RING-CHAIN TAUTOMERISM OF DIACETYL AND BENZIL THIOACYLHYDRAZONES

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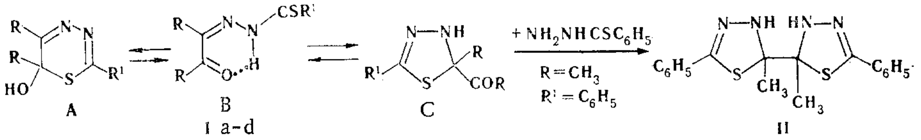
The products of condensation of thiobenzohydrazide with diacetyl and benzil have the structures of the corresponding 1,3,4-thiadiazol-2-ines; the same diketones and phenylthioacetylhydrazine were used to synthesize derivatives that display in solutions the ability to undergo thioacylhydrazone—1,3,4-thiadiazoline tautomerism. A bis derivative, viz., 5-(2'-phenyl-5'-methyl-1,3,4-thiadiazolin-2-yl)-5-methyl-2-phenyl-1,3,4-thiadiazol-2-ine, was obtained in the condensation of excess thiobenzohydrazide with diacetyl.

It has been previously shown that thioacylhydrazones of monocarbonyl compounds display the phenomenon of ring-chain tautomerism [1-5], whereas ring-chain tautomerism with the participation of various heterorings is characteristic for acetylacetone thiobenzoylhydrazone [6]. In the present paper we discuss the peculiarities of the structures of the products of condensation of thiobenzo- and phenylthioacetohydrazides with the simplest α-diketones, viz., diacetyl and benzil, regarding which there has been a previous report [7] without detailed proof for the structures of the products obtained. These subjects are of interest in connection with the fundamental possibility of the realization of yet another ring-chain variant of A $\rightleftarrows$ B tautomerism.



a R=CH_3, R^1=C_6H_5; b R=R^1=C_6H_5; c R=CH_3, R^1=$CH_2C_6H_5$; d R=C_6H_5, R^1=$CH_2C_6H_5$

We found that condensation products with splitting out of water in a radio of 1:1 are formed in high yields in all cases. If, however, one uses excess thiobenzohydrazide, the principal product in the reaction with diacetyl is the bis adduct (II).*

According to the IR and PMR spectral data, thiobenzohydrazide derivatives Ia, b exist in single tautomeric form C in various solvents. The hydrazone structure should be excluded, since the ^{13}C NMR spectra of Ia, b contain only two signals of sp^2-hydrid carbon atoms. Thiadiazine tautomer A is also impossible, since an intense absorption band of a carbonyl group at 1700-1730 cm^{-1} is present in the IR spectra of Ia, b. All of the IR and PMR spectral data are in complete agreement with structure C (Table 1). Let us especially note that the ^{13}C NMR spectra contain a signal of the $C_{(5)}$ atom at 80-90 ppm that is characteristic for 1,3,4-thiadiazol-2-ines [4]. The thiadiazoline structure of Ia is confirmed by its mass spectrum (see the experimental section), in which the primary fragmentation is ejection of an acetyl group from the molecular ion. The remaining fragment ions are typical for the mass spectra of 2-phenyl-1,3,4-thiadiazol-2-ines [4].

The bis(thiadiazolinyl) structure of II is in agreement with the NMR and mass-spectral data. The formation of an equimolar mixture of diastereomers in derivative II is manifested in doubling of the signals of the monotypic carbon atoms in ^{13}C NMR spectrum and in the anisochromicity of the diastereotopic methyl groups in the PMR spectrum (solution in d_6-DMSO, 1.95 and 1.97 ppm). For this compound, cleavage of the $C_{(5)}$—$C_{(5')}$ bond is most characteristic

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*Only the known [8] 2-benzoyl-5-phenyl-1,3,4-thiadiazole was isolated in the region with a keto aldehyde of phenylglyoxol.

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TABLE 1. Physicochemical Constants and ^{1}H and ^{13}C NMR Spectra of Ia-d and II

