as the mass standard. The 10 principal ions in the mass spectrum of II, m/z (relative intensity, %): 154 (61), 126 (66), 125 (8), 111 (84), 94 (9), 93 (11), 72 (7), 70 (100), 67 (10), 42 (22).

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REACTION OF METHYL PROPIOLATE WITH THIOSEMICARBAZONES

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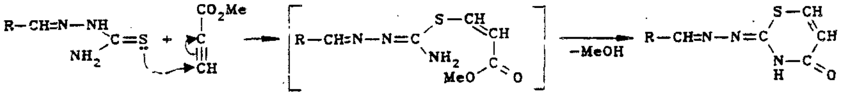
Methyl propiolate reacts with thiosemicarbazones in methanol in the presence of triethylamine to give 2-benzylidene(thenylidene, or furfurlidene)azino-3H-1,3-thiazin-4-ones.

Continuing a study of the reactions of nitrogen and sulfur-containing ambifunctional compounds with activated acetylenes [1], we have now examined the reactions of thiosemicarbazones with methyl propiolate.

1-Acetylthiosemicarbazide is known to react with methyl propiolate in methanol on warming to give a mixture of cis,cis- and cis,trans-dimethyl β-thiodiacrylic ethers [55% yield). Similar compounds have been obtained by reacting thiobenzamide and thioacetamide with methyl propiolate in methanol at 20°C, the yields being 77 and 70% respectively. However, the reaction of ethyl propiolate with thiobenzamide in the absence of a solvent on heating proceeds vigorously to give 2-phenyl-1,3-thiazin-4-one [4]. Arylthiohydrazides react with methyl propiolate on heating in methanol to give 60-65% of substituted 1,3,4-thiadiazoles [5, 6]. The reaction of propiolate esters with thiourea and its derivatives affords 1,3-thiazin-4-ones [7-9].

We have now examined the reaction of thiosemicarbazones (I) of various types with methyl propiolate (II) in equimolar amounts, in methanol at 60°C in the presence of catalytic amounts of triethylamine, to give 2-benzylidene (thenylidene, or furfurylidene)azino-3H-1,3-thiazin-4-ones (IVa-e).



Ia-e II IIIa-e IVa-e

III—IV a R=Ph; b R=p-Br—C_6H_4; c R=p-NO_2—C_6H_4; d R=α-C_4H_3S; e R=α-C_4H_3O

The reaction clearly involves the intermediate formation of the S-monoadducts, which cyclize readily to (IVa-e) with the removal of a molecule of alcohol. The intermediate

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TABLE 1. Properties of Compounds Obtained

Compound	mp, °C	PMR spectrum, ppm	Found, %				Empirical formula	Claculated, %				Yield, %
			C	H	N (Br)	S		C	H	N (Br)	S	
IIIa	94—96	—	54,5	5,0	15,8	12,2	$C_{12}H_{13}N_3O_2S$	54,8	4,9	16,0	12,2	23
IIIb	162—164		41,9	3,7	12,3 (23,6)	9,6	$C_{12}H_{13}BrN_3O_2S$	42,0	3,8	12,2 (23,3)	9,3	35
IVa	217—220	6,33 (1H, d. COCH=); 8,44 (1H, s N—CH=); 7,5—7,9 (7H, m, Ar, NH, S—CH=)	56,9	4,0	18,3	13,7	$C_{11}H_9N_3OS$	57,1	3,9	18,2	13,9	42
IVb	222—224	6,34 (1H, d, COCH=); 8,42 s (1H, s, N—CH=); 7,7—7,9 (6H, m, Ar, NH, S—CH=)	42,8	2,6 (25,6)	13,3	10,3	$C_{11}H_8BrN_3OS$	42,6	2,6	13,6 (25,8)	10,3	37
IVc	266—267	6,40 (1H, d, COCH=); 8,57 (1H, s, N—CH=); 7,7—8,6 (6H, m, Ar, NH, S—CH=)	48,0	2,9	19,9	11,5	$C_{11}H_8N_4O_3S$	47,8	2,9	20,2	11,6	26
IVd	222—223	6,22 (1H, d, COCH=); 8,58 (1H, s N—CH=); 7,2—7,8 (5H, m, thienyl S—CH=, NH)	45,9	3,1	17,4	27,1	$C_9H_7N_3OS_2$	45,6	3,0	17,7	27,0	37
IVe	196—198	6,33 (1H, d, COCH=); 8,25 (1H, s N—CH=); 7,75 (1H, d, S—CH=); 6,7—7,5 (4H, m, furyl, NH)	48,7	3,2	19,2	14,4	$C_9H_7N_3O_2S$	48,9	3,2	19,0	14,5	20

