CONCLUSIONS

Stable complexes of chloronitroacetamide with Cu^{2+} and Ni^{2+} ions were synthesized. The molecular structure of bis(chloronitroacetamidato)tetramminecopper(II) was determined by x-ray diffraction structural analysis.

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REACTION OF 1-ACYL-2-PHENYLACETYLENES WITH THIOSEMICARBAZIDE

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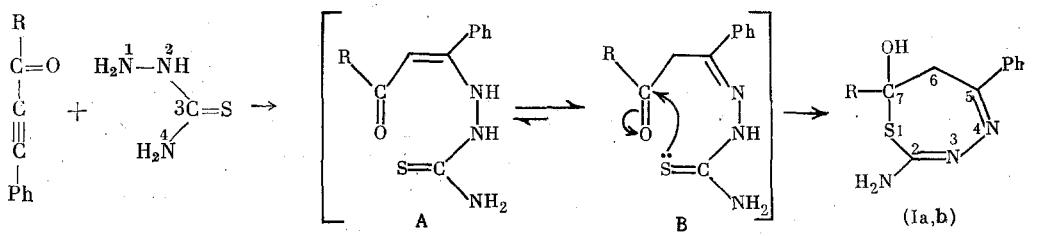
The dimethyl ester of acetylenedicarboxylic acid reacts with thiosemicarbazide (TSC) and its 1-substituted derivatives to give 2-hydrazino-5-methoxycarbonylmethylene-1,3-thiazolin-4-ones [1], while this ester reacts with 4-substituted derivatives of TSC to give 3-amino-2-imino-6-methoxycarbonyl-1,3-thiazin-4-ones [2]. The reaction of terminal α-acetylenic ketones with 1-phenyl TSC in methanol at 20°C gives 2-aceylmethyl-5-imino-3-phenyl-4H-1,3,4-thiadiazoles [3].

We have found that the reaction of 1-acyl-2-phenylacetylenes with TSC in equimolar ratio in methanol at 60°C leads to the formation of 2-amino-7-hydroxy-6,7-dihydro-1,3,4-thiadiazepines (Ia) and (Ib) in 71-75% yield.



R = Ph(a), α-C_4H_3S(b).

The 1-NH_2 group in TSC is more nucleophilic than the 4-NH_2 group [2, 4]. Thus, adducts A are formed initially and rapidly convert to more stable adducts B, as indicated by Lown and Ma [2]. Adducts B undergo intramolecular cyclization to form (Ia) and (Ib). The structures of the products were supported by IR, UV, ^1H and ^{13}C NMR, and mass spectroscopy.

The IR spectra for (Ia) and (Ib) in chloroform show bands at 708-712 (CS), 1520-1545 (C=N), 3505-3510 and 3375-3380 cm^{-1} (NH_2). The presence of broad bands for the associated OH group at 3240-3300 cm^{-1} indicates intramolecular OH...NH_2 hydrogen bonding. A decrease in the concentration to $5 \cdot 10^{-4}$ mole/liter does not lead to a change in the relative intensity of the OH band, which indicates the lack of intermolecular association [5].

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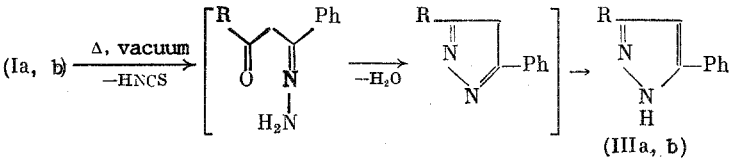
The UV spectra of (Ia) and (Ib) have a band at 219-225 nm characteristic for the conjugated =C=N–N=C= system in the heterocycle [6]. The PMR spectra of (Ia) and (Ib) show an AB pattern for the 6-CH_2 protons at 3.42-3.80 ppm ($^2J_{HH}$ = 19.0 Hz) due to the free asymmetric C^7 atom.

