

REACTIONS OF VINYLENE DIISOTHIOCYANATE WITH ANILINE, N-BENZYLIDENEMETHYLAMINE AND N,N'-DICYCLOHEXYLCARBODIIMIDE

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Reaction of vinylene diisothiocyanate with aniline, N-benzylidenemethylamine and N,N'-dicyclohexylcarbodiimide affords the stable 1-(anilinothiocarbonyl)-4-imidazoline-2-thione and 1,3,5-thiadiazine derivatives, respectively.

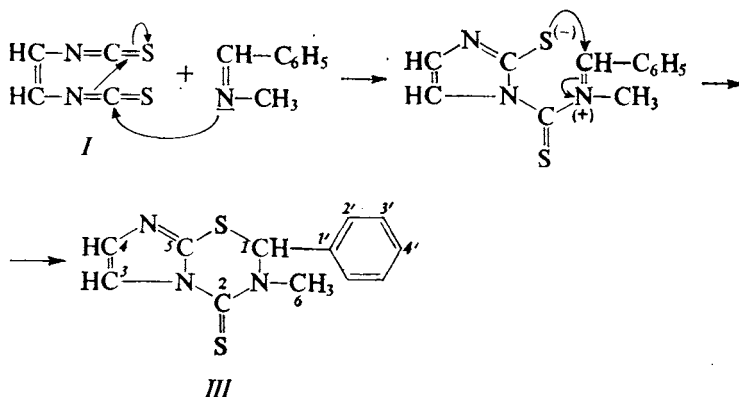
Vinylene diisothiocyanate^{1,2} (*I*) reacts with many nucleophiles³, e.g. *p*-chloroaniline, cyclohexylamine, morpholine, isoquinoline, triethylamine, and sodium azide to form the respective substituted thiocarbonylimidazolines. The addition product of *p*-chloroaniline to diisothiocyanate *I* easily undergoes decomposition to yield *p*-chlorophenyl isothiocyanate and imidazole-2-thione. The dithione, obtained from cyclohexylamine, was stable under similar conditions. Secondary amines are able to react with diisothiocyanate *I* to afford the 1 : 1 or 2 : 1 adducts in contrast to primary amines; phenylhydrazine and ethanol furnish exclusively 2 : 1 adducts.

The aim of this paper was to study reactions of vinylene diisothiocyanate (*I*) with some further nucleophiles. Thus, reaction of *I* with aniline gave the anticipated 1-(anilinothiocarbonyl)-4-imidazoline-2-thione (*II*) which is stable in contrast to the product obtained by reacting *I* with *p*-chloroaniline³.

The ¹H NMR spectrum of *II* revealed signals of aromatic ring and N-bound protons and those of a —CH=CH— group (7.37 ppm, 8.26 ppm). The ¹H NMR spectrum was also measured at 30°C; nonetheless signals of decomposition products did not appear. The ¹³C NMR spectrum showed signals of two C=S groups in agreement with the presumed structure.

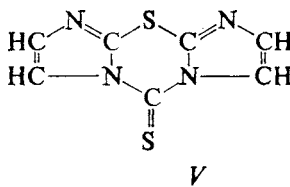
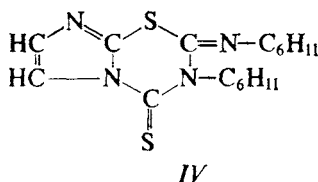
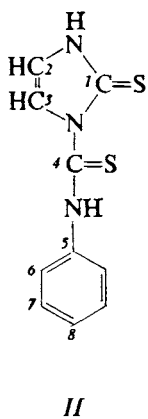
Compound *I* gave with N-benzylidenemethylamine 2-phenyl-3-methyl-4-thioxoimidazo[1,2-*e*][1,3,5]-thiadiazine (*III*, Scheme 1). We suppose that this reaction proceeds *via* ionic intermediate similarly as with *o*-phenylene diisothiocyanate⁴. Structure of the cycloadduct *III* was evidenced by spectral methods. The IR spectrum disclosed absorption bands of stretching vibrations at 1 520 cm⁻¹ and 1 480 cm⁻¹ ($\nu(\text{C}=\text{C})$) and 1 075 cm⁻¹ ($\nu(\text{C}=\text{S})$). The ¹H NMR spectrum displayed signals associated with the —CH=CH— group (7.07 ppm and 8.12 ppm) and H-2 proton

(6.87 ppm) in addition to those belonging to aromatic ring and methyl group. The ^{13}C NMR spectrum is characteristic of the presence of a thiocarbonyl group at 172.75 ppm and other signals agreeing in positions with those of monosubstituted imidazoles⁵. The molecular radical ion and further fragments in the mass spectrum are in line with fragmentation pattern of 1,3,5-thiadiazines.



