Synthesis of Heterocycles. Part II. New Routes to Acetylthiadiazolines and Alkylazothiazoles (1)

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Methylglyoxalyl chloride arylhydrazones (III) react with an ethanolic solution of thiourea to give 2-amino-4-methyl-5-arylazothiazoles (XII) instead of the expected 2-acetyl-4-aryl-5-imino-Δ^2-1,3,4-thiadiazolines (V) which were obtained from III and potassium thiocyanate. 3-Thiocyanato-2,4-pentanedione (IV) coupled with diazotized anilines to give V. The postulated routes to formation of V and XII from III are given. Nitrosation of V gave the corresponding *N*-nitroso derivatives (VI) which decomposed upon refluxing in dry xylene to give 2,4-disubstituted-Δ^2-1,3,4-thiadiazolin-5-ones (VII). Boiling of either V or VI with hydrochloric acid gave the hydrochloride salt (VIII). The thiadiazolines V gave the respective *N*-acyl derivatives (IX) and (X) with acetic anhydride and benzoyl chloride in pyridine.

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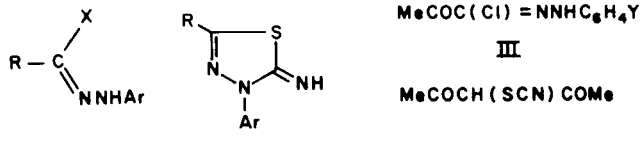
Reactions of the hydrazonyl halides of type (I) with either thiourea or potassium thiocyanate were shown (3,4) to give 2,4-disubstituted-5-imino-Δ^2-1,3,4-thiadiazolines (II). In this work, we have investigated the effect of the presence of a carbonyl group conjugated with the hydrazone group on the course of such reactions using methylglyoxalyl chloride arylhydrazone III. Also, we studied the



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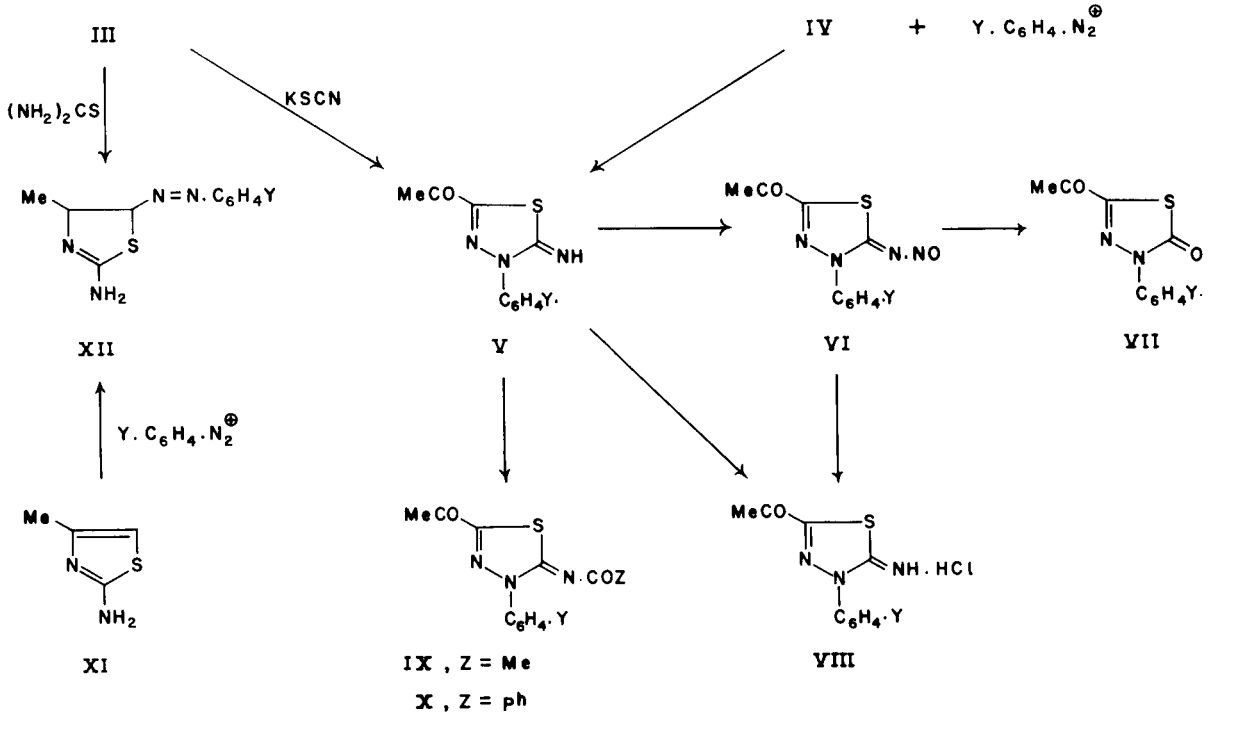

