RESEARCH ON ACYL ISOCYANATES AND THEIR DERIVATIVES

XI.* REACTIONS OF ACYL ISOCYANATES WITH BENZIMIDAZOLINETHIONE, ITS ACYL DERIVATIVES, AND THIOUREA

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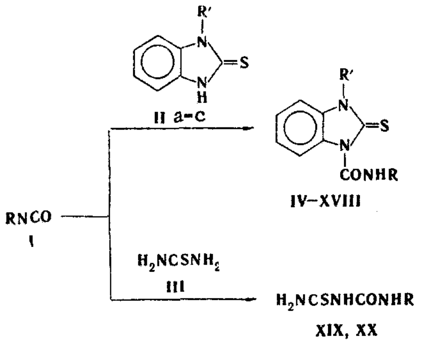
1-Substituted benzimidazolinethiones, 3-substituted 1-acylbenzimidazolinethiones, and acyl thiobiurets, respectively, are formed in the reaction of acyl, alkyl, and aryl isocyanates with benzimidazolinethione, its 1-acyl derivatives, and thiourea. The IR and UV spectra of the compounds obtained are analyzed.

Benzimidazolinethione [2] and thiourea in the crystalline state and in solution exist in the thione form. Despite this, aryl isocyanates react with benzimidazolinethione to give products involving acylation at sulfur [4], while thiourea reacts to give products involving acylation at nitrogen [5].

Although they are of undoubted theoretical and practical interest, the reactions of benzimidazolinethione and its acyl derivatives with acyl isocyanates have not been investigated previously. The reaction of acyl isocyanates with thiourea was investigated only in the case of high aliphatic isocyanates, and it was shown that products of acylation at nitrogen are formed [6].

In the present research we have studied the reaction of acyl isocyanates (I) with benzimidazolinethione (IIa), its 1-benzoyl (IIb) and 1-acetyl (IIc) derivatives, and thiourea (III), For comparison, we also studied the reactions of some alkyl and aryl isocyanates with the indicated reagents under comparable conditions. 1-Acylcarbamoyl derivatives IV-VIII, X, XI, XVII, and XVIII, which are presented in Table 1, and 1-benzoylthiobiuret (XIX), respectively, were obtained by the action of acyl isocyanates on II and III via the scheme presented below. Similarly, alkyl or arylcarbamoyl derivatives of benzimidazolinethione (IX, XII-XVI, see Table 1) and 1-(4-chlorophenyl)thiobiuret (XX) were obtained by the action of alkyl or aryl isocyanates on II-III.



II a R'=H; b R'=COC_6H_5; c R'=$COCH_3$

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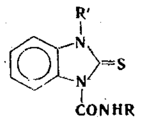
* See [1] for communication X.

All-Union Scientific-Research Institute of Chemical Agents for the Protection of Plants, Moscow. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 695-698, May, 1973. Original article submitted December 20, 1971.