Compound	mp, °C	Solvent	PMR spectrum, ppm						^{13}C NMR spectrum, ppm (J, Hz)				Found, %		Empirical formula	Calc., %		Yield, %
			R	RCO	R^1	NH	form	B:C	C=O	C=N	C-5 (C=S)	other signals	C	H		C	H	
Ia	Oil	CCl_4	1,75	2,21	7,2—7,9 m	7,10	C	0 : 100	204,2	143,2	84,7	22,3 ($^1J_{CH}$=130,5); 22,7 ($^1J_{CH}$=132,0)	59,9	5,5	$C_{11}H_{12}N_2OS$	60,0	5,5	65
Ib	113	CCl_4	7,1—7,7m			6,95	C	0 : 100	194,7	145,0	89,8	—	73,3	4,8	$C_{21}H_{16}N_2OS$	73,2	4,7	75
Ic	Oil	CCl_4	1,65	2,22	3,65; 7,0—7,3 m	6,41	C	30 : 70	204,8, ($^2J_{CCH}$=4,5)	143,6	86,6	10,5 ($^1J_{CH}$=132,0); 24,1 ($^1J_{CH}$=132,0); 36,2 ($^1J_{CH}$=135,0)	61,5	6,1	$C_{12}H_{14}N_2OS$	61,5	6,0	55
			1,96	2,32	4,36; 7,0—7,3 m	10,30	B		191,7, ($^2J_{CCH}$=5,0)	149,2	206,1 ($^2J_{CCH}$=6,0)	23,1 ($^1J_{CH}$=130,5); 24,7 ($^1J_{CH}$=130,5); 48,0						
			1,60	2,27	3,72; 7,1—7,4 m	7,60	C											
		d_6-DMSO	2,05	2,33	4,42; 7,1—7,4 m	12,35	B	40 : 60										
Id	Oil	CCl_4	7,0—8,0m		3,55, 3,71 (J_{AB}=15,0) 7,0—8,0m	—[a]	C	35 : 65	196,6	140,0	92,6	38,1	74,5	5,0	$C_{23}H_{18}N_2OS$	74,6	4,9	70
			7,0—8,0m		4,20; 7,0—8,0 m	—[b]	B		172,5	148,8	207,6	38,6						
		d_6-DMSO	7,1—8,0m		3,75; 7,1—8,0 m	8,48	C	45 : 55										
			7,1—8,0m		4,35; 7,1—8,0 m	13,05	B											
II	151	CCl_4	1,80		7,2—7,6 m	6,35	—	—	—	141,4; 142,2	91,3; 92,5	25,5 ($^1J_{CH}$=130,3); 26,3 ($^1J_{CH}$=130,3)	61,0	5,2	$C_{18}H_{18}N_4S_2$	61,0	5,1	60

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[a] Masked by the signals of the aromatic ring protons. [b] Not localized.

under the influence of electron impact. The subsequent fragmentation of the fragment ions is similar to that observed for 1,3,4-thiadiazol-2-ines [4].

Phenylthioacetylhydrazine derivatives Ic, d exist in solutions as equilibrium mixtures of two forms. In addition to the thiadiazoline tautomers C, the spectral characteristics of which are similar to the data for Ia, b, yet another form, the fraction of which increases as the polarity of the solvent increases, appears. The second isomer should be assumed to be hydrazone B; this is in agreement with the detection in the IR spectrum of an absorption band of yet another carbonyl group at 1680-1700 cm^{-1}. The position of the band of stretching vibrations of an NH bond (at 3300 cm^{-1}) indicates the formation of an intramolecular hydrogen bond. This is also confirmed by the absence of a temperature dependence of the position of the weak-field NH signal in the PMR spectra. As one should have expected for the B form, three signals of sp^2-hybrid carbon atoms are observed in the ^{13}C spectra.

Thus existence in thiadiazine form A is not characteristic for the products of condensation of thioacylhydrazines with α-diketones, and the development of linear tautomer B for the phenylthioacetylhydrazine derivatives is associated with a decrease in the acceptor capacity of the substituent in the thioamide fragment.

EXPERIMENTAL

The IR spectra of solutions of the compounds in CCl_4 were recorded with a Specord 75 IR spectrometer. The PMR spectra were obtained with a Tesla BS-497 spectrometer (100 MHz) with hexamethyldisiloxane as the internal standard, while the ^{13}C NMR spectra were recorded with a CFT-20 spectrometer with tetramethylsilane as the internal standard. The mass spectra were recorded with an MKh-1303 mass spectrometer with direct introduction of the samples into the ion source the ionizing voltage was 70 eV, the emission current was 0.6 mA, and the temperature was 170°C. The individuality of all of the compounds obtained was confirmed by chromatography on a thin layer of Silufol with chloroform as the eluent.

Reaction of Thiohydrazides with α-Diketones. A 0.05-mole sample of the corresponding hydrazide in 25 ml of methanol was added with stirring to 0.05 mole of the corresponding diketone in 25 ml of methanol (cooling of the reaction mixture to −20°C was necessary for the preparation of Ia). After 24 h, the methanol was removed *in vacuo*, and the residue was recrystallized from hexane.

Mass spectra of Ia and II (m/z, relative intensities of the ions in percent relative to the maximum ion peak): Ia: 220 (8), 177 (47), 176 (100), 149 (67), 135 (23), 121 (39), 117 (38), 116 (35), 104 (69), 103 (90), 91 (50), 77 (69), 76 (47), 51 (32); II: 178 (15), 177 (100), 176 (6), 136 (6), 121 (13), 109 (6), 105 (8), 104 (19), 103 (10), 77 (34), 76 (9), 74 (9), 59 (10), 51 (21).

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