Y = a, H; b, p-Me; c, p-MeO; d, p-Cl; e, p-NO_2; f, m-CH_3; g, m-Cl; h, m-NO_2.

Scheme 1

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Table I

Methylglyoxalyl Chloride Arylhydrazones (III)
$MeCOC(Cl)=NNHC_6H_4Y$

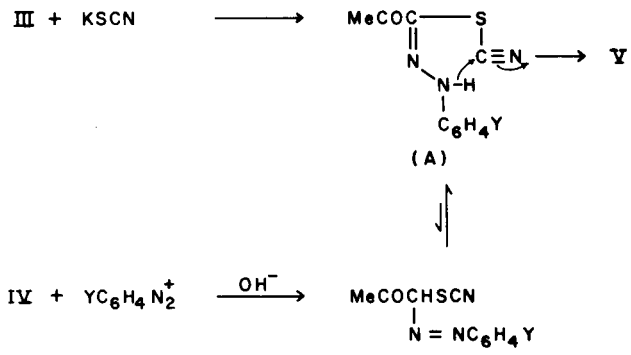
Compound	Y	M.p., °C	Molecular Formula	Calcd. % C	H	N	Cl	Found % C	H	N	Cl
IIIa	H	143 (a)	$C_9H_9ClN_2O$	54.96	4.58	14.25	18.07	55.03	4.52	14.24	18.03
IIIb	*p*-Me	152	$C_{10}H_{11}ClN_2O$	57.01	5.22	13.30	16.86	56.98	5.21	13.36	16.92
IIIc	*p*-MeO	120	$C_{10}H_{11}ClN_2O_2$	52.99	4.89	12.36		52.95	4.84	12.27	
IIId	*p*-Cl	180	$C_9H_8Cl_2N_2O$	46.78	3.49	12.12	30.70	46.74	3.43	12.19	30.72
IIIe	*p*-NO_2	236-238	$C_9H_8ClN_3O_3$	44.74	3.33	17.38		44.78	3.29	17.39	
IIIf	*m*-Me	149	$C_{10}H_{11}ClN_2O$	57.01	5.22	13.30	16.86	56.96	5.18	13.25	16.79
IIIg	*m*-Cl	190	$C_9H_8Cl_2N_2O$			12.12	30.70			12.08	30.67
IIIh	*m*-NO_2	208	$C_9H_8ClN_3O_3$			17.38				17.36	

(a) Lit. m.p. 139° (7).

azo coupling of 3-thiocyanato-2,4-pentanedine (IV) as an example of the use of the thiocyanato group to activate the carbon-hydrogen bond of aliphatic methylene compounds in their coupling reactions. The results of these studies are summarized in Scheme 1.

Results and Discussion.

In an ethanolic sodium acetate buffered solution, 3-thiocyanato-2,4-pentanedione IV couples with aryldiazonium salts to give 2-acetyl-4-aryl-5-imino-Δ^2-1,3,4-thiadiazolines V. The structures of compounds V were inferred from their analytical and spectral data (Table II), their chemical reactions, and independent synthesis. Thus, the ir spectra of V revealed the presence of an imino NH (3310 cm^{-1}), unsaturated acetyl C=O (1690 cm^{-1}), and a C=N (1610 cm^{-1}) bands. No bands were observed in the regions 2200-2100 and 740-720 cm^{-1} due to a free SCN group. The uv absorption pattern of V showed, in each case, three maxima in the 350-335, 255-240, and 230-215 nm regions (Table II). The nmr spectrum of V (Y = *p*-methoxy) for example, in deuterated chloroform showed a multiplet at δ 7.2-7.9 (5H, aromatic and imino NH), a singlet at δ 3.6-3.9 (3H, CH_3OAr) and a singlet at δ 2.2-2.6 (3H, CH_3CO) ppm. Upon shaking with deuterium oxide a new singlet appeared at δ 4.45 ppm assignable to DOH proton and the multiplet at δ 7.3-8.1 ppm corresponding to four protons only. Furthermore, the treatment of III (Table I) with excess potassium thiocyanate in ethanol at elevated temperature afforded products that proved to be identical in every respect with the corresponding V prepared earlier. The above results indicate that both the reaction of III with potassium thiocyanate and the azo coupling of IV proceed *via* one and the same intermediate. The latter is undoubtedly the hydrazone (A), which cyclizes readily to give V (Scheme 2).



