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# FORMATION OF IMIDAZOLIDINE DERIVATIVES FROM DIMETHYL (2,2-DIMETHYLHYDRAZINO)SUCCINATE IN REACTIONS WITH ALLYL AND PHENYL ISOTHIOCYANATES*

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UDC 547.467.1'784.
2:548.737

The reaction of (2,2-dimethylhydrazino)succinic acid ester with allyl and phenyl isothiocyanates leads to esters of 1-substituted (3-dimethylamino-5-oxo-2-thioxo-4-imidazolidinyl)acetic acids, which in protic solvents undergo a slight degree of elimination of dimethylamine to give esters of 1-substituted (5-oxo-2-thioxoimidazolidin-4-ylidene)acetic acids. The structure of methyl (1-allyl-5-oxo-2-thioxoimidazolidin-4-ylidene)acetate was proved by x-ray diffraction analysis.

Within the framework of a systematic study of the reactivities of hydrazino carboxylic acids [1, 2] we have investigated the reaction of dimethyl (2,2-dimethylhydrazino)succinate (I) with allyl and phenyl isothiocyanates. In the reaction of allyl isothiocyanate with ester I at high temperatures in ethanol we obtained two products in the form of a light-yellow oily liquid and a small amount of yellow crystals. The corresponding thiosemicarbazides are usually formed in the reaction of trisubstituted hydrazines with isothiocyanates [3]. However, an analysis of the spectra of the compounds obtained showed that neither of them is

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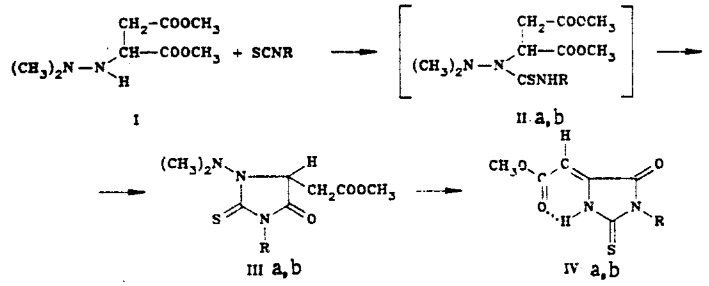
*Communication 3 from the series "Derivatives of hydrazino carboxylic acids," See [1] for communication 2.

Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga 226006. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1219-1223, September, 1987. Original article submitted May 23, 1986.

0009-3122/87/2309-0974$12.50

an acyclic thiosemicarbazide II. It might be assumed that the initially formed adduct II undergoes cyclization to ester III under the reaction conditions:



II–IV a $R=CH_2CH=CH_2$; b $R=C_6H_5$

The IIIa structure proposed for the liquid compound is in good agreement with data from the PMR, IR, and mass spectra (see the experimental section).

An analysis of the PMR spectrum of the crystalline reaction product showed that this compound does not contain a dimethylamine fragment and that, instead of signals from a $CHCH_2CO$ grouping, only resonance peaks of isolated CH and NH protons are observed. On the basis of this, it was assumed that the crystalline product is formed from ester III by splitting out of dimethylamine. The possibility of this transformation was proved by obtaining a small amount of yellow crystals by refluxing the yellow component in ethanol. The formation of imidazolidine IV is most likely as a result of the transformation; this was also indicated by the similarity between the spectral data obtained and the data known for 1-substituted (5-oxo-2-thioxoimidazolidin-4-ylidene)acetic acids obtained by oxidation of the corresponding derivatives of (5-oxo-2-thioxoimidazolidin-4-yl)acetic acids with bromine [4] or by reaction of primary amines with esters of isothiocyanatofumaric acid [5].

