# MESOIONIC 2-ACYLIMINO-1,3,4-THIADIAZOLES

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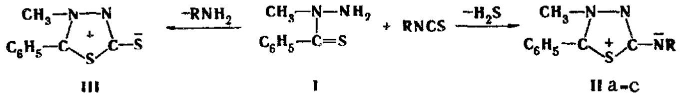
UDC 547.794.3

Mesoionic 2-carbamoylimino-, 2-thiocarbamoylimino-, and 2-methacryloylimino-1,3,4-thiadiazoles were obtained by reaction of α-alkylthioacylhydrazines with the appropriate acyl isothiocyanates. Mesoionic 1,3,4-thiadiazole-2-thione is also formed in the reaction with diethylthiocarbamoyl isothiocyanate.

We have previously described [1] the reaction of α-alkylthioacylhydrazines (I) with acyl isothiocyanates, which gives the corresponding mesoionic 2-acylimino-1,3,4-thiadiazoles. We found it was possible to use this reaction for the synthesis of mesoionic 2-carbamoyl-, 2-thiocarbamoyl-, and 2-methacryloylimino-1,3,4-thiadiazoles (IIa-c). The reaction with thiocarbamoyl isothiocyanate proceeds in two directions [2, 3], and IIb and III were isolated after chromatographic separation in a layer of aluminum oxide.



IIa $R=(C_2H_5)_2NCO$; b $R=(C_2H_5)_2NCS$; c $R=CH_2=C(CH_3)CO$

## EXPERIMENTAL METHOD

The carbamoyl and thiocarbamoyl isothiocyanates were obtained in solution immediately prior to their use [4].

The melting points were determined with a heating stage. The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The UV spectra of acetonitrile solutions of the compounds were recorded with an SF-4 spectrophotometer. The PMR spectra of $CDCl_3$ solutions were recorded with a BS 487C spectrometer with an operating frequency of 80 MHz with tetramethylsilane as the standard. Thin-layer chromatography (TLC) was accomplished on silica gel (fixed layer on a terephthalate film) with $CHCl_3$ as the solvent, $CHCl_3$–acetone (9.5 : 0.5) as the eluent, and development by iodine vapors.

Mesoionic 2-Diethylcarbamoylimino-1,3,4-thiadiazole (IIa). A mixture of 4.8 g (45 mmole) of $C_2H_5NCOCl$ and 11.5 g (43 mmole) of PbNCS was refluxed for 30 min in 30 ml of absolute acetonitrile, after which the mixture was filtered, 2.5 g (15 mmole) of I was added to the filtrate, and the mixture was refluxed for another 3 h. It was then vacuum-evaporated, and the residue was recrystallized from ether to give 1.04 g (25%) of II with mp 155.5-156° and $R_f$ 0.37. UV spectrum: $\lambda_{max}$ 356 and 262 nm (log ε 3.96 and 4.18). IR spectrum: 1588, 1475, 1460, and 1380 $cm^{-1}$. PMR spectrum, τ, ppm: 5.95 ($N-CH_3$, s), 2.38 ($C_6H_5$ s), 6.42 ($N-CH_2$, m), and 8.80 ($CH_2CH_3$, t). Found: C 57.2; H 6.3; S 11.2%. $C_{14}H_{18}N_4OS$. Calculated: C 57.9; H 6.2; S 11.0%.

Mesoionic 2-Diethylthiocarbamoylimino-1,3,4-thiadiazole (IIb). A 2-g (16 mmole) sample of $C_2H_5NCSCl$ and 1.3 g (13 mmole) of KNCS were refluxed in 30 ml of absolute tetrahydrofuran (THF) for 1 h, after which the mixture was filtered, 1.8 g (11 mmole) of I was added to the filtrate, and the mixture was refluxed for another 9 h. The solvent was removed in vacuo, and the residue was recrystallized from alcohol to give 1.45 g of a mixture of two compounds with $R_f$ 0.48 and 0.68. A 0.5-g sample of the mixture was separated preparatively in a layer of aluminum oxide (with a thickness of 2 mm, elution by chloroform).

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Institute of Chemistry, Academy of Sciences of the USSR, Gorki. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 648-649, May, 1975. Original article submitted November 11, 1973; revision submitted November 4, 1974.

A total of 0.30 g of IIb, with mp 169-170° and $R_f$ 0.48, was isolated from the zone located closer to the front. UV spectrum: $\lambda_{max}$ 362 and 244 nm (log ε 4.01 and 4.37). IR spectrum: 1500, 1430, 1365, and 1270 $cm^{-1}$. PMR spectrum, τ, ppm: 5.95 ($N-CH_3$, s), 2.40 ($C_6H_5$, s), 6.04 ($N-CH_2$, m), and 8.75 ($CH_2CH_3$, t). Found: C 54.7; H 6.0; S 20.4%. $C_{14}H_{18}N_4S_2$. Calculated: C 54.9; H 5.9; S 20.9%. A total of 0.07 g of a compound identical to mesoionic 4-methyl-5-phenyl-1,3,4-thiadiazole-2-thione (III) [2] was isolated from the zone near the start.

Mesoionic 2-Methacryloylimino-1,3,4-Thiadiazole (IIc). A solution of 1.7 g (17 mmole) of methacrylolyl isothiocyanate [5] and 2.1 g (13 mmole) of I in 25 ml of absolute toluene was refluxed for 8 h, after which the solvent was removed by vacuum evaporation, and the residue was recrystallized from toluene and washed with ether to give 1.53 g (80%) of IIc with mp 166.5-167.5° and $R_f$ 0.37. UV spectrum: $\lambda_{max}$ 334 and 260 nm (log ε 4.07 and 3.94). IR spectrum: 1548, 1480, 1405, and 1380 $cm^{-1}$. PMR spectrum, τ, ppm: 5.88 ($N-CH_3$ s), 2.38 ($C_6H_5$, s), 7.88 ($CH_3-C$, s), and 3.65 and 4.48 ($=CH_2$, s, s). Found: C 60.4; H 5.2; S 13.0%. $C_{13}H_{13}N_3OS$. Calculated: C 60.2; H 5.0; S 12.4%.

## LITERATURE CITED

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