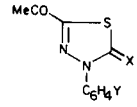
Scheme 2

Treatment of a solution of V in glacial acetic acid with aqueous sodium nitrite solution gave the red 2-acetyl-4-aryl-5-nitrosoimino-Δ^2-1,3,4-thiadiazolines VI. Ir spectra of VI showed no NH band but contained a common band at 1660 cm^{-1} (C=O). Their uv spectra in ethanol (Table II) showed two common maxima in the 490-460 (log $\epsilon < 2$) and 350-340 (log $\epsilon > 4$) nm regions. These are assigned to the n-π^* and π-π^* transitions of the nitrosoimino group (5). The finding that the former maximum shifts to shorter wavelength by changing solvents from non-polar to polar ones, whereas the latter absorption (350-340 nm) did not alter by change in the solvent polarity, supports the above-mentioned assignments. The nmr spectrum of VI (Y = *p*-methoxy) exhibits a singlet at δ 2.1-2.5 (3H, CH_3CO), a singlet at δ 3.6-3.9 (3H, CH_3OAr), and a multiplet at δ 7.2-8.0 (4H, aromatic) ppm.

Compounds VI decomposed to the corresponding 2-acetyl-4-aryl-Δ^2-1,3,4-thiadiazolin-5-ones VII when heated in dry xylene. The latter compounds showed no absorption in the visible region but, however, showed two maxima in the 320-310, and 250-230 nm regions (Table II). The ir spectra of VII revealed two common CO absorption bands around 1690 ($CH_3COC=$) and 1710 (5-keto group) cm^{-1}. The nmr spectrum of VII (Y = *p*-methoxy) showed a multiplet in the aromatic region δ 7.2-8.2 (4H, aromatic), a

Table II

Disubstituted Δ^2-1,3,4-Thiadiazolines (V-X)