The validity of the hypothesis of the formation of imidazolidine IVa was confirmed definitively by an x-ray diffraction study. The crystals of IVa, like the crystals of methyl [1-(4-bromophenyl)-5-oxo-2-thioxoimidazolidin-4-ylidene]acetate (V), the structure of which was previously established by x-ray diffraction analysis [5], also belong to monoclinic syngony. The bond lengths and bond angles in the fragment of the molecule (without the allyl substituent) that is similar to ester V coincide within the limits of the experimental error. The atoms that form the hydantoin heteroring of the molecule are situated in the plane in which the $C_{(6)}$ and $C_{(7)}$ atoms are also located. The S and $O_{(14)}$ atoms deviate from this plane on different sides by 0.017(1) and 0.043(1) Å, respectively. An intramolecular $N_{(3)}-H_{(3)}\ldots O_{(8)}$ hydrogen bond with an interatomic $N_{(3)}\ldots O_{(8)}$ distance of 2.838(6) Å [$N_{(3)}-H_{(3)}$ 0.79(6), $H_{(3)}\ldots O_{(8)}$ 2.35(6) Å, angle $N_{(3)}H_{(3)}O_{(8)}$ 120° (5)] is evidently formed in the molecule; this is due to the slight deviation [0.040(6) Å] of the $O_{(8)}$ atom from the plane of the $C_{(7)}$, $C_{(6)}$, $C_{(4)}$, $N_{(3)}$, and $H_{(3)}$ atoms. The bond lengths in the allyl substituent have less pronounced character of single and double bonds than in the allylthiourea molecule [6]. The plane drawn through the $C_{(11)}$, $C_{(12)}$, and $C_{(13)}$ atoms forms an angle of 83.6° with the ring. The packing of the molecules in the crystal is realized at greater or equal van der Waals distances, except for the close contact of the sulfur atom with $O_{(8)}$ at a distance of 3.103(4) Å. This contact is evidently realized by interaction of the oxygen atom of the carbonyl group, which bears a partial negative charge, with the partially positively charged sulfur atom, which is due to its conjugation with the hydantoin heteroring; this is indicated by the shortening to 1.646(5) Å of the S=C bond length.

In the reaction of hydrazino ester I with phenyl isothiocyanate the yield of hydantoin IVb is 4.8%, while the yield of its analog IVa under the same conditions is 1.3%. The difference in the yields is evidently associated with the greater electron-acceptor effect of the phenyl group as compared with the allyl group; this promotes an increase in the lability of the hydrogen atom attached to the chiral center in hydantoin III. It might be assumed that the elimination of dimethylamine is facilitated by attack of the base at this hydrogen atom. It is characteristic that heating hydantoin IIIb in an aprotic solvent (for example, in dioxane) both in the presence and absence of starting hydrazine I does not lead to splitting out of dimethylamine. The formation of trace amounts of hydantoin IVb is observed when methanol or ethanol is added to the reaction mixture. Further acceleration of the reaction was achieved when catalytic amounts of a base or acid were added. Of the protic solvents, water has the greatest effect on this process. Consequently, the elimination of dimethylamine from hydantoin III occurs only when a proton donor and a proton acceptor (preferably

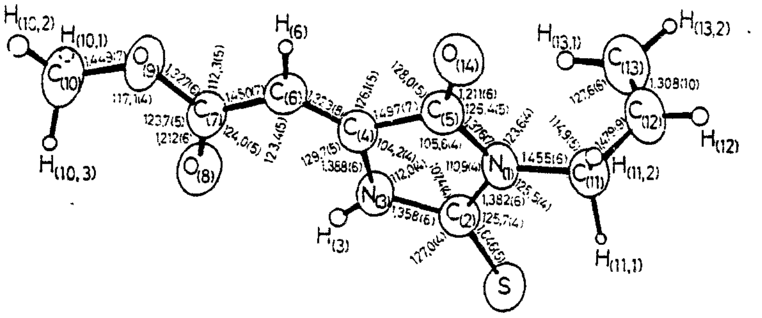
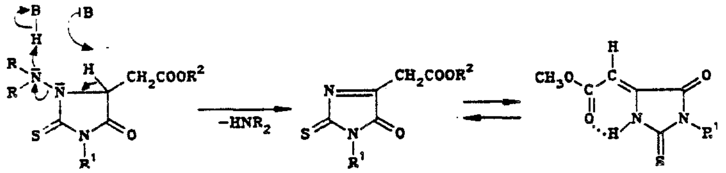


Fig. 1. Structure of the methyl (1-allyl-5-oxo-2-thioxoimidazolidin-4-ylidene)acetate molecule.

water and a base or acid) are simultaneously present. Proceeding from what we have stated above, the mechanism of splitting out of dimethylamine can be represented in the form of simultaneous attack of a basic agent at the 4-H atom and of a proton of the solvent (acid) at the dialkylamino group of hydantoin III:



## EXPERIMENTAL

The PMR spectra were recorded with a Brucker WH 90/DS spectrometer on the δ scale with tetramethylsilane (TMS) as the internal standard. The melting points were determined with a Kofler stage and were not corrected. The mass spectra were recorded with an MS-50 AEI spectrometer. The IR spectra were obtained from suspensions in mineral oil with a Perkin–Elmer 580 B spectrometer. Thin-layer chromatography (TLC) was carried out on Silufol UV-254 plates in the mobile phases ether–petroleum ether (1:1) and ether–carbon tetrachloride (1:1) for the allyl and phenyl derivatives, respectively.