TABLE 1. Benzimidazolinethiones



Compound	R	R′	Reaction conditions		mp, °C[a]	Empirical formula	N, %		IR spectrum (KBr), cm⁻¹		UV spectrum, λ_{max}^{MeOH}, nm (log ε)		Yield, %
			t, °C	time, h			found	calculated	$\nu(NHC{=}S)$	$\delta\left(\begin{smallmatrix}N\\N\end{smallmatrix}\!>C{=}S\right)$	NC(S)N	NHC(S)NC(O)	
IV	C_6H_5CO	H	20	24	185—187	$C_{15}H_{11}N_3O_2S$	14,0, 13,9	14,1	1450	595	250 (4,54)	305 (4,40)	97
V	$4\text{-}ClC_6H_4CO$	H	20	24	220 (dec.)	$C_{15}H_{10}ClN_3O_2S$	12,8, 12,7	12,7	1445	610	246 (4,56)	304 (4,48)	98
VI	$C_6H_5OCH_2CO$	H	20	24	123—125	$C_{16}H_{13}N_3O_3S$	12,6, 12,5	12,8	1450	600	248 (4,23)	306 (4,27)	99
VII	$2\text{-}CH_3\text{-}4\text{-}ClC_6H_3OCH_2CO$	H	20	24	152—153	$C_{17}H_{14}ClN_3O_3S$	11,5, 11,4	11,2	1460	600	250 (4,48)	306 (4,54)	96
VIII	$2\text{-}CH_3C_6H_4OCH_2CO$	H	20	24	206—208	$C_{17}H_{15}N_3O_3S$[b]	12,6, 12,5	12,3	1460	610			96
IX	$4\text{-}ClC_6H_4$	H	80	6	156—158	$C_{14}H_{10}ClN_3S$	13,5, 13,6	13,8	1470	595			93
X	C_6H_5CO	C_6H_5CO	20	1	166—168	$C_{22}H_{15}N_3OS$	10,1, 10,2	10,5	1470	600			97
XI	$C_6H_5OCH_2CO$	C_6H_5CO	20	1	170	$C_{23}H_{17}N_3O_4S$	10,0, 9,8	9,7					98
XII	CH_3	C_6H_5CO	80	1	235	$C_{16}H_{13}N_3O_2S$	13,5, 13,6	13,5					98
XIII	$CH_3(CH_2)_3$	C_6H_5CO	80	1	158—160	$C_{19}H_{19}N_3O_2S$	12,2, 12,2	11,9					96
XIV	$2\text{-}ClC_6H_4$	C_6H_5CO	80	1	200—202	$C_{21}H_{14}ClN_3O_2S$	11,0, 11,2	11,2					92
XV	$3\text{-}ClC_6H_4$	C_6H_5CO	80	1	183—184	$C_{21}H_{14}ClN_3O_2S$	11,3, 11,4	11,2			inflection 248 (4,56)	306 (4,69)	85
XVI	$4\text{-}ClC_6H_4$	C_6H_5CO	80	1	204—205	$C_{21}H_{14}ClN_3O_2S$	11,2, 11,2	11,2			262 (4,58)	308 (4,49)	92
XVII	CH_5CO	CH_3CO	80	3	163—165	$C_{17}H_{13}N_3O_3S$	12,4, 12,6	12,4	1445	610			72
XVIII	$C_6H_5OCH_2CO$	CH_3CO	80	3	120—121	$C_{18}H_{15}N_3O_4S$[c]	11,2, 11,3	11,4	1470	595	249 (4,32)	301 (4,28)	70

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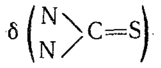
[a] Recrystallized from acetone (IV), alcohol–acetone (V–VIII), benzene–isooctane (X–XIII), and benzene (X, XIII–XVIII). [b] Found: C 60.2, 59.8; H 4.2, 4.2%. Calculated: C 59.8; H 4.1%. [c] Found: C 58.8, 58.7; H 4.2, 4.2%. Calculated: C 58.8; H 4.1%.

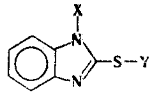
Depending on the structure of the starting reagents, the indicated reactions proceeded with different degrees of ease in benzene. On the whole, acyl isocyanates display greater reactivity than alkyl or aryl isocyanates. In the first case, the reactions proceed at room temperature, while in the case of alkyl and aryl isocyanates, the reactions proceed only on refluxing in benzene. It was found that the reactivity with respect to isocyanates increases in the order III < IIa < IIb. While the reactions of acyl isocyanates with IIb are complete after 1 h at room temperature, the reactions with IIc require refluxing (in benzene) for 3 h. Aryl isocyanates do not react with IIc even on heating for 48 h.

The structure of the 1,3-disubstituted benzimidazolinethiones was proved by alternative synthesis. Thus the corresponding 3-benzoyl derivatives (X, XI, and XVI), which are identical with respect to IR spectra and melting points to samples synthesized from acyl isocyanates and IIa, were obtained by the action of benzoyl chloride on 1-(acylcarbamoyl)benzimidazolinethiones (IV, VI, and IX).

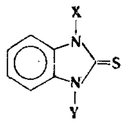
The structures of the compounds, the characteristics of which are given in Table 1, were confirmed by analysis of their IR and UV spectra. The IR spectra of thiobiurets XIX and XX are characterized [3] by the presence of bands of a thioureido grouping [NC(=S)] at 1460 cm^{-1}. The IR spectra of the benzimidazolinethione derivatives and the starting II contain characteristic bands of a thioureido grouping and bands of


$\delta\left(\begin{smallmatrix}N\\N\end{smallmatrix}\!>\!C{=}S\right)$ deformation vibrations at 600 cm^{-1} [3] (see Table 1).