Compound (f)	X	Y	M.p., °C	Molecular Formula	N, % Calcd.	N, % Found	S, % Calcd.	S, % Found	λ max (log ε) nm
Va	NH	H (a)	74-76	$C_{10}H_9N_3OS$ (b)	19.16	19.08	14.62	14.56	342 (3.78), 245 (4.04), 216 (4.05)
Vb	NH	*p*-Me (a)	88-89	$C_{11}H_{11}N_3OS$	18.01	17.91	13.74	13.67	344 (3.81), 245 (4.16), 220 (4.12)
Vc	NH	*p*-MeO (a)	145	$C_{11}H_{11}N_3O_2S$	16.86	16.79	12.86	12.85	344 (3.92), 246 (4.25), 222 (4.23)
Vd	NH	*p*-Cl (a)	127	$C_{10}H_8ClN_3OS$	16.58	16.55	12.63	12.58	340 (4.03), 248 (4.28), 228 (4.23)
Ve	NH	*p*-NO_2 (a)	194-195	$C_{10}H_8N_4O_3S$	19.99	19.87	11.44	11.37	346 (4.18), 247 (4.24), 230 (4.20)
Vf	NH	*m*-Me (a)	52-53	$C_{11}H_{11}N_3OS$	18.01	17.90	13.74	13.66	342 (4.03), 245 (4.19), 215 (4.19)
Vg	NH	*m*-Cl (a)	81	$C_{10}H_8ClN_3OS$	16.58	16.53	12.63	12.61	343 (4.03), 245 (4.20), 215 (4.23)
Vh	NH	*m*-NO_2 (a)	147	$C_{10}H_8N_4O_3S$	19.99	19.89	11.44	11.38	338 (3.98), 252 (4.29), 218 (4.20)
VIa	NNO	H	114 dec.	$C_{10}H_8N_4O_2S$ (c)	22.57	22.42	12.91	12.80	465 (1.72), 347 (4.23), 275 (4.22) (d)
VIb	NNO	*p*-Me	105 dec.	$C_{11}H_{10}N_4O_2S$	21.36	21.27	12.22	12.13	465 (1.74), 345 (4.01), 273 (3.96)
VIc	NNO	*p*-MeO	118 dec.	$C_{11}H_{10}N_4O_3S$	20.13	19.98	11.52	11.47	465 (1.82), 347 (4.35), 284 (4.33)
VId	NNO	*p*-Cl	88 dec.	$C_{10}H_7ClN_4O_2S$	19.82	19.73	11.34	11.21	465 (1.85), 347 (3.95), 278 (4.47)
VIe	NNO	*p*-NO_2	118 dec.	$C_{10}H_7N_5O_4S$	23.88	23.71	10.93	10.81	466 (1.81), 348 (4.27), 279 (4.39)
VIf	NNO	*m*-Me	112 dec.	$C_{11}H_{10}N_4O_2S$	21.36	21.25	12.22	12.11	465 (1.73), 347 (3.73), 276 (3.45)
VIg	NNO	*m*-Cl	92 dec.	$C_{10}H_7ClN_4O_2S$	19.82	19.76	11.34	11.22	465 (1.81), 347 (3.81), 275 (3.52)
VIh	NNO	*m*-NO_2	105 dec.	$C_{10}H_7N_5O_4S$	23.88	23.76	10.93	10.81	464 (1.82), 347 (3.82), 275 (4.09)
VIIa	O	H	57	$C_{10}H_8N_2O_2S$ (e)	12.71	12.62	14.56	14.44	304 (3.98), 240 (3.93) sh
VIIb	O	*p*-Me	84-86	$C_{11}H_{10}N_2O_2S$	11.96	11.84	13.68	13.54	310 (3.99), 242 (3.96) sh
VIIc	O	*p*-MeO	125	$C_{11}H_{10}N_2O_3S$	11.19	11.05	12.81	12.73	315 (3.91), 243 (4.06)
VIId	O	*p*-Cl	82	$C_{10}H_7ClN_2O_2S$	10.99	10.84	12.59	12.48	304 (4.05), 229 (4.12) sh
VIIe	O	*p*-NO_2	123-125	$C_{10}H_7N_3O_4S$	15.84	15.72	12.09	12.00	304 (4.23), 238 (4.61)
VIIf	O	*m*-Me	60-62	$C_{11}H_{10}N_2O_2S$	11.96	11.80	13.68	13.54	305 (3.98), 235 (3.85) sh
VIIg	O	*m*-Cl	84	$C_{10}H_7ClN_2O_2S$	10.99	10.83	12.59	12.44	304 (3.98), 236 (3.88) sh
VIIh	O	*m*-NO_2	135	$C_{10}H_7N_3O_4S$	15.84	15.70	12.09	12.01	304 (4.02), 240 (3.92)
VIIIa	NHHCl	H	217	$C_{10}H_{10}ClN_3OS$	16.43	16.33	12.54	12.49	
VIIIf	NHHCl	*m*-Me	209 dec.	$C_{11}H_{12}ClN_3OS$	15.56	15.48	11.88	11.80	
IXa	NCOMe	H	119	$C_{12}H_{11}N_3O_2S$	16.08	16.02	12.27	12.20	315 (4.07), 285 (4.23), 228 (3.96) sh
IXb	NCOMe	*p*-Me	132	$C_{13}H_{13}N_3O_2S$	15.32	15.25	11.60	11.58	317 (4.08), 285 (4.26), 228 (3.96) sh
IXc	NCOMe	*p*-MeO	115	$C_{13}H_{13}N_3O_3S$	14.47	14.36	11.04	10.98	317 (3.97), 283 (4.24), 227 (4.01) sh
IXd	NCOMe	*p*-Cl	148-149	$C_{12}H_{10}ClN_3O_2S$	14.21	14.12	10.84	10.77	308 (4.37), 275 (4.31), 229 (3.99) sh
IXe	NCOMe	*p*-NO_2	172	$C_{12}H_{10}N_4O_4S$	18.29	18.18	10.47	10.38	316 (4.42), 270 (4.27), 232 (4.25) sh
IXf	NCOMe	*m*-Me	127	$C_{13}H_{13}N_3O_2S$	15.32	15.23	11.69	11.58	314 (3.88), 283 (3.81), 228 (3.85) sh
IXg	NCOMe	*m*-Cl	131	$C_{12}H_{10}ClN_3O_2S$	14.21	14.13	10.84	10.79	315 (3.79), 285 (3.88), 225 (3.88) sh
IXh	NCOMe	*m*-NO_2	141	$C_{12}H_{10}N_4O_4S$	18.29	18.18	10.47	10.40	314 (3.96), 280 (3.91), 224 (3.78) sh
Xa	NCOPh	H	240-241	$C_{17}H_{13}N_3O_2S$	12.99	12.89	9.91	9.88	332 (4.40), 287 (4.29) sh, 238 (3.99)
Xb	NCOPh	*p*-Me	177	$C_{18}H_{15}N_3O_2S$	12.49	12.43	9.53	9.46	335 (4.31), 282 (4.26) br, 240 (4.06)
Xc	NCOPh	*p*-MeO	178	$C_{18}H_{15}N_3O_3S$	11.92	11.83	9.10	9.00	330 (4.17), 272 (4.25) sh, 235 (4.21)
Xd	NCOPh	*p*-Cl	188-189	$C_{17}H_{12}ClN_3O_2S$	11.74	11.65	8.96	8.79	330 (4.22), 282 (4.23), 234 (4.03)
Xe	NCOPh	*p*-NO_2	183	$C_{17}H_{12}N_4O_4S$	15.21	15.11	8.70	8.61	325 (4.39), 272 (4.31) br, 246 (4.27)
Xf	NCOPh	*m*-Me	201	$C_{18}H_{15}N_3O_2S$	12.49	12.37	9.53	9.49	330 (4.30), 285 (4.19) sh, 237 (4.11)
Xg	NCOPh	*m*-Cl	195	$C_{17}H_{12}ClN_3O_2S$	11.74	11.70	8.96	8.84	330 (4.05), 283 (4.11) sh, 238 (3.98)
Xh	NCOPh	*m*-NO_2	206	$C_{17}H_{12}N_4O_4S$	15.21	15.18	8.70	8.61	328 (3.98), 279 (4.20) br, 242 (3.87)