Reaction of Allyl Isothiocyanate with Dimethyl (2,2-Dimethylhydrazino)succinate (I). A 9.92-g (0.1 mole) sample of allyl isothiocyanate was added to 20.42 g (0.1 mole) of I in 50 ml of ethanol, and the reaction mixture was maintained at 20°C for 30 min and then refluxed for 1.5 h. The solvent was removed at reduced pressure, and the reaction product was distilled at 0.005 mm with collection of the fraction with bp 95-135°C. The distillate was treated with a mixture of ether with methanol, and the yellow crystalline precipitate was removed by filtration, washed with methanol, and dried in vacuo at 50°C to give 0.29 g (1.3%) of yellow crystals with mp 119-121°C (from methanol). PMR spectrum ($CDCl_3$): 3.84 (3H, s, $COOCH_3$), 4.49 (2H, d, $NCH_2$), 5.1-5.4 (2H, m, $=CH_2$), 5.6-6.1 (1H, m, N–C–CH=), 5.86 (1H, s, =CH–CO), and 10 ppm (1H, broad s, NH). IR spectrum: 1670 (C=C), 1700 (N–C=O), 1744 (O–C=O), and 3255 $cm^{-1}$ (N–H). Mass spectrum:* 226 (54, $M^+$), 211 (43), 194 (64), 179 (22), 166 (43), 100 (46), 99 (57), 72 (51), 69 (30), 68 (100), 57 (33), 55 (31), 41 (77). Found: C 47.8; H 4.5; N 12.2%. $C_9H_{10}N_2O_2S$. Calculated: C 47.8; H 4.5; N 12.4%.

The filtrate was evaporated at reduced pressure to give a light-colored oil (16.5 g) in which admixed hydantoin IVa was not detected by chromatography. PMR spectrum ($CDCl_3$): 3.03 and 2.88 (each 1H, AB part of an ABX system, $^2J = 16.5$ Hz, $^3J = 4.0$ and 4.0 Hz, $CH_2CO$), 2.96 (6H, s, $NCH_3$), 3.69 (3H, s, $COOCH_3$), 4.23 (1H, t, $^3J = 4.0$ Hz, NCHCO), 4.41 (2H, d, $N–CH_2–C$), 5.1-5.4 (2H, m, $=CH_2$), and 5.6-6.1 ppm (1H, m, N–C–C–CH=). Mass spectrum: 271 (5, $M^+$), 229 (66), 228 (100), 213 (19), 200 (28), 169 (75), 168 (38), 155 (41), 153 (25), 99 (22), 44 (56).

Reaction of Phenyl Isothiocyanate with Dimethyl (2,2-Dimethylhydrazino)succinate (I). A. A mixture of 10.21 g (0.05 mole) of I and 6.76 g (0.05 mole) of phenyl isothiocyanate in 15 ml of dioxane was maintained at 20°C for 4 days, after which it was treated with methanol, and the precipitate was removed by filtration, washed with methanol, and dried in vacuo at 50°C to give 2.90 g of colorless large crystals of ester IIIb with mp 118-120°C.

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*Here and subsequently, the m/z values (relative intensities, %) are presented.

An additional 2.84 g of ester IIIb was isolated from the filtrate for an overall yield of 5.74 g (37%). PMR spectrum ($CDCl_3$): 3.01 (6H, s, $NCH_3$), 3.15 and 3.04 (each 1H, AB part of an ABX system, $^2J$ = 17.2 Hz, $^3J$ = 4.0 and 4.0 Hz, $CH_2CO$), 3.37 (3H, s, $COOCH_3$), 4.33 (1H, t, $^3J$ = 4.0 Hz, CH), and 7.4 ppm (5H, m, $C_6H_5$). IR spectrum: 1597 ($C_6H_5$), 1730 and 1750 $cm^{-1}$ (C=O). Mass spectrum: 307 (2, $M^+$), 265 (34), 264 (100), 205 (56), 204 (46), 203 (32), 84 (29), 77 (30), 68 (30), 54 (30), 44 (34), 43 (45), 42 (38). Found: C 54.8; H 5.8; N 13.5%. $C_{14}H_{17}N_3O_3S$. Calculated: C 54.7; H 5.6; N 13.7%.

