REACTIONS OF ISOCYANATES WITH AZOMETHINES

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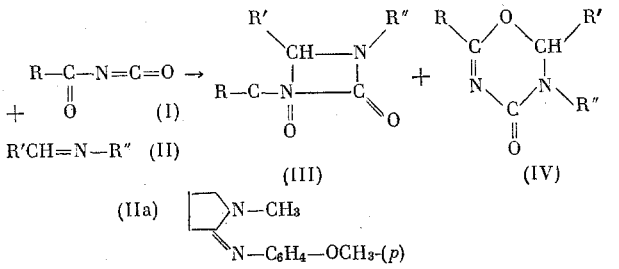
In the present communication are given the data on the reactions of the benzoyl and trichloroacetyl isocyanates with some azomethines, which proceed with the formation of the cyclic 1:1 adducts, and specifically 1,3-diazetidin-2-one (III) and 1,3,5-oxadiazin-4-one (IV) derivatives (Table 1).



For (II), (III) (IV)

	R′	R″		R′	R″
b	$Et_2NC_6H_4$	C_6H_5	g	(p)-$O_2NC_6H_4$	$C_6H_5CH_2$
c	(p)-$CH_3OC_6H_4$	C_6H_5	h	(p)-BrC_6H_4	C_6H_5
d	C_6H_5	(p)-$CH_3OC_6H_4$	i	(p)-ClC_6H_4	C_6H_5
e	(p)-$O_2NC_6H_4$	(p)-$CH_3OC_6H_4$	k	(p)-$O_2NC_6H_4$	(p)-$O_2NC_6H_4$
f	C_6H_5	C_6H_5			

As can be seen from Table 1, azomethines (IIa)–(IIe) react with the benzoyl and trichloroacetyl isocyanates to give (III) and (IV). The ratio of (III) and (IV) depends on the temperature, the reaction time, and the character of the substituent in the p-position of the C-aryl- and N-arylazomethines. A similar effect of the reaction conditions and the character of the substituent in the azomethines on the competition of the 2 + 2- and 2 + 4-cycloaddition reactions was observed by us previously [1]. Compound (IIa) reacts with isocyanates only on the type of 2 + 2-cycloaddition. Compound (IIf) reacts with benzoyl isocyanate to give the 2 + 2-cycloadduct (IIIf), and with trichloroacetyl isocyanate to give the 2 + 4-cycloadduct (IVf). The insertion of electron-acceptor substituents in the p-position of the C-aryl- and N-arylazomethines shifts the direction of the reaction toward 2 + 4-cycloaddition. Thus, azomethines (IIg)–(IIk) react with isocyanates to give only the (IV) isomer. Acyl and aroyl isocyanates react with benzalbenzylamine [2, 3] and p-substituted benzalbenzylamines [3] in the same way (2 + 4-cycloaddition).

All of the obtained adducts are crystalline compounds. The (III) and (IV) compounds were separated by fractional crystallization from ether, CCl_4 or benzene. The structure of the adducts was confirmed by the IR spectral data. The IR spectra of the (III) compounds have the absorption bands of the stretching vibrations of the C=O group in the 1672-1688 and 1768-1781 cm^{-1} regions. The spectra of the (IV) compounds have the bands of the stretching vibrations of the C=N and C=O bonds in the 1614-1634 and 1672-1704 cm^{-1} regions.

The order in which the isocyanates add to azomethines was established by acid hydrolysis in acetone, as described in [1]. The elemental analysis of all of the obtained compounds for C, H, N and Cl showed satisfactory agreement with the calculated values.