SCHEME 1

As known, isothiocyanates react with carbodiimides through the $\text{C}=\text{S}$ bond giving rise to the respective cycloadducts⁶⁻⁸. Since the unsaturated 1,2-diisothiocyanates consist of two $-\text{NCS}$ groups linked by a multiple bond, it was of interest to investigate which one undergoes the reaction with carbodiimides. Reaction of *I* with *N,N'*-dicyclohexylcarbodiimide afforded 2-cyclohexylimino-3-cyclohexyl-4-thioxoimidazo[1,2-*e*][1,3,5]-thiadiazine (*IV*). Its IR spectrum contains an ab-



sorption band at $1\,650\text{ cm}^{-1}$, indicative of an exocyclic $\text{C}=\text{N}$ bond, and another one at $1\,575\text{ cm}^{-1}$ due to stretching vibrations $\nu(\text{C}=\text{N})$ of the ring⁹. The ^1H NMR spectrum showed signals of cyclohexyl protons and those of the $-\text{CH}=\text{CH}-$ group (7.37 ppm, 8.87 ppm). Mass spectrum of the cycloadduct *IV* displayed characteristic peaks at m/z 348 ($\text{M}^{+\bullet}$), 206, and 142; both latter peaks are consistent with molecular mass of the starting products. Another crystalline product was obtained from the filtrate. It was identified as bisimidazo[2,1-*b*:1',2'-*e*][1,3,5]-thiadiazine-4-thione (*V*) formed from two molecules of vinylene diisothiocyanate by the loss of CS_2 . Its physicochemical constants accorded with those reported². The unreacted $\text{N,N}'$ -dicyclohexylcarbodiimide afforded a small amount of dicyclohexylurea⁹.

The results reported together with ours entitle to propose that reactions of vinylene diisothiocyanate (*I*) with N -benzylidenemethylamine and $\text{N,N}'$ -dicyclohexylcarbodiimide proceed probably *via* ionic intermediates.

EXPERIMENTAL

The IR spectra were measured with a Specord 75 IR spectrophotometer in the $800-4\,000\text{ cm}^{-1}$ range. The ^1H and ^{13}C NMR spectra were taken with Tesla BS 487 A (80 MHz) and Tesla BS 567 (25.15 MHz) apparatuses, respectively, tetramethylsilane being the internal reference. The ^{13}C NMR signals were assigned from the noise decoupled and off-resonance spectra. The mass spectra were recorded with an MS 902 S (AEI Manchester) instrument at 70 eV and 100°C ionization chamber temperature.

Vinylene diisothiocyanate (*I*) was prepared according to². IR spectrum, cm^{-1} (CHCl_3): 3 020 ($\nu(\text{C}-\text{H})$), 2 000–2 120 ($\nu(\text{NCS})$), 1 620 ($\nu(\text{C}=\text{C})$); the only product was immediately dissolved in dichloromethane and filtered. N -Benzylidenemethylamine (b.p. $92-93^\circ\text{C}/4.5\text{ kPa}$) was synthesized according to¹⁰ and $\text{N,N}'$ -dicyclohexylcarbodiimide had (m.p. $33-35^\circ\text{C}$).

Reaction of Vinylene Diisothiocyanate (*I*) with Aniline

The dichloromethane solution of *I* was evaporated and the red oil obtained (2.64 g, 18 mmol) was dissolved in ether (40 ml), filtered and added to aniline (1.85 g, 21 mmol) in ether (20 ml) with stirring at room temperature. The solvent was after 24 h of stirring removed *in vacuo* and the product was crystallized from chloroform–heptane. 1-(Anilinothiocarbonyl)-4-imidazoline-2-thione (*II*), yellow crystals, m.p. $219-220^\circ\text{C}$, yield 2.69 g, (62%). For $\text{C}_{10}\text{H}_9\text{N}_3\text{S}_2$ (235) calculated: 51.06% C, 3.82% H, 17.87% N; found: 50.61% C, 3.43% H, 18.11% N. IR spectrum, cm^{-1} (KBr): $\nu(\text{NH})$ 3 450, $\nu(\text{C}-\text{H})$ 2 875, $\nu(\text{C}=\text{C})$ 1 630, 1 590, $\delta(\text{NH})$ 1 430. ^1H NMR spectrum, ppm ($(\text{C}^2\text{H}_5)_2\text{SO}$, δ): 7.37 (d, 1 H, $=\text{CH}$, $J_{\text{AB}} = 3.0\text{ Hz}$), 8.26 (d, 1 H, $=\text{CH}$, $J_{\text{AB}} = 3.0\text{ Hz}$), 8–7.43 (m, 5 H, arom), 13.25 (s, 1 H, NH), 14.65 (s, 1 H, NH). ^{13}C NMR spectrum, ppm ($\text{C}^2\text{HCl}_3 + (\text{C}^2\text{H}_5)_2\text{SO}$, δ): 159.81 (s, $\text{C}_{(1)}$), 119.35 (d, $\text{C}_{(2)}$), 114.20 (d, $\text{C}_{(3)}$), 175.34 (s, $\text{C}_{(4)}$), 137.72 (s, $\text{C}_{(5)}$), 128.68 (d, $\text{C}_{(6)}$), 126.74 (d, $\text{C}_{(7)}$), 124.06 (d, $\text{C}_{(8)}$).