B. The reaction was carried out in ethanol as in the reaction of ester I with allyl isothiocyanate. After cooling, the reaction mass was filtered to give 1.25 g (4.8%) of methyl (1-phenyl-5-oxo-2-thioxoimidazolidin-4-ylidene)acetate (IVb) in the form of yellow crystals with mp 231-232°C (from methyl ethyl ketone; the crystals began to sublime at ~170-180°C). According to the data in [5], this compound had mp 222-223°C. PMR spectrum ($CDCl_3$): 3.86 (3H, s, $COOCH_3$), 5.94 (1H, s, =CH—CO), 7.4 (5H, m, $C_6H_5$), and 10.2 ppm (1H, broad s, NH). IR spectrum: 1597 ($C_6H_5$), 1667 (C=C), 1700 (N—C=O), 1750 (O—C=O), and 3220 $cm^{-1}$ (N—H). Mass spectrum: 262 (100, $M^+$), 231 (44), 202 (25), 174 (18), 135 (28), 111 (29), 83 (26), 77 (62), 69 (19), 51 (26), 44 (28), 41 (20). Found: C 54.9; H 3.6; N 11.0%. $C_{12}H_{10}N_2O_3S$. Calculated: C 55.0; H 3.8; N 10.7%. As in the case described above, the filtrate yielded 10.4 g (34%) of imidazolidine IIIb, which had a similar PMR spectrum and did not depress the melting point of an authentic sample.

Conversion of Methyl (1-Allyl-3-dimethylamino-5-oxo-2-thioxoimidazolidin-4-yl)acetate (IIIa) in Ethanol. A solution of 3.85 g (0.014 mole) of IIIa in 5 g of ethanol was refluxed for 1.5 h. Ester IVa was detected in the reaction mixture by chromatography ($R_f$ 0.54, did not absorb in UV light, developed in iodine vapors; $R_f$ for IIIa 0.34, dark-blue spot in UV light). Ethanol (5 g) was added, and the mixture was refluxed for another 3 h. Treatment with methanol, as indicated above, gave 0.13 g (3%) of hydantoin IVa.

Conversion of Methyl (1-Phenyl-3-dimethylamino-5-oxo-2-thioxoimidazolidin-4-yl)acetate (IIIb). A. A solution of 0.3 g (1 mmole) of chromatographically pure IIIb in a mixture of 3 g of dioxane and 3 g of ethanol was refluxed for 2 h. Ester IVb was detected by chromatography ($R_f$ 0.4, did not absorb in UV light, yellowish, developed in iodine vapors; $R_f$ for IIIb 0.67, dark-blue spot in UV light). Hydantoin IVb did not crystallize when the mixture was cooled. Crystals of ester IVb [the yield was 0.01 g (5%) in both cases] could be obtained in subsequent experiments by the addition to the reaction mixture of three drops of triethylamine or trichloroacetic acid with cooling. The reaction products obtained were identical to a genuine sample of IVb (monitoring by TLC).

B. A 0.3-g (1 mmole) sample of IIIb was refluxed in 5 ml of dioxane for 4 h (the formation of ester IVb could not be detected by TLC). Changes in the composition of the mixture were not observed when 5 ml of methanol was added and the mixture was heated additionally for 8 h. After the addition of 5 ml of water and heating for another 5 h, it was established by TLC that the solution contained ester IVb, which crystallized upon cooling. The mixture was treated with methanol to give 3.7 mg (1.4%) of light-yellow crystals of imidazolidine IVb.

C. A 0.3-g (1 mmole) sample of IIIb was similarly treated in the presence of 0.27 g (1 mmole) of the ester. Refluxing in 5 ml of dioxane for 8 h did not give imidazolidine IVb (monitored by TLC). Traces of IVb were detected by chromatography after refluxing for 8 h

