(β-chloroethyl)benzothiazolin-2-one (2.13 g, 10 mmol) which had been placed in an ice salt bath. A solution of fuming nitric acid (1.5 ml) in conc. sulfuric acid (1.2 ml) was then added dropwise such that the temperature did not exceed 10°C. The reaction mixture was left in the ice bath for 0.5 h, held for 1 h at about 20°C, and poured onto ice (50 g). The precipitate was filtered off, washed with water, ammonia solution, and then methanol and was then dried to give compound **2** (1.8 g, 70%); mp 171-173°C (dioxane).

Alternative Synthesis of Compound 3. A suspension of amine **1a** (1.95 g, 10 mmol), ethylene oxide (2.5 ml), and acetic acid (10 ml) was left for 30 days in a sealed ampule with periodic shaking. The contents of the ampul were evaporated to dryness and extracted with water (2 × 10 ml) and the aqueous solution was neutralized with base. The precipitated product was filtered off to give **3** (0.55 g, 23%); mp 201-203°C (water).

Alternative Synthesis of Compound 4. A. 3-(β-Hydroxyethyl)benzothiazolin-2-one (2.75 g, 14 mmol) was dissolved in conc. sulfuric acid (2.5 ml), cooled to 0°C, and a mixture of fuming nitric acid (1.6 ml) and conc. sulfuric acid (1.6 ml) was added dropwise such that the temperature did not exceed 10°C. The reaction mixture was held at this temperature for 0.5 h, at about 20°C for 0.5 h, and then poured into ice (50 g) and extracted with benzene (5 × 20 ml). The benzene solution was evaporated to give the product **4** (0.5 g, 15%); mp 152-153°C (benzene).

B. Ethylene chlorohydrin (0.66 g, 8.2 mmol) was added dropwise to a suspension of 6-nitrobenzothiazolin-2-one (1.45 g, 7.4 mmol) and KOH (0.42 g, 7.4 mmol) in water (4 ml). The reaction mixture was stirred on a boiling water bath for 8 h and held at about 20°C for 15 h. The precipitate was filtered off, washed with water, and chromatographed on a column eluting the product with benzene to give compound **4** (0.85 g, 48%).

Mixed samples of compounds **2-4** obtained by the alternative syntheses with the corresponding samples separated before did not give a depression of melting point.

6-(β-Hydroxyethyl)amino-2-iminobenzothiazoline Dihydrochloride (7). 2,6-Diaminobenzothiazole (0.83 g, 5 mmol) was refluxed for 3 h in ethylene chlorohydrin (2 ml). The reaction mixture was cooled, extracted with ether (3 ml) and then methanol (2 × 3 ml). The residue gave product **7** (0.51 g, 39%); mp 208-209°C (methanol).

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