SYNTHESIS AND TAUTOMERISM OF TETRAHYDRO-2,4-DIOXO-6-ALKYLIDENE-1,3,5-THIADIAZINES

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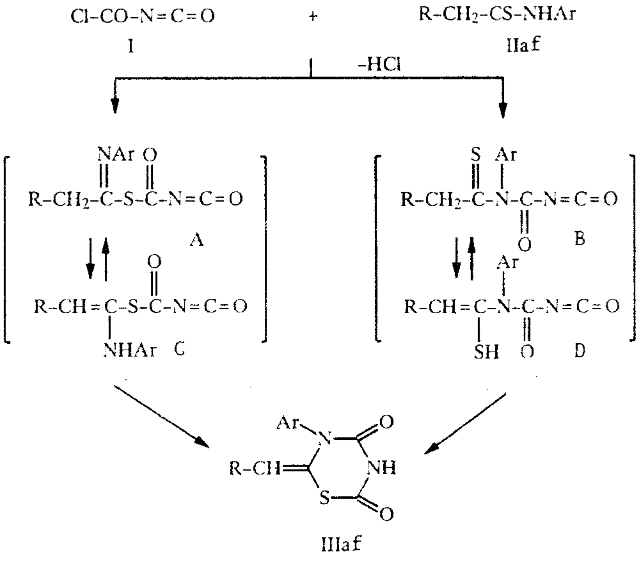
The reaction of chlorocarbonylisocyanate with N-substituted thioamides of alkanecarboxylic acids has led to the synthesis of tetrahydro-2,4-dioxo-6-alkylidene-1,3,5-thiadiazines, for which tautomeric transformations to the corresponding ureidocarbonylthioacetylenes have been observed.

Chlorocarbonylisocyanate (I) is being widely used as an effective reagent in the synthesis of various kinds of heterocyclic compounds [1, 2]. The majority of cyclocondensations based on I occurs in reactions with ambidentate nucleophilic reagents. On the other hand, the reactions of this isocyanate with thiocarbonyl compounds with ambidentate nature have hardly been studied. In particular, the reactions of I with thioureas [3] and thiosemicarbazides [4] have been described in the literature.

The present communication offers the data obtained in the reaction of the isocyanate I with N-substituted thioamides of alkanecarboxylic acids (IIa-f).

Scheme 1



II, IIIa R = H, Ar = C_6H_5; b R = H, Ar = 4-BrC_6H_4; c R = H, Ar = 4-FC_6H_4 ; d R = H, Ar = 4-$CH_3C_6H_4$; e R = H, Ar = 4-$CH_3C_6H_4$; f R = CH_3, Ar = C_6H_5

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TABLE 1. Characteristics of Compounds IIIa-f

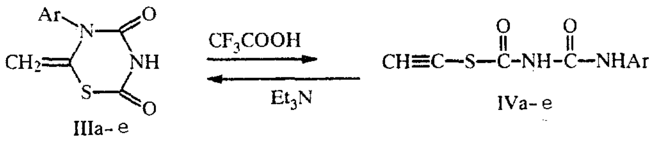
Compound	Empirical formula	mp. °C	IR spectrum, ν, cm^{-1}			^{1}H NMR, ppm SSCC (J)	^{13}C NMR, ppm	Yield, %
			N–H	C=O	C=C			
IIIa	$C_{10}H_8N_2OS$	189...190	3340, 3200	1720	1640	4,11 (1H, d, CH), J = 3,0; 4,62 (1H, d, CH), J = 3,0; 7,23...7,54 (5H, m, C_6H_5); 10,31 (1H, broad s, NH)	97,7 (CH_2); 127,6, 127,8, 128,6, 133,3 (C_6H_5), 136,9 ($C_{(6)}$), 147,8 ($C_{(4)}$), 161,1 ($C_{(2)}$)	69
IIIb	$C_{10}H_7BrN_2O_2S$	139...140	3320, 3200	1710	1640	4,18 (1H, d, CH), J = 3,0; 4,67 (1H, d, CH), J = 3,0; 7,32 (2H, d, CH_2), J = 8,0; 7,76 (2H, d, CH_2), J = 8,0; 10,52 (1H, broad s, NH)	99,7 (CH_2), 122,7, 131,7, 133,4, 134,8 (C_6H_4), 137,9 ($C_{(6)}$), 149,4 ($C_{(4)}$), 162,7 ($C_{(2)}$)	57
IIIc	$C_{10}H_7FN_2O_2S$	127...128	3320, 3250	1715	1635	4,20 (1H, d, CH), J = 3,1; 4,70 (1H, d, CH), J = 3,1; 7,18...7,44 (4H, m, C_6H_4); 10,44 (1H, broad s, NH)	97,2 (CH_2), 124,6, 130,5, 133,5, 134,3 (C_6H_4), 137,4 ($C_{(6)}$), 148,2 ($C_{(4)}$), 162,0 ($C_{(2)}$)	70
IIId	$C_{11}H_{10}N_2O_2S$	195...196	3340, 3250	1720	1625	2,24 (3H, s, CH_3); 4,07 (1H, d, CH), J = 3,0; 4,54 (1H, d, CH), J = 3,0; 6,95...7,52 (4H, m, C_6H_4); 10,40 (1H, broad s, NH)	21,8 (CH_3), 97,6 (CH_2), 126,9, 127,6, 128,9, 133,5 (C_6H_4), 136,7 ($C_{(6)}$), 149,3 ($C_{(4)}$), 150,1 ($C_{(2)}$)	63
IIIe	$C_{11}H_{10}N_2O_3S$	122...123	3320, 3200	1720	1630	3,79 (3H, s, CH_3O); 4,13 (1H, d, CH), J = 3,0; 4,59 (1H, d, CH), J = 3,0; 6,98...7,29 (4H, m, C_6H_4); 10,45 (1H, broad s, NH)	53,9 (CH_3O), 97,2 (CH_2), 124,3, 127,1, 128,8, 132,5 (C_6H_4), 136,6 ($C_{(6)}$), 147,9 ($C_{(4)}$), 163,1 ($C_{(2)}$)	54
IIIf	$C_{11}H_{10}N_2O_2S$	148...149	3320, 3205	1710	1625	1,59 (3H, d, CH_3), J = 6,0; 4,95 (1H, qu, CH), J = 6,0; 7,30...7,52 (5H, m, C_6H_5); 10,12 (1H, broad s, NH)	13,3 (CH_3), 116,6 (CH), 129,1, 129,6, 129,9, 130,4 (C_6H_4), 140,2 ($C_{(6)}$), 150,0 ($C_{(4)}$), 163,8 ($C_{(2)}$)	71