TABLE 1. Coordinates of the Atoms of IVa

| Atom | *x* | *y* | *z* | Atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| S | 0,0692(1) | 0,1007(3) | 0,0883(1) | $C_{(12)}$ | 0,2378(7) | −0,2447(14) | 0,2304(2) |
| $O_{(8)}$ | 0,1882(4) | −0,5207(8) | −0,0708(2) | $C_{(13)}$ | 0,1239(8) | −0,4110(16) | 0,2141(3) |
| $O_{(9)}$ | 0,3452(4) | −0,8650(8) | −0,0677(1) | $H_{(3)}$ | 0,155(7) | −0,251(12) | 0,006(3) |
| $O_{(14)}$ | 0,4788(4) | −0,5728(8) | 0,1503(2) | $H_{(6)}$ | 0,416(6) | −0,776(10) | 0,034(2) |
| $N_{(1)}$ | 0,2993(4) | −0,2379(9) | 0,1345(2) | $H_{(10,1)}$ | 0,179(6) | −0,971(10) | −0,135(2) |
| $N_{(3)}$ | 0,1999(5) | −0,2815(9) | 0,0389(2) | $H_{(10,2)}$ | 0,324(9) | −1,040(17) | −0,147(4) |
| $C_{(2)}$ | 0,1898(5) | −0,1404(10) | 0,0866(2) | $H_{(10,3)}$ | 0,284(6) | −0,732(11) | −0,150(2) |
| $C_{(4)}$ | 0,3141(5) | −0,4716(10) | 0,0532(2) | $H_{(11,1)}$ | 0,318(4) | 0,061(10) | 0,188(2) |
| $C_{(5)}$ | 0,3789(5) | −0,4428(11) | 0,1181(2) | $H_{(11,2)}$ | 0,458(7) | −0,169(12) | 0,215(3) |
| $C_{(6)}$ | 0,3576(6) | −0,6459(12) | 0,0191(2) | $H_{(12)}$ | 0,284(7) | −0,192(12) | 0,271(3) |
| $C_{(7)}$ | 0,2888(6) | −0,6654(11) | −0,0436(2) | $H_{(13,1)}$ | 0,099(7) | −0,482(12) | 0,174(3) |
| $C_{(10)}$ | 0,2802(7) | −0,9098(18) | −0,1300(3) | $H_{(13,2)}$ | 0,070(5) | −0,479(11) | 0,243(2) |
| $C_{(11)}$ | 0,3327(6) | −0,1339(14) | 0,1940(2) | | | | |

in a mixture of 5 ml of dioxane and 5 ml of methanol. Imidazolidine IVb crystallized after refluxing reagents I and IIIb for 8 h in a mixture of 5 ml of dioxane, 5 ml of methanol, and 5 ml of water. The product was isolated by treatment with methanol. The yield was 0.014 g (5.2%).

X-Ray Diffraction Analysis of Methyl (1-Allyl-5-oxo-2-thioxoimidazolidin-4-ylidene) acetate (IVa). The light-yellow single crystals of IVa ($C_9H_{10}N_2O_3S$), which were grown from methanol, were characterized by the following crystallographic parameters: $a$ = 9.068(2), b = 5.062(2), c = 23.624(7) Å, β = 105.44(2)°, V = 1045.3(5) Å$^3$, M = 226.24, $d_{calc}$ = 1.44 g·cm$^{-3}$, Z = 4, space group $P2_1/c$. The cell parameters and the intensities of 1700 reflections were measured with a Syntex $P2_1$ automatic diffractometer (Cu Kα emission, graphite monochromator, θ/2θ scanning up to $2\theta_{max}$ 150°). To decode the structure we used 1215 independent reflections with $I \geq 2\sigma_I$. The calculations were made with a Nova-1200 minicomputer by means of programs of the XTL system. The structure was decoded by the direct method by means of the MULTAN program and was refined by the total-matrix method of least squares within the anisotropic approximation for the nonhydrogen atoms and within the isotropic approximation for the hydrogen atoms (the coordinates of which were localized from differential synthesis) with the use of the weight scheme $I/W = \sigma_F^2 + (0.01F_0)^2$ up to a final value R = 0.068.

The coordinates of the atoms thus obtained are presented in Table 1.

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# 1,2,4-TRIAZOL-3-ONE IN REACTION WITH ACETYLENE

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UDC 547.792'314.2.07:
543.422.25

Depending on the conditions, the reaction of 1,2,4-triazol-3-one with acetylene leads to the addition of one or two molecules of acetylene to give, in the latter case, a mixture of divinyl isomers, $N_{(2)}N_{(4)}$, $N_{(1)}O$, and $N_{(2)}O$.

1,2,4-Triazole-3-thione and its 5-methyl(phenyl)-substituted derivatives react with acetylene in the presence of an alkaline catalyst primarily at the more nucleophilic sulfur atom to form the corresponding triazolyl vinyl sulfides [1-4]. The use of cuprous chloride or cadmium acetate promotes the addition of a second molecule of acetylene to one of the nitrogen atoms to give a mixture of isomers with respect to the $N_{(1)}$ and $N_{(2)}$ atoms.

In the present research we studied the behavior of the oxygen analog of the thione — 1,2,4-triazol-3-one (I) — in the reaction with acetylene. Under the usual conditions for the synthesis of triazolyl vinyl sulfide (KOH, 180°C) the reaction of triazole I with acetylene proceeds with the formation of a very small amount of 4-vinyl-1,2,4-triazol-3-one (IIa). Increasing the reaction temperature to 240°C leads to a certain increase in the yield of IIa to 15%, but starting I remains unchanged. We were able to accomplish the complete conversion

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Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Irkutsk 664033. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1224-1226, September, 1987. Original article submitted May 19, 1986.

0009-3122/87/2309-0978$12.50