THE DUAL REACTIVITY OF 3-AMINORHODANINE

L. I. Petlichnaya

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 3, No. 4, pp. 649–652, 1967

UDC 547.78:542.953.3

3-Aminorhodanine in ethanol reacts in the hydrazine form with aromatic aldehydes to give 3'-arylidene derivatives, while in ammonia it reacts in the tautomeric thiol form to give 5-arylidene derivatives. 3',5-Diarylidene derivatives of 3-aminorhodanine can be obtained by reacting aromatic aldehydes with 3'-aminorhodanine in glacial acetic acid, with 3-arylideneminorhodanines in ammonia solution, or with 5-aryliden-3-aminorhodanines in ethanol.

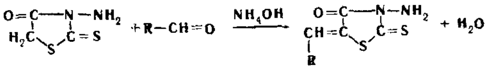
Though methods of synthesizing 3-aminorhodanine were described long ago [1, 2], up to the present it has not been adequately investigated chemically. The assigned structure 2-thio-1,3,4-thiadiazon-5-one, but not 2-thio-3-aminothiazolid-4-one [3], was rejected [4] because treatment of 3-aminorhodanine with HNO_2 gives rhodanine, while treatment with benzaldehyde gives a dibenzylidene derivative, because the molecule contains a free amino group. The IR and UV absorption spectra also confirm the thiazolidine structure of 3-aminorhodanine.

The problem of why 3-aminorhodanine is not basic has not been solved. Electrometric data showed [5] that 3-aminorhodanine is characterized by acidic properties ($pK_a = 9.2$), equal to those of boric acid, which can be explained by the presence of a free mercapto group. According to [6], unsubstituted rhodanine has two characteristic UV absorption maxima, at 251 nm (thioamide band) and 295 nm (dithiocarbonate band). At the same time unsubstituted 3-aminorhodanine has only one absorption maximum at 290–295 nm. Thus the thioamide band is absent for 3-aminorhodanine.

3-Aminorhodanine reacts with aromatic aldehydes in ammonia solution, to give monoarylidene derivatives, though it can give Schiff's bases (hydrazine derivatives) and 5-arylidene derivatives (rhodanine derivatives). To confirm that the Schiff's base formation reaction is unaffected by the nature of the solvent, some hydrazines, e. g. phenylhydrazine, p-nitrophenylhydrazine, benzoylhydrazide, and dioxalylhydrazide, were condensed with benzaldehyde, salicylaldehyde, and p-dimethylamino benzaldehyde in ammonia, and in all 12 cases the corresponding hydrazones were obtained in good yield. Hence hydrazines react with aldehydes in ammonia just as readily as in ethanol.

Because 3-aminorhodanine can be regarded as a hydrazine derivative, it should react with aldehydes in ethanol. Actually reaction of 3-aminorhodanine with aromatic aldehydes in ethanol gives 3'-arylidene derivatives (Table 1).

When the condensation of 3-aminorhodanine with aromatic aldehydes was effected by Girard's method [7], i. e. in ammonia, the expected products were 3',5-diarylidene derivatives, but only nonoarylidene derivatives were obtained (see Table 2), which were not 3-arylidenerhodanines. Thus in ammonia solution 3-aminorhodanine does not behave like a hydrazine derivative, and gives 5-arylidene derivatives:

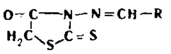


Hence the dual reactivity of 3-aminorhodanine is to be ascribed to its tautomerism:

The ammonia medium promotes displacement of the equilibrium to the right because the ammonium salt of the thio form is formed. The occurrence of a tautomeric thio form explains the acid properties of 3-aminorhodanine, and the lack of a thioamide absorption band.

If the condensation of 3-aminorhodanine is run with excess aldehyde in glacial acetic acid, 3',5-diarylidene derivatives are formed (Table 3):

Table 1



3-Arylidenaminorhodanines

R	Mp, °C	Formula	Found, %			Calculated, %			Yield, %
			C	H	N	C	H	N	
C_6H_5	136*	$C_{10}H_8N_2OS_2$	—	—	11.94	—	—	11.86	99.0
p-ClC_6H_4	142	$C_{10}H_7ClN_2OS_2$	44.64	3.02	10.46	44.34	2.61	10.26	68.7
p-BrC_6H_4	130	$C_{10}H_7BrN_2OS_2$	38.29	2.44	8.77	38.07	2.23	8.84	89.0
o-$HOOCC_6H_4$	192	$C_{11}H_8N_2O_3S_2$	47.04	3.16	10.42	47.13	2.88	9.99	25.2
p-$NO_2C_6H_4$	194	$C_{10}H_7N_3O_3S_2$	42.26	2.84	15.13	42.70	2.51	14.93	95.0
m-$NO_2C_6H_4$	168	$C_{10}H_7N_3O_3S_2$	42.06	2.98	14.89	42.70	2.51	14.93	86.0

*[8] gives mp 136°.