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TABLE 1

Starting compounds	Weight, g	Experimental conditions			Yield, %	T. mp., °C
		solvent	T., °C	time, h		
C_6H_5CONCO	1,47	CCl_4	18—20	2	(III), 21	117—119
(IIa)	2,04					
(IIa)	2,04	"	18—20	24	(III), 48	117—119
(IIa)	2,04	"	70—80	2	(III), 61,3	117—119
CCl_3CONCO	1,89	"	18—20	10	(III), 25,3	123—125
(IIa)	2,04					
(IIa)	2,04	"	18—20	144	(III), 61,4	123—125
CCl_3CONCO	1,5	Ether	18—20	4	(III), 46,4	135—137
(IIb)	2,0					
(IIb)	2,0	"	18—20	1 week	(III), 74,1	135—137
					(IV), 12,1	171—172
(IIb)	2,0	CCl_4	90	1	(III), 45,3	135—137
(IIb)	2,0	"	70—80	16	(III), 50	135—137
					(IV), 35	171—172
C_6H_5CONCO	1,47	"	18—20	4	(III), 65	107—108
(IIb)	2,52					
(IIb)	2,52	"	18—20	48	(III), 57	107—108 [1]
					(IV), 27	162—163
(IIb)	2,52	"	50—55	6	(III), 83	107—108
					(IV), 12	162—163
C_6H_5CONCO	1,39	Ether	18—20	10	(III), 62,6	120,5—122
(IIc)	2,0				(IV), 24,8	132—133
(IIc)	2,0	CCl_4	18—20	8	(III), 86,4	120,5—122
(IIc)	2,0		18—20	250	(III), 5	120,5—122
		"			(IV), 88	132—133
CCl_3CONCO	2,3	Ether	18—20	6	(III), 85,2	128—129
(IIc)	2,5					
(IIc)	2,5	CCl_4	70—80	4	(III), 42,6	128—129
					(IV), 39,9	185—187
(IIc)	2,5	"	70—80	20	(III), 32,1	128—129
					(IV),53,4	185—187
CCl_3CONCO	2,23	Ether	18—20	2 weeks	(III), 13,4	131—132
(IId)	2,5				(IV), 57,9	174—175
(IId)	2,5	CCl_4	70—80	20	(III), 16	131—132
					(IV), 85,4	174—175
CCl_3CONCO	1,89	"	70—80	1 week	(III), 18,4	117—119
(IIe)	2,56				(IV), 40,1	141,5—142,5
(IIe)	2,56	Ether	18—20	"	(III), 27,6	117—119
					(IV), 61,1	141,5—142,5
C_6H_5CONCO	2,3	CCl_4	70—80	10	(III), 14,2	109—110,5
(IIe)	4,0				(IV), 60,7	127—129
(IIe)	4,0	"	70—80	15	(III), 5	109—110,5
					(IV), 61,4	127—129
C_6H_5CONCO	1,6	"	70—80	48	(III), 30	114—115,5
(IIf)	2,0					
(IIf)	2,0	"	70—80	10	(III), 10	114—115,5
(IIf)	2,0	Ether	18—20	1 week	(III), 5,7	114—115,5
CCl_3CONCO	2,08	"	18—20	"	(IV), 20	160—162
(IIf)	2,0					
(IIf)	2,0	CCl_4	70—80	25	(IV), 25	160—162
CCl_3CONCO	1,89	Ether	18—20	48	(IV), 84,3	117—119
(IIg)	2,4					
CCl_3CONCO	1,89	"	70—80	3	(IV), 71,6	127—128
(IIh)	2,6					
CCl_3CONCO	2,18	Ether	70—80	1	(IV), 68,4	115—117
(IIi)	2,5					
CCl_3CONCO	1,89	CCl_4	70—80	7	(IV), 34,1	137—138
(IIk)	2,71					

The IR spectra were taken in Nujol and in CCl_4 on a UR-10 instrument. The experimental reaction conditions are given in Table 1. The adducts were hydrolyzed as described in [1].

CONCLUSIONS

The benzoyl and trichloroacetyl isocyanates react with azomethines on the type of both 2 + 2- and 2 + 4-cycloaddition. The temperature, reaction time, and the electronic effects of the substituents, all exert an effect on the ratio of the isomers.

LITERATURE CITED

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