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THE REACTION OF TERMINAL α-ACETYLENIC KETONES WITH THIOSEMICARBAZONES

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The reaction of terminal α-acetylenic ketones with thiosemicarbazones gives a series of 5-amino- and 5-anilino-3-acylvinyl-Δ^4-1,3,4-thiadiazolines. These products react with perchloric acid to give the corresponding perchlorates.

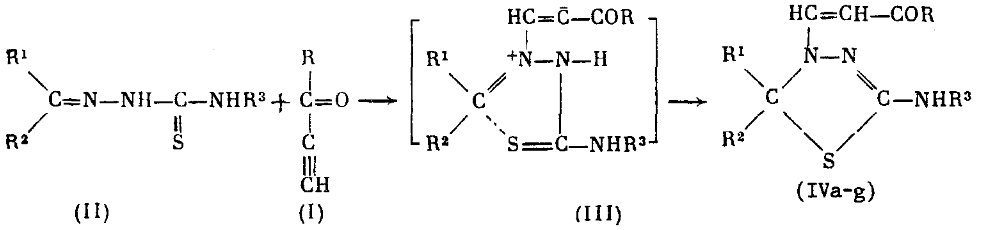
The prolonged heating of thiobenzhydrazide with excess ketone or aldehyde in benzene or methanol gave cyclic 1,3,4-thiadiazoline instead of linear hydrazones [1-4].

A study was carried out on the isomerization of the thiosemicarbazones of acetone, 2-butanone, 3-pentanone, etc., to give 1,3,4-thiadiazolines in acid media [5-7].

The prolonged reaction of 1,4-diphenylthiosemicarbazide with formaldehyde in dioxane at 20°C also gave isomeric cyclic structures, namely, 1,4-diphenyl-1,2,4-triazolidine-3-thione and 4-phenyl-2-phenylamino-1,3,4-thiadiazolidine in a 25:1 ratio [8].

We have found that the reaction of terminal α-acetylenic ketones (I) and thiosemicarbazones (II) with an equimolar reagent ratio at room temperature in the absence of catalyst gives 5-amino- and 5-anilino-3-acylvinyl-Δ^4-1,3,4-thiadiazolines (IVa)-(IVg) in a high yield (81-97%).

As a result the reaction of thiosemicarbazones (II) with acylacetylene (I) most likely proceeds by an addition of acetylene fragments to N^1 atoms of thiosemicarbazene (II) forming the intermediate (III). The last conditions easily lead to cyclization to the corresponding 1,3,4 thiadiazolines (IVa-g). An analogous mechanism for the formation of substituted 1,3,4-thiadiazolines has been proposed for the reaction of thiosemicarbazones with acylating reagents such as acetyl chloride and acetic anhydride [9-11].



R = Ph, R^1 = 2-thienyl $R^2 = R^3$ = H (a); R = R^1 = 2-thienyl $R^2 = R^3$ = H (b); R = $R^1 = R^3$ = Ph, R^2 = H (c); R = R^3 = Ph, $R^1 + R^2 = (CH_2)_5$ (d); R = 2-thienyl $R^1 + R^2 = (CH_2)_5$, R^3 = Ph (e); R = 2-thienyl $R^1 + R^2 = (CH_2)_5$, R^3 = H (f); R = Ph, $R^1 + R^2 = (CH_2)_5$, R^3 = H (g).

We may propose that the starting thiosemicarbazones (II) under the synthesis conditions initially cyclize to the corresponding 1,3,4-thiadiazolines and, then, the acylvinyl fragment adds to N^3 in the ring. However, cyclization

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TABLE 1. Indices of the Compounds Synthesized

Compound	Yield, %	mp, °C	Chemical formula	Found/Calculated, %				^{13}C NMR spectrum, δ, ppm					
				C	H	N	S	C^2	C^5	CO=CH=	N—CH=	C=O	R, R^1, R^2, R^3
(IVa)	94	130–131	$C_{15}H_{13}N_3OS_2$	57,48/57,14	4,15/4,13	13,05/13,33	19,91/20,32	68,4	154,1	143,2	93,1	185,8	126,6–142,8
(IVb)	93	138–139	$C_{13}H_{11}N_3OS_3$	48,35/48,60	3,69/3,43	13,07/13,08	29,73/29,91	68,9	155,1	142,8	92,7	178,7	127,3–147,6
(IVc)	97	162–164	$C_{23}H_{19}N_3OS$	71,80/71,69	4,95/4,94	11,02/10,91	7,95/8,31	71,1	149,1	144,1	93,7	186,1	122,1–140,0
(IVd)	81	178–179	$C_{22}H_{23}N_3OS$	70,38/70,03	5,98/6,10	11,24/11,14	8,24/8,49	86,6	149,1	140,3	94,1	186,3	118,2–140,3
(IVe)	81	177–179	$C_{20}H_{21}N_3OS_2$	62,74/62,66	5,40/5,48	10,90/10,97	16,58/16,71	86,7	149,1	139,6	94,1	178,9	118,1–147,6
(IVf)	88	167–169	$C_{14}H_{17}N_3OS_2$	54,42/54,72	5,68/5,54	13,48/13,68	20,74/20,85	87,6	154,4	139,4	92,7	178,3	128,1–147,0
(IVg)	83	147–148	$C_{16}H_{19}N_3OS$	63,55/63,79	6,22/6,31	13,65/13,95	10,45/10,63	87,5	154,2	140,0	93,1	185,2	126,9–140,7