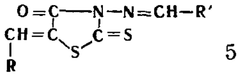


Table 2

5-Arylidene-5-aminorhodanines

R	Mp, °C	Formula	Found, %			Calculated, %			Yield, %
			C	H	N	C	H	N	
C_6H_5	196*	$C_{10}H_8N_2OS_2$	—	—	11.95	—	—	11.86	45.5
p-ClC_6H_4	204	$C_{10}H_7ClN_2OS_2$	44.09	2.48	10.26	44.34	2.61	10.26	74.3
p-BrC_6H_4	214	$C_{10}H_7BrN_2OS_2$	38.67	3.01	8.56	38.07	2.23	8.84	98.1
o-$HOOCC_6H_4$	200	$C_{11}H_8N_2O_3S_2$	47.59	3.22	9.91	47.13	2.80	9.99	77.0
p-$NO_2C_6H_4$	176**	$C_{10}H_7N_3O_3S_2$	—	—	15.09	—	—	14.93	41.0
m-$NO_2C_6H_4$	235	$C_{10}H_7N_3O_3S_2$	42.30	2.89	15.04	42.70	2.51	14.93	39.2

*[8] gives mp 196°.

**[8] gives mp 176°.

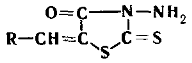


Table 3

3', 5-Diarylidene-3-aminorhodanines

Run No.	R, R′	Mp, °C	Formula	Element	Found, %	Calculated, %	Yield, %
1	$R=R'=C_6H_5$	171*	$C_{17}H_{12}N_2OS_2$	C H N	62.51 4.00 8.75	62.94 3.74 8.64	50.8
2	$R=R'=$p-ClC_6H_4	181	$C_{17}H_{10}Cl_2N_2OS_2$	C H N	52.36 2.56 7.10	51.91 2.56 7.13	75.2
3	$R=R'=$p-BrC_6H_4	201	$C_{17}H_{10}Br_2N_2OS_2$	C H N	42.57 2.80 6.05	42.33 2.09 5.81	62.4
4	$R=R'=$o-$HOOCC_6H_4$	238	$C_{19}H_{12}N_2O_3S_2$	C H N	55.23 3.15 6.46	55.35 2.93 6.80	46.3
5	$R=R'=$p-$NO_2C_6H_4$	175	$C_{17}H_{10}N_4O_5S_2$	C H N	49.50 2.89 13.01	49.27 3.06 13.52	61.1
6	$R=R'=$m-$NO_2C_6H_4$	265**	$C_{17}H_{10}N_4O_5S_2$	C H N	49.70 3.54 13.72	49.27 3.06 13.52	41.5
7	$R=R'=C_6H_5$	167	$C_{17}H_{12}N_2OS_2$	—	—	—	49.3
8	$R=R'=C_6H_5$	167	$C_{17}H_{12}N_2OS_2$	—	—	—	49.5
9	$R=C_6H_4OH$-o; $R'=C_6H_5$	150	$C_{17}H_{12}N_2O_2S_2$	N S	8.63 19.09	8.24 18.84	24.6
10	$R=C_6H_5$; $R'=C_6H_4OH$-o	120	$C_{17}H_{12}N_2O_2S_2$	C H N	60.10 3.93 8.22	59.98 3.55 8.24	50.5

*[8] gives mp 171°.

**[8] gives mp 268°.

To identify the monoarylidene derivatives obtained both in ethanol and in ammonia, some of the 3'-arylidene derivatives were further submitted to Girard condensation with aldehydes in ethanol, and some 5-arylidene derivatives reacted with aldehydes in ethanol or acetic acid, all to give diarylidene derivatives (Table 3).

Thus for compounds 7 and 10 the starting materials were the 3'-arylidene derivatives, and they were reacted further by the Girard method, while the compounds corresponding to 8 and 9 were obtained by refluxing 5-derivatives in ethanol or acetic acid. The correctness of our reasoning was proved by the compounds under nos. 7 and 8 being 3', 5-dibenzylidene derivatives.

EXPERIMENTAL

3-(Arylidenamino)rhodanines (Table 1). The appropriate aldehyde was added to a rapidly stirred solution of 1.48 g (0.01 mole) 3-aminorhodanine in 30 ml warm MeOH. A precipitate suddenly formed, the whole was stirred for 1 hr, and left overnight. The precipitate was filtered off and recrystallized from EtOH or AcOH.

5-Arylidene-3-aminorhodanines (Table 2). 2 ml conc NH_4OH, 1 g NH_4Cl in 2 ml water, and an equivalent quantity of aldehyde were added to a warm, stirred solution of 0.01 mole 3-aminorhodanine in 10 ml MeOH. After stirring for 1 hr the mixture was left overnight, the precipitate was filtered off, washed with EtOH, and recrystallized from AcOH.

3', 5-Diarylidene-3-aminorhodanines. 0.01 mole 3-aminorhodanine was boiled with 0.02 mole aldehyde in 30 ml glacial AcOH for 2 hr. After cooling, the precipitate was filtered off and washed with boiling MeOH or benzene (Table 3).

3', 5-Diarylaminorhodanines were also obtained from 3'-arylidene derivatives by condensing the latter further using the Girard method, or else from 5-derivatives, in the way described above.

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22 December 1965

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