The ^{13}C NMR spectra of (Ia) and (Ib) in $CDCl_3$ lack signals for a carbonyl carbon. The signals at 92.32-95.83 ppm were assigned to C^7 since the signal of the asymmetric carbon atom of the analogous fragment in the spectrum of a model compound, 2-phenacyl-2-phenyl-1,3-oxathiolane (II) is found at 95.45 ppm [7].

The mass spectra of (Ia) and (Ib) have molecular ion peaks. The major type of fragmentation upon electron impact for (Ia) and (Ib) is the formation of ions of the corresponding 3,5-disubstituted pyrazoles which give the strongest mass peaks. $[HNCS]^+$ions are also recorded.

Heating of (Ia) and (Ib) in vacuum leads to the opening of the 1,3,4-thiadiazepine ring and loss of isothiocyanic acid and the formation of 3,5-disubstituted pyrazoles (IIIa) and (IIIb).



R = Ph(a), R = α-C_4H_3S(b).

Opening of the 1,3,4,-thiadiazepine ring is observed upon passing dry gaseous HCl through a solution of (Ia) in $CHCl_3$ and the hydrochloride salt of (IIIa) is isolated as the only product.

EXPERIMENTAL

The IR spectra were taken for KBr pellets or in chloroform solution on an IR-75 spectrometer. The UV spectra were taken on a Specord spectrophotometer. The PMR spectra were taken on a Tesla BS-487C spectrometer at 80 MHz in $CDCl_3$ or DMSO relative to TMS or HMDS. The ^{13}C NMR spectra were taken on an FX-900 spectrometer at 22.49 MHz in $CDCl_3$ or DMSO-d_6 relative to DMSO related to TMS). The mass spectra were taken on an MKh-1303 mass spectrometer with direct sample inlet to the ion source and 30 eV ionizing voltage.

2-Amino-7-hydroxy-5,7-diphenyl-6,7-dihydro-1,3,4-thiadiazepine (Ia). A solution of 0.92 g (10 mmoles) TSC in 40 ml methanol was added to a solution of 2.06 g (10 mmoles) 1-benzoyl-2-phenylacetylene in 40 ml methanol, heated to reflux and stirred for 2 h. The mixture was cooled to 20°C. The precipitate formed was filtered off and recrystallized from acetone to give 2.1 g (71%) (Ia) as white crystals with mp 107-108°C (from benzene). ^{13}C NMR spectrum (in $CDCl_3$, ν, ppm): 153.09 (C^2). 175.95 (C^5), 51.46 (C^6), 95.83 (C^7), 124.1-144.2 (arom CH). Mass spectrum, m/z (rel. intensity, %): 297 (7) $[M]^+$, 220 (100) $[M–HNCS–H_2O]^+$, 178 (20) $[M–PhCOCH_2]^+$, 105 (15) $[PhCO]^+$, 77 (17) $[Ph]^+$, 59 (7) $[NHCS]^+$. Found: C 64.31; H 5.12; N 14.09; S 10.90%. Calculated for $C_{16}H_{13}N_3OS$: C 64.69; H 5.14; N 14.09; S 10.82%.

2-Amino-7-hydroxy-7-(thienyl-2-)-5-phenyl-6,7-dihydro-1,3,4-thiadiazepine (Ib) was obtained by analogy to (Ia) from 1.06 g (5 mmoles) 1-thenoyl-2-phenylacetylene and 0.47 g (5 mmoles) TSC in 40 ml methanol. The product was obtained in 75% yield (1.1 g) as white crystals with mp 114-116°C (from benzene). ^{13}C NMR spectrum in $CDCl_3$: 150.34 (C^2), 174.45 (C^5), 50.23 (C^6), 92.32 (C^7), 121.5-147.7 (benzene and thiopene ring CH). Mass spectrum: 303 (13) $[M]^+$, 226 (100) $[M–HNCS–H_2O]^+$, 178 (27) $[M–C_4H_2SCOCH_2]^+$, 111 (17) $[C_4H_3SCO]^+$, 77 (10) $[Ph]^+$, 59 (15) $[HNCS]^+$. Found: C 55.21; H 4.19; N 13.82; S 21.30%. Calculated for $C_{14}H_{11}N_3OS_2$: C 55.11; H 4.28; N 13.90; S 21.13%.