Reaction of Vinylene Diisothiocyanate (*I*) with N -Benzylidenemethylamine

Solution of N -benzylidenemethylamine (2.6 g, 22 mmol) in acetonitrile (20 ml) was added to the filtered solution of *I* (2.85 g, 20 mmol) in acetonitrile (30 ml). The mixture was stirred for 4 h at room temperature. The solid portion of the product was filtered off and crystallized from

ethanol. 2-Phenyl-3-methyl-4-thioxoimidazo[1,2-*e*][1,3,5]-thiadiazine (*III*), beige crystals, m.p. 174.5–175°C, yield 2.72 g (52%). For $C_{12}H_{11}N_3S_2$ (261) calculated: 55.21% C, 4.21% H, 16.09% N; found: 54.81% C, 3.94% H, 16.31% N. IR spectrum, cm^{-1} (KBr): $\nu(C-H)$ 2900, $\nu(C=C)$ 1520, 1480, $\nu(C=S)$ 1075. 1H NMR spectrum, ppm ($(C^2H_3)_2SO$, δ): 3.91 (s, 3 H, CH_3), 6.87 (s, 1 H, H-2), 7.07 (s, 1 H, $=CH$), 8.12 (d, 1 H, $=CH$, $J_{AB} = 1.5$ Hz), 7.62–7.15 (m, 5 H, arom). ^{13}C NMR spectrum, ppm ($(C^2H_3)_2SO$, δ): 63.28 (d, $C_{(1)}$), 172.72 (s, $C_{(2)}$), 121.88 (dd, $C_{(3)}$), 129.2 (dd, $C_{(4)}$), 43.35 (q, $C_{(6)}$), 136.59 (s, $C_{(1')}$), 124.87 (d, $C_{(2')}$), 128.45 (d, $C_{(3')}$), 124.05 (d, $C_{(4')}$). Mass spectrum, m/z (rel. intensity, %): 261 (22.6), 260 (10), 203 (26.6), 187 (4.6), 170 (4), 149 (5.3), 142 (26.6), 122 (5.3), 121 (10), 119 (18), 118 (53.3), 91 (10.6), 89 (6), 77 (22.6), 28 (100).

Reaction of Vinylene Diisothiocyanate (*I*) with *N,N'*-Dicyclohexylcarbodiimide

Solution of *N,N'*-dicyclohexylcarbodiimide (3.8 g, 18 mmol) in ether (40 ml) was dropwise added in a nitrogen atmosphere to the filtered solution of *I* (2.53 g, 18 mmol) in ether (60 ml) at ambient temperature. The light yellow 2-cyclohexylimino-3-cyclohexyl-4-thioxoimidazo[1,2-*e*][1,3,5]-thiadiazine (*IV*) which separated after a 4 h-stirring was filtered off; m.p. 180 to 181°C (ethanol-ether 1 : 10); yield 2.9 g (47%). For $C_{17}H_{24}N_4S_2$ (348) calculated: 58.68% C, 6.95% H, 16.09% N; found: 59.05% C, 6.90% H, 16.28% N. IR spectrum, cm^{-1} ($CHCl_3$): $\nu(C-H)_{alic}$ 2930, $\nu(C=N)_{exo cycl}$ 1650, $\nu(C=N)_{cycl}$ 1575. 1H NMR spectrum, ppm (C^2HCl_3 , δ): 1.05–1.95 (m, 20 H, cyclohexyl), 2.5–3.0 (m, 1 H, 1-cyclohexyl-N<), 3.3–3.87 (m, 1 H, 1-cyclohexyl-N=), 7.37 (s, 1 H, $=CH$), 8.87 (s, 1 H, $=CH$). Mass spectrum, m/z (rel. intensity, %): 348 (0.1), 224 (9.6), 208 (13.4), 206 (15.3), 191 (10), 177 (15.3), 164 (23), 163 (40.4), 151 (19.9), 142 (9.6), 140 (8.6), 125 (38.4), 124 (36.5), 123 (7.6), 109 (7.6), 97 (34.6), 83 (96), 43 (100). The filtrate after evaporation of the solvent furnished the yellow bisimidazo[2,1-*b*:1',2'-*e*][1,3,5]-thiadiazine-4-thione (*V*), m.p. 186–187°C, yield 0.77 g (21%). 1H NMR spectrum, ppm ($(C^2H_3)_2SO$, δ): 7.58 (d, 2 H, $-CH=CH-$, $J_{AB} = 2.0$ Hz), 8.5 (d, 2 H, $-CH=CH-$, $J_{AB} = 2.0$ Hz). Mass spectrum, m/z (rel. intensity, %): 208 (100), 181 (7.1), 150 (31.2).

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