S-monoadducts (III) could be isolated by reacting benzaldehyde and p-bromobenzaldehyde thiosemicarbazones (Ia and Ib) with methylpropiolate in equimolar proportions. When the reactant ratio (I):(II) was 1:2, the sole products in all instances were the 1,3-thiazin-4-ones (IVa-e).

The IR spectra of (IIIa, b) showed absorption for the C—S bond at 690-708, for C=C and C=N at 1580-1595, for C=O at 1680-1720, and two bands for the primary amino group at 3250-3300 and 3420-3430 cm^{-1}. In the PMR spectra of (IIIa, b), singlets were present for the olefinic protons COCH= at 6.10 and 6.15 ppm, J = 8 Hz (for the cis isomer), singlets for the methine protons N=CH at 8.23 and 8.32 ppm, CH_3 groups (3.66 and 3.73 ppm), and multiplets for the benzene ring protons and the NH groups at 7.4-8.1 ppm.

The structures of the 1,3-thiazin-4-ones (IVa-e) were confirmed by their IR and PMR spectra (Table 1).

In the IR spectra of the 1,3-thiazin-4-ones (IVa-e), absorption was present for the bonds C—S (690-705), thiazine ring C=C (1580-1585), C=N (1620), C=O (1670), and ring NH (2820-2900 cm^{-1}).

EXPERIMENTAL

IR spectra were obtained on a UR-20 spectrometer in KBr disks, and PMR spectra on a Tesla BS-487C spectrometer (80 MHz) in CD_3OD or $CDCl_3$, internal standard HMDS.

The properties of the compounds obtained are given in Table 1.

2-Benzylideneazo-3H-1,3-thiazin-4-one (IVa). To a solution of 0.66 g (3.6 mmole) of benzaldehyde thiosemicarbazone (Ia) in 15 ml of methanol was added slowly, dropwise with stirring, a solution of 0.3 g (3.6 mmole) of methyl propiolate in 15 ml of methanol, followed by 0.2 ml of triethylamine, and the mixture was heated on a water bath to 60°C and stirred for 6 h. The solid which separated on cooling to 0°C was filtered off, recrystallized from ethanol, and dried in vacuo to give 0.36 g (42%) of bright yellow crystals, mp 217-220°C.

Compounds (IVb-e) were obtained similarly.

Benzaldehyde S-Methoxycarbonylvinylthiosemicarbazone (IIIa). To a solution of 0.89 g (5 mmole) of benzaldehyde thiosemicarbazone (Ia) in 20 ml of glacial acetic acid was added a solution of 0.42 g (5 mmole) of methyl propiolate in 10 ml of glacial acetic acid, and the mixture stirred at 20°C for two days. The solvent was partially removed, and the product isolated by precipitation with ether at 0°C, yield 0.3 g (23%).

p-Bromobenzaldehyde S-Methoxycarbonylvinylthiosemicarbazone (IIIb). Following the removal of the 1,3-thiazin-4-one (IV), as described for (IVa), the methanolic solution was partially evaporated under reduced pressure, cooled to 0°C, and the solid which separated filtered off and recrystallized from ethanol. Yield 0.6 g (35%).

When the molar ratio of thiosemicarbazone (Ia) to methyl propiolate (II) was 1:2, only (IVa) was isolated, in 28% yield.

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