(a) Prepared according to procedures 1 and 2 (*cf.* Experimental). (b) *Anal.* Calcd.: C, 54.78, H, 4.14. Found: C, 54.73, H, 4.12. (c) *Anal.* Calcd.: C, 48.38, H, 3.25. Found: C, 48.34, H, 3.19. (d) VIa (chloroform): λ max (log ε) 485 (1.73), 355 (4.36), 278 (4.25) nm. VIa (acetic acid): λ max (log ε) 460 (1.77), 345 (4.09), 275 (2.98) nm. (e) *Anal.* Calcd.: C, 54.54, H, 3.66. Found: C, 54.50, H, 3.63. (f) Abbreviations: dec. = decomposition; sh = shoulder; br = broad.

Table III

2-Amino-4-methyl-5-arylazothiazoles(XII)

Compound	Y	M.p., °C	Lit. M.p., °C	Molecular Formula	N, % Calcd.	N, % Found	S, % Calcd.	S, % Found	λ max (log ε) nm
XIIa	H (a)	183 dec. (b)	184 (10)	$C_{10}H_{10}N_4S$	25.67	25.59	14.69	14.53	395 (4.47), 243 (4.32)
XIIb	*p*-Me (a)	187 dec.	189-190 (10)	$C_{11}H_{12}N_4S$	24.22	24.13	13.86	13.74	399 (4.39), 250 (4.29)
XIIc	*p*-MeO (a)	186 dec.	—	$C_{11}H_{12}N_4OS$	22.66	22.60	12.96	12.83	415 (4.46), 250 (4.35)
XIId	*p*-Cl (a)	168 dec.	167 (11)	$C_{10}H_9ClN_4S$	22.17	22.03	12.68	12.60	413 (4.19), 248 (4.33)
XIIe	*p*-NO_2 (a)	207 dec.	206 (10)	$C_{10}H_9N_5O_4S$	26.60	26.53	12.18	12.05	410 (4.38), 252 (4.31)