The reaction of the reactants I and IIa-f takes place at room temperature in benzene solution in the presence of triethylamine as acceptor of hydrogen chloride; it leads to 57-71% of the corresponding tetrahydro-2,4-dioxo-6-alkylidene-1,3,5-thiadiazines (IIIa-f) (Scheme 1). Taking into account literature data on the reactions of chlorocarbonylisocyanate with N-substituted amides [5] and of 1-chloroalkylisocyanates with N-substituted thioamides [6] it can be assumed that in the first case the process passes through a stage of formation of N-isocyanatocarbonylation products (A) and in the second case through the formation of S-isocyanatocarbonylation products (B), capable on account of a prototropic shift of isomerizing to the isocyanates (C) and (D) respectively, which then undergo an intramolecular cyclization.

The spectral characteristics of the obtained substances (see Table 1) confirm the structure of the thiadiazines IIIa-f. Thus, their IR spectra contain strong absorption bands of stretching vibrations in the region 3200-3340 (NH), 1710-1720 (C=O), and 1625-1640 cm^{-1} (C=C). In the ^{1}H NMR spectra of compounds IIIa-e the signals of the protons of the methylene group appear as two doublets in the interval 4.07-4.70 ppm (J = 3.0 Hz) (system AX). On the other hand, the thiadiazine IIIf is characterized by a doublet of methyl protons in the region 1.59 ppm (J = 6.0 Hz) and by a quadruplet of the methyne proton in the region 4.95 ppm (J = 6.0 Hz). The ^{13}C NMR spectra of all compounds contain, besides signals of the C atoms of the exocyclic alkylidene and aromatic substituents, signals of the C atoms of the heterocycle: $C_{(6)}$ 136.6-140.2, $C_{(4)}$ 147.8-150.0, and $C_{(2)}$ 161.1-163.8 ppm.

When the compounds IIIa-e are in contact with catalytic amounts of inorganic (HCl) or organic (CF_3COOH) acids they can undergo a tautomeric transformation to ureidocarbonylthioacetylenes IVa-e. The IR spectra of solutions of the investigated compounds (in benzene, CH_2Cl_2, or $CHCl_3$) contain, after the addition of catalytic amounts of the acid, additional medium-intensity bands in the region 2045-2055 cm^{-1}, characteristic for acetylene thioethers [7], and in the region 3430-3450 cm^{-1}(NH). In the ^{1}H NMR spectra of compounds IIIa-e in $CDCl_3$ additional signals appear of the acetylene protons in the interval 2.64-2.71 [8] and N–H protons in the interval 8.79-8.84 ppm. The subsequent treatment of the obtained solutions with an organic base is accompanied by a full shift of the equilibrium to the cyclic form III and by the restoration of the original spectra. This fact leads us to the conclusion that the III ⇄ IV conversion is reversible and that it is an example for a new type of ring-chain enamidine tautomerism (Scheme 2).

Scheme 2



EXPERIMENTAL

The ^{1}H NMR and ^{13}C NMR spectra were taken on a Varian Gemini-200 spectrometer, using HMDS and TMS as internal standards. The IR spectra were taken on a UR-20 spectrometer in chloroform. The elemental analysis data for C, H, N, and S correspond to the calculated values.

Tetrahydro-2,4-dioxo-6-alkylidene-1,3,5-thiadiazine (IIIa-f). A suspension of 0.01 mole of thioamide IIa-f in 40 ml anhydrous benzene is treated with 1.05 g (0.01 mole) I and, with stirring, with 1.0 g (0.01 mole) triethylamine in 10 ml benzene. The reaction mixture is stirred for 2 h, heated to 65-70°C and filtered hot. The filtrate is evaporated and the residue crystallized from a hexane–benzene mixture.

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