N-(3,4-DIARYLTHIAZOLYL-2)-N'-BENZALHYDRAZINES

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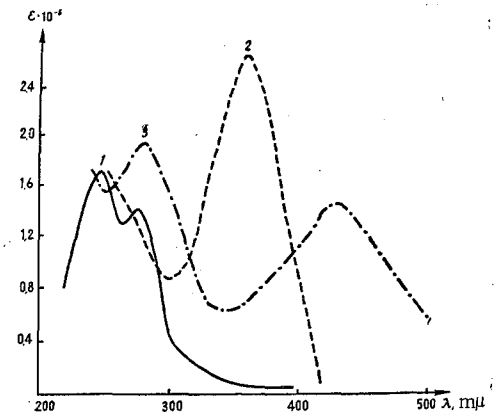
Reaction of 4-arylthiosemicarbazones of aromatic aldehydes with ω-bromoacetophenone gives N-(3, 4-diarylthiazoyl-2)-N'-benzalhydrazines.

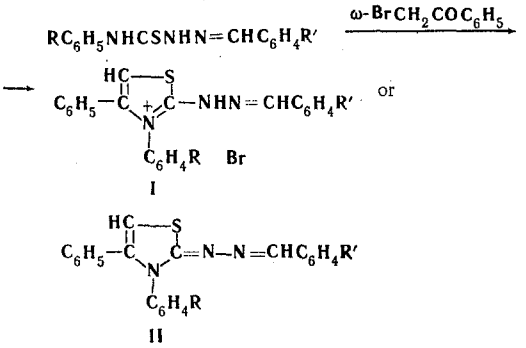
In a previous paper, we described the preparation of a number of substituted 4-phenylthiosemicarbazides from the corresponding phenylisothiocyanates and hydrazine hydrate in aqueous ethanol [1]. Substituted 4-phenylthiosemicarbazones of aromatic aldehydes are prepared by heating 4-arythiosemicarbazides with aromatic aldehydes in ethanol [2, 3]. It is known that a number of arylthiosemicarbazones exhibit antitubercular action [4, 5]. It was of interest to synthesize and investigate N-(3,4-diarylthiazolyl-2)-N'-benzalhydrazines.



Absorption curves in ethanol (c-$5 \cdot 10^{-5}$ M): 1) 4-p-bromophenylthiosemicarbazide; 2) p-nitrobenzaldehyde 4-p-bromophenylthiosemicarbazone; 3) n-[3-(p-bromophenyl)-4-phenylthiazolyl-2]-N'-(p-nitrobenzal) hydrazine.

These compounds resemble derivatives of hydrazides of acids, among which have recently been found compounds with valuable physiological properties [6–8].

Substituted N-3,4-diarylthiazolyl-2)-N'-benzalhydrazines were synthesized by boiling substituted 4-phenylthiosemicarbazones of aldehydes with ω-bromoacetophenone [9].



Some compounds are obtained as hydrobromides I, but in the main synthesis yields the free bases II. Column chromatography on alumina causes salts I to lose hydrogen bromide, and leads to isolation of the free bases II (table). They are bright orange to red crystalline compounds, slightly soluble in most organic solvents, and crystallizing from ethanol.

Comparison of absorption spectra of 4-(p-bromophenyl) thiosemicarbazide (1), p-nitrobenzaldehyde 4-(p-bromophenyl) thiosemicarbazone (2), and N-[3-(p-bromophenyl)-4-phenylthiazolyl-2]-N'-(p-nitrobenzal) hydrazine (3) shows that on passing from the substituted 4-phenylthiosemicarbazide (1) to the corresponding thiosemicarbazone (2) there

N-(3,4-Diarylthiazolyl-2)-N-benzalhydrazines (II)

R	R'	Mp, °C,	Formula	Element	Found, %	Calculated, %	Yield, %
p-CH_3O	p-$N(CH_3)_2$	176–177	$C_{25}H_{24}N_4OS$	N	13.24; 13.40	13.08	77
p-C_3H_7O		159–160	$C_{27}H_{28}N_4OS$	N	11.97; 11.95	12.28	86
o-Cl		188–190	$C_{24}H_{21}ClN_4S$	N	12.94; 13.04	12.95	54
m-Cl		222–223	$C_{24}H_{21}ClN_4S$	N	12.65; 12.87	12.95	85
o-CH_3	p-NO_2	212–213	$C_{23}H_{18}N_4O_2S$	N	13.34; 13.50	13.53	100
p-CH_3O		198–199	$C_{23}H_{18}N_4O_3S$	S	7.62; 7.70	7.44	35
p-C_2H_5O		205–206	$C_{24}H_{20}N_4O_3S$	N	12.38; 12.48	12.61	85
p-C_3H_7O		194–195	$C_{25}H_{22}N_4O_3S$	N	12.37; 12.44	12.22	79
p-NH_2SO_2		209–210	$C_{22}H_{17}N_5O_4S_2$	N	14.61; 14.68	14.61	100
p-$COOC_2H_5$		198–199	$C_{25}H_{20}N_4O_4S$	N	11.84; 11.81	11.86	100
o-Cl		199–200	$C_{22}H_{15}ClN_4O_2S$	N	13.16; 13.26	12.88	100
m-Cl		219–220		N	12.84; 12.90	12.88	100
p-Cl		175–176		S	7.54; 7.56	7.36	42
p-$COOC_2H_5$	o-OH	194–195	$C_{25}H_{21}N_3O_3S$	N	9.97; 9.88	9.48	86
p-Br	o-OH	191–192	$C_{22}H_{16}BrN_3OS$	N	9.16; 9.36	9.33	100

is an 88 mμ bathochromic shift, and that the hydrazine derivative (3) absorbs at 70 mμ lower than the 4-arylthiosemicarbazone derivative, from which it is obtained.

EXPERIMENTAL

N-3-(m-Chlorophenyl)-4-phenylthiazolyl-2-N'-(p-dimethylaminobenzal)hydrazine. 2 g p-dimethylaminobenzaldehyde m-chlorophenylthiosemicarbazone was dissolved in 50 ml EtOH, 1.2 g ω-bromoacetophenone added, and the mixture refluxed on a water-bath for 15–20 min. On cooling yellowish-orange crystals separated; they were filtered off, washed with EtOH, and dried. Yield 2.5 g (85%), mp 222–223° (ex EtOH). The compounds tabulated were prepared similarly.

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