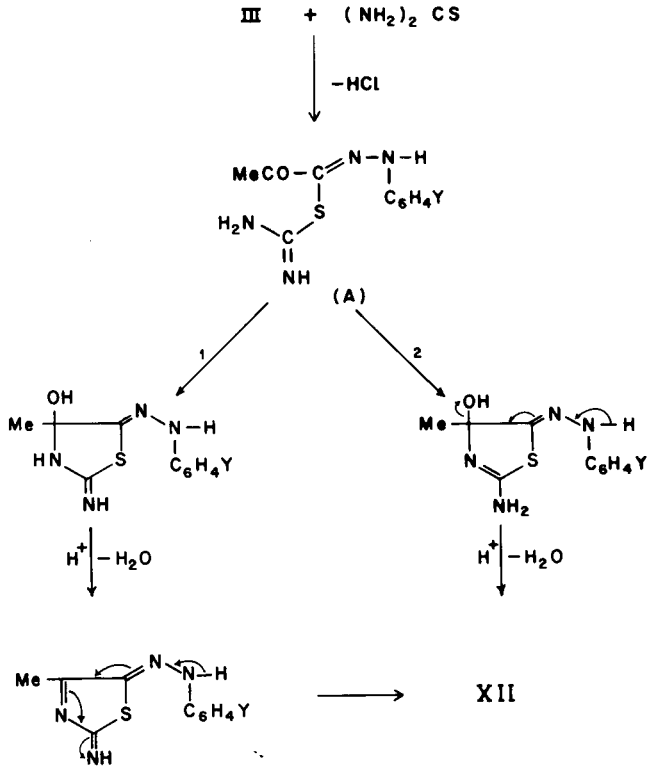
(a) Prepared according to procedures 1 and 2 (*cf.*, Experimental). (b) dec. = decomposition.

singlet at δ 3.7-3.9 (3H, CH_3OAr), and a singlet at δ 2.1-2.3 (3H, CH_3CO) ppm.

Boiling of either V or VI with hydrochloric acid gave the hydrochloride salt VIII (Table II). In addition, while acylation of compounds V (or VIII) with acetic anhydride yielded the corresponding 2-acetyl-4-aryl-5-*N*-acetylimino-Δ^2-1,3,4-thiadiazolines IX, their (V or VIII) benzoylation with benzoyl chloride in pyridine afforded the corresponding 2-acetyl-4-aryl-5-*N*-benzoylimino-Δ^2-1,3,4-thiadiazolines X. The elemental and spectral data of IX and X were in accordance with the structures assigned. Ir spectra of IX contained bands at 1690 ($CH_3COC=$) and 1630 ($CH_3CON=$) cm^{-1}. The nmr spectrum of IX (Y = *p*-methoxy) in deuteriochloroform revealed the presence of a multiplet at δ 7.2-8.0 (4H, aromatic), a singlet at δ 3.7-3.9 (3H, CH_3OAr), a singlet at δ 2.4-2.7 (3H, $CH_3COC=$), and a singlet at δ 2.1-2.3 (3H, CH_3CON) ppm. The uv data are shown in Table II.

On the other hand, treatment of III with excess thiourea in ethanol yielded 5-arylazo-4-methyl-2-aminothiazoles XII. The structures of XII were deduced from their analytical and spectral data (Table III). The nmr spectrum (in deuteriochloroform) of each of compounds XII showed an NH_2 singlet at δ 5.65 ppm, which disappeared upon addition of deuterium oxide and a new singlet appeared at δ 4.55 ppm. The electronic spectra of compounds XII were different from those of V as each of the former compounds showed two intense maxima (log ε > 4) in the 415-390 and 255-240 nm regions. Further confirmation of the structures of XII was achieved by comparison with authentic samples prepared from 2-amino-4-methylthiazole (XI) and the appropriate aryldiazonium salts.