products (1,3,4-thiadiazolines) are not found even upon the maintenance of the thiosemicarbazones of benzaldehyde and thiophene-2-aldehyde for 72 h in acetonitrile at 20°C in the absence of acylacetylenes (I).

Only the starting reagents were isolated upon carrying out the reaction of the thiosemicarbazones of benzaldehyde and thiophenaldehyde with substituted acetylenic ketones, namely, 1-benzoyl-2-phenyl- and 1-thionyl-2-phenylacetylenes, under the same conditions in acetonitrile or methanol at 20°C for 3 h or for a prolonged period. This finding supports the reaction mechanism proposed above. When substituted acetylenic ketones are used in the reaction, steric factors hinder the formation of intermediate zwitterions (III) and the products of their cyclization, namely, substituted 1,3,4-thiadiazolines (IV).

The IR spectra of 1,3,4-thiadiazolines (IVa)-(IVg) have bands for the C—S bond at 705-720 cm^{-1}, C—N bond at 1280-1320 cm^{-1}, C=C bond at 1580-1585 cm^{-1}, C=N bond in the ring at 1610-1620 cm^{-1}, conjugated C=O group at 1630-1650 cm^{-1}, NH_2 group in (IVa), (IVb), (IVf), and (IVg) at 3130-3150 and 3280-3310 cm^{-1}, and the NH group in (IVc)-(IVe) at 3220-3255 cm^{-1}.

The corresponding perchlorate was obtained in 52% yield upon treating 5-amino-3-benzoylvinyl-2-(thienyl-2)-Δ^4-1,3,4-thiadiazoline (IVa) with perchloric acid in glacial acetic acid.

EXPERIMENTAL

The IR spectra were taken on a UR-75 spectrometer in KBr pellets, while the ^{13}C NMR spectra were taken on a Tesla BS 567A spectrometer at 100 MHz in DMSO-d_6.

The indices for the compounds synthesized and the ^{13}C NMR spectral data are given in Table 1.

5-Amino-3-benzoylvinyl-2-(thienyl-2)-Δ^4-1,3,4-thiadiazoline (IVa). A sample of 0.47 g (25 mmoles) of the thiosemicarbazone of thiophene-2-aldehyde (II) was added to a solution of 0.33 g (25 mmoles) benzoylacetylene in 15 ml acetonitrile and stirred for 3 h at 20°C. The precipitate formed was filtered off, recrystallized from acetonitrile, and dried in vacuum to give 0.75 g (94%) (IVa) as yellow crystals with mp 130-131°C.

A yield of 0.54 g (68%) (IVa) was obtained under analogous conditions in benzene, while a yield of 0.42 g (53%) (IVa) was obtained when methanol was used as the reaction medium.

Products (IVb)-(IVg) were obtained by analogy (see Table 1).

5-Amino-3-benzoylvinyl-2-(thienyl-2)-Δ^4-1,3,4-thiadiazolinium Perchlorate. A sample of 0.43 ml 26% $HClO_4$ in 15 ml 95% acetic acid was slowly added with stirring to a solution of 0.47 g (1.5 mmole) (IVa) at 20°C and stirred for 1 h. The precipitate formed was filtered off, washed with cold acetic acid, and dried in vacuum to give 0.32 g (52%) perchlorate as white crystals with mp 211-212°C. IR spectrum (ν, cm^{-1}): 690 (C—S), 1100 (ClO_4^-), 1320 (C—N), 1585 (C=C), 1620 (ring C=N), 1670 (C=O), 3100-3420 (HN^+, NH_2). Found: Cl, 8.42; N, 9.90; S, 15.42%. Calculated for $C_{15}H_{14}ClN_3O_5S_2$: Cl, 8.67; N, 10.12; S, 15.42%.

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