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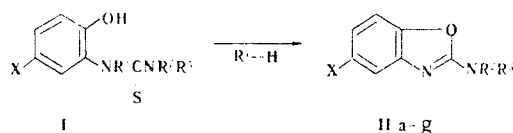
# SYNTHESIS OF 2-AMINO BENZOXAZOLES AND 2-IMINO BENZOXAZOLINES

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The cyclization of sulfonamide derivatives of alkylated 2-hydroxyphenylthioureas in the presence of an ammoniacal solution of silver oxide gives 2-alkylamino-benzoxazole-5-sulfonamides or the corresponding 3-alkyl-2-alkyliminobenzoxazolines. Alkyl-substituted 2-aminobenzoxazole-5-sulfonamides were also obtained by the reaction of benzoxazolythione with secondary amines and aniline.

We have previously shown that the corresponding 2-hydroxyphenylthioureas (I) are obtained in the reaction of primary amines with benzoxazolythione derivatives [1]. We have found that sulfonamide derivatives of I ( $X = SO_2NH_2$ ) with alkyl substituents in the 3 position are cyclized by an ammoniacal solution of silver nitrate to give good yields of 2-alkylaminobenzoxazole-5-sulfonamides (IIa-d,  $R^3 = H$ ).



We also obtained 5-sulfonamide derivatives of substituted 2-aminobenzoxazoles (IIe-g) by another method — by substitution of the thiol group of benzoxazolythione by reaction with secondary amines (piperidine and morpholine) and aniline (see Table 1). In this case the opening of the oxazole ring that is observed in the reaction with strong aliphatic amines [2] does not occur.

Cyclization of 1,3-dialkyl-substituted thioureas I and their sulfonamide derivatives ( $X = H, SO_2NH_2, R^1 = CH_3$ ) gives the corresponding 3-methyl-2-alkyliminobenzoxazolines (III). The 2-iminobenzoxazoline derivatives have an exocyclic azomethine group, the stretching vibrations of which have unusually high frequencies — 1700–1740  $cm^{-1}$  (the IR spectra of these compounds were the subject of a separate communication [3]).

TABLE 1. 2-Aminobenzoxazole-5-sulfonamides (IIa-g)

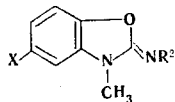
Compound	$R^2$	$R^3$	Reaction time, h	mp, °C	Found, %		Calc., %		Yield, %
					N	S	N	S	
IIa	$C_2H_5$	H	2	209–211		13,2		13,3	75
IIb	$C_4H_9$	H	2	176–178	15,5		15,9		91
IIc	$C_6H_{11}$	H	2	212–214	14,5		14,2		82
IId	$CH_2C_6H_5$	H	2	210–212	14,1		13,8		88
IIe	$-(CH_2)_4-$		5	233–235		11,4		11,4	59
IIf	$-(CH_2)_2O(CH_2)_2-$		4	216–218		11,3		11,3	51
IIg	$C_6H_5$	H	3*	237–239	14,6		14,5		81

\*The reaction was carried out at 130–140°C.

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TABLE 2. 2-Imino-3-methylbenzoxazolines (IIIa-h)



Com- pound	R <sup>2</sup>	X	mp, °C	N, %		Yield, %
				found	calc.	
IIIa	C <sub>2</sub> H <sub>5</sub>	H	43—45	15,7	15,9	
IIIb	C <sub>3</sub> H <sub>7</sub>	H	16—18	14,6	14,7	80
IIIc	C <sub>6</sub> H <sub>11</sub>	H	82—84	12,2	12,2	88
IIId	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	H	55—57	11,8	11,8	86
IIIe	C <sub>3</sub> H <sub>7</sub>	SO <sub>2</sub> NH <sub>2</sub>	202—203	15,6	15,6	83
IIIf	C <sub>4</sub> H <sub>9</sub>	SO <sub>2</sub> NH <sub>2</sub>	157—159	14,7	14,8	80
IIIg	C <sub>6</sub> H <sub>11</sub>	SO <sub>2</sub> NH <sub>2</sub>	183—185	13,9	13,6	70
IIIh	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	SO <sub>2</sub> NH <sub>2</sub>	210—212	13,3	13,2	73

## EXPERIMENTAL

2-Aminobenzoxazoles (IIa-d). A solution of 3.6 mmole of thiourea I in 40 ml of alcohol was heated with 5 ml of an ammoniacal solution of 7.5 mmole of AgNO<sub>3</sub> at 40–50° for 1 h with continuous stirring, after which another 5 ml of concentrated ammonium hydroxide was added, and the mixture was stirred for another hour. The precipitated Ag<sub>2</sub>S was separated, the filtrate was acidified with dilute HCl, and the precipitated AgCl was separated. The filtrate was concentrated, and the concentrate was made alkaline with 5% NaOH. The precipitated 2-aminobenzoxazole (II) was removed by filtration and recrystallized from dilute alcohol. The physical constants and yields of the compounds are presented in Table 1.

2-Aminobenzoxazoles (IIe-g). A mixture of 4.2 mmole of 2-thioxobenzoxazolyl-5-sulfonamide and 2 mmole of amine was heated on a water bath for several hours, after which it was acidified with 5% HCl and filtered. The filtrate was made alkaline with 6% alkali solution (see Table 1).

2-Alkylimino-3-methylbenzoxazolines (IIIa-e). A solution of 11 mmole of AgNO<sub>3</sub> in 5 ml of ammonia was added to a solution of 4.7 mmole of 1,3-dialkylthiourea I in 40 ml of alcohol, after which the mixture was stirred at 40–50° for 2 h. The precipitated Ag<sub>2</sub>S was separated, and the filtrate was worked up as in the first experiment. See Table 2 for the physical constants and yields of the compounds.

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