2-Phenacyl-2-phenyl-1,3-oxathiolane (II) was obtained according to our previous procedure [7] from 3.09 g (15 mmoles) 1-benzoyl-2-phenylacetylene and 1.17 g (15 mmoles) β-mercaptoethanol in 40 ml dry $CHCl_3$ in the presence of K_2CO_3 at 60°C. The product was obtained in 30% yield (1.2 g), mp 101-102°C [7]. ^{13}C NMR spectrum (in DMSO-d_6): 95.45 (C^2), 67.72 (C^4), 33.04 (C^5), 195.94 (CO), 51.84 (CH_2), 126.1-136.8 (arom CH). Found: C 71.70; H 5.62; S 11.19%. Calculated for $C_{17}H_{16}O_2S$: C 71.81; H 5.58; S 11.29%.

Heating (Ia) in Vacuum. A sample of 0.3 g (Ia) was placed in a sublimation apparatus and heated for 1 h at 105-110°C at 1.33 GPa. White crystals with mp 200-201°C sublime on

the cool part of the apparatus. The yield was 0.2 g (91%). The compound obtained was 3,5-diphenylpyrazole (IIIa) [8]. IR spectrum (ν, cm^{-1}, KBr): 1405-1575 (C=N and C=C in the pyrazole ring), 3425 (NH). Found: C 82.05; H 5.49; N 12.81%. Calculated for $C_{15}H_{12}N_2$: C 81.85; H 5.50; N 12.70%.

Analogously, 0.37 g (Ib) upon heating in vacuum to 95-100°C gives 0.07 g (30%) 5-(thienyl-2)-3-phenylpyrazole with mp 186-187°C. Found: C 68.93; H 4.86; N 12.25; S 13.93%. Calculated for $C_{13}H_{10}N_2S$: C 69.02; H 4.86; N 12.39; S 14.15%.

Preparation of the Hydrochloride Salt of 3,5-diphenylpyrazole (IVa). A sample of 0.3 g (IIIa) was dissolved in 40 ml dry chloroform and dry HCl was passed through this solution for 2 h at 20°C. The precipitate formed was filtered off, washed with cold chloroform and dried in vacuum to give 0.21 g (82%) hydrochloride salt of (IVa) as white crystals with mp 233-234°C (232-233°C [8]). Found: C 70.02; H 5.21; Cl 14.02; N 10.81%. Calculated for $C_{15}H_{12}N_2 \cdot HCl$: C 69.93; H 5.12; Cl 14.20; N 10.92%.

CONCLUSIONS

The reaction of 1-acyl-2-phenylacetylenes with thiosemicarbazide in methanol at 60°C gives 2-amino-7-hydroxy-6,7-dihydro-1,3,4-thiadiazepines which, upon heating in vacuum fragment with the formation of 3,5-disubstituted pyrazoles.

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TELOMERIZATION OF 1-HEXENE BY DIETHYL PHOSPHITE IN THE PRESENCE OF DECACARBONYLDIMANGANESE AND PEROXIDES

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Radical telomerization involving heteroorganic compounds which react on account of cleavage of the element–hydrogen bond holds interest as a method for the synthesis of telomers with various functional groups containing a heteroatom in the hydrocarbon chain. The initiation of telomerization of metal complex systems derived from binuclear manganese or rhenium carbonyls in the case of silicon hydrides and mercaptans [1] has a number of interesting features which considerably expand the range for the use of binuclear carbonyls as radical reaction initiators.

Great interest is naturally found in the clarification of the general nature of the observed effects and the use of metal complex catalysis in reactions involving organophosphorus telogens containing the readily homolyzable P–H bond.

The addition of diethyl phosphite (DEP) to α-olefins catalyzed by Bz_2O_2 or UV light has been reported by Pudovik [2]. In the present work, we studied the telomerization of 1-hexene (M) by DEP with initiation by tert-butyl peroxide (TBP) or $Mn_2(CO)_{10}$

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