The two possible pathways that account for the formation of XII from III and thiourea are shown in Scheme 3. The first step involves the formation of a carbon-sulfur bond by elimination of a molecule of hydrogen chloride to give (A). This is similar to the reported reaction of thioamides with α-halocarbonyl compounds (6). In the second step, ring closure occurs through direct attack by the amino (route 1) or the imino nitrogen atom (route 2) on the carbonyl carbon with the elimination of a molecule of water.



Scheme 3

These results show that, unlike hydrazonyl halides of type I, α-ketohydrazonyl chlorides give different products in their reactions with thiourea and potassium thiocyanate. Besides, the azo coupling of active methylene thiocyanates constitutes a useful route to the synthesis of substituted thiadiazolines.

EXPERIMENTAL

All melting points were determined on Electrothermal melting point apparatus, and are uncorrected. Elemental analyses were performed by Prof. Dipl.-Ing. Dr. H. Malissa and G. Reuter, West Germany. Spectra were recorded with a Pye-Unicam SP1000 Infrared spectrophotometer (potassium bromide wafer technique), and Pye-Unicam SP8000 Visible and ultraviolet spectrophotometer (in Ethanol). ^{1}H-Nmr spectra in

deuteriochloroform were recorded on a Varian-T60A spectrometer using TMS as an internal standard.

Methylglyoxalyl chloride arylhydrazones III (7), 3-thiocyanato-2,4-pentanedione IV (8), and 2-amino-4-methylthiazole XI (9) were prepared as previously reported.

2-Acetyl-4-aryl-5-imino-Δ^2-1,3,4-thiadiazolines (V).

Procedure 1.

The appropriate aryl diazonium salt (0.01 mole) was added to a stirred cold solution of IV (0.01 mole) and sodium acetate (1.2 g.) in ethanol (50 ml.), and then left in ice for 10 hours. The solid formed was collected, washed with water, and recrystallized from methanol to give compounds V in 84-88% yield (Table II).

Procedure 2.

A solution of potassium thiocyanate (0.01 mole) in water (10 ml.) was added, while stirring, to a suspension of the appropriate III (0.005 mole) in ethanol (50 ml.). The mixture was then stirred for 5 hours at room temperature, during which dissolution took place and a new solid was formed. The latter was collected, washed with water, and recrystallized from methanol. Compounds V were obtained in 85-90% yields and showed the same physical and spectral data as those of the products obtained by procedure 1 (Table II).

2-Acetyl-4-aryl-5-nitrosoimino-Δ^2-1,3,4-thiadiazolines (VI).

General Procedure.

A solution of V in acetic acid (25 ml.) was treated with an aqueous solution of sodium nitrite while stirring (1 hour). The bright reddish product which precipitated was filtered and recrystallized from the appropriate solvent to give VI in quantitative yields (Table II).

2-Acetyl-4-aryl-Δ^2-1,3,4-thiadiazolin-5-ones (VII).

General Procedure.

Compound VI (1 g.) was refluxed in xylene (50 ml.) for 1 hour and left overnight at room temperature. Removal of the solvent under reduced pressure gave a solid residue which was crystallized from methanol. The products VII (Table II) were obtained in almost quantitative yields.

Hydrochloride Salt Formation of V or VI. General.

Hydrogen chloride gas was bubbled into a solution of compound V or VI (0.5 g.) in ether (30 ml.) for 30 minutes.

The crude salt which precipitated was collected and recrystallized from ethanol-ether to give VIII (Table II) in 95% average yield.

Acylation of V. General Procedure.

Compound V (1 g.) was refluxed in acetic anhydride (25 ml.) for 20 minutes, cooled and poured onto ice. The crude product which precipitated was filtered and recrystallized from ethanol to give IX in quantitative yields (Table II). Benzoylation of V was affected by refluxing with an equimolecular amount of benzoyl chloride in pyridine for 30 minutes. The reaction mixture was then cooled, poured on ice, and the product recrystallized from acetic acid to give X in 76-90% yields (Table II).

2-Amino-4-methyl-5-arylazothiazoles (XII).

Procedure 1.

A mixture of the appropriate III (0.01 mole) and thiourea (0.02 mole) in ethanol (50 ml.) was refluxed for 5 hours, then poured on ice. The solid was collected, washed with water