The conclusions regarding the addition of benzimidazolinethiones to the isocyanates under consideration to give N-substituted benzimidazolinethiones are also confirmed by an examination of the UV spectra of the compounds obtained. It is known [7] that the UV spectra of 2-methylmercaptobenzimidazole (type A) differ sharply with respect to the shape and position of the absorption bands (λ_{max} 248-258 and 283-292 nm) from the spectra of 1,3-dimethyl- or 1-benzoylbenzimidazolinethione (type B) (λ_{max} 242-252 and 298-311 nm); this makes it possible to make a choice between the S or N derivatives in the benzimidazolinethione series [8]. It is apparent from Table 1 that the UV spectra of IV-VI, XIV-XVI, and XVIII contain absorption maxima that are characteristic for structure B rather than A. On the basis of the principles that we previously devloped in an analysis of the UV spectra of thioureas, benzoylthioureas, and thiouracils [9], the indicated absorption maxima of these compounds can be assigned, respectively, to the NC(=S)N and NC(=S)-NC(=O) systems (see Table 1).



A



B

Thus, despite the differences in the acylation reactions of benzimidazolinethiones from those of thioureas (see [10, 11]), on the one hand, and of isocyanates of various structures, on the other, the reagents indicated above form only N-acyl derivatives in reactions with acyl isocyanates.

EXPERIMENTAL

The IR spectra of KBr pellets were recorded with a UR-10 spectrometer, while the UV spectra of methanol solutions were recorded with a Specord spectrophotometer.

Benzimidazolinethione (IIa) was obtained by the method in [12]. 1-Acetyl- (IIc) and 1-benzoylbenzimidazolinethione (IIb) were synthesized by the method in [8]. The acyl isocyanates were obtained as described in [13].

1-(Benzoylcarbamoyl)benzimidazoline-2-thione (IV). A solution of 1.47 g (10 mmole) of benzoyl isocyanate in 15 ml of absolute benzene was added at room temperature to a solution of 1.50 g (10 mmole) of IIa in 20 ml of absolute benzene. The mixture was stirred for 24 h, and the resulting precipitate was removed by filtration and recrystallized from acetone to give 2.73 g (92%) of thione IV with mp 185-187°.

The characteristics of benzimidazolinethione derivatives IV-XVIII and the conditions used to prepare them are presented in Table 1.

1-Benzoylcarbamoyl-3-benzoylbenzimidazoline-2-thione (X). A solution of 1.41 g (10 mmole) of benzoyl chloride in 15 ml of dimethylformamide was added with stirring at room temperature to a solution of

2.97 g (10 mmole) of thione IV and 1.01 g (10 mmole) of triethylamine in 20 ml of DMF. Stirring was then continued for 3 h, after which the mixture was poured into water. The aqueous mixture was filtered to give 3.60 g (90%) of X with mp 166-168° (from benzene–isooctane). No melting-point depression was observed for a mixture of this product with a sample obtained from 1-benzoylbenzimidazolinethione and benzoyl isocyanate.

Benzoylation of VI and IX under the same conditions gave XI and XVI.

1-Benzoylthiobiuret (XIX). A solution of 2.06 g (14 mmole) of benzoyl isocyanate in 10 ml of benzene was added with stirring to a solution of 1.06 g (14 mmole) of thiourea in 20 ml of benzene, after which the mixture was stirred for 36 h. The precipitate was removed by filtration and washed with benzene to give 2.72 g (87%) of thiobiuret XIX with mp 165-166° (from acetone). IR spectrum, ν, cm^{-1}: 1690, 1710 (C = O) and 1460 (NHC = S). Found: N 18.4%. $C_9H_9N_3O_2S$. Calculated: N 18.3%.

1-(4-Chlorophenyl)thiobiuret (XX). As in the preceding experiment, 2.18 g (80%) of thiobiuret XX, with mp 172-173° (from acetone), was obtained by refluxing 0.91 g (12 mmole) of thiourea and 1.82 g (12 mmole) of 4-chlorophenyl isocyanate in 20 ml of benzene for 6 h. Found: N 18.4%. $C_8H_8ClN_3OS$. Calculated: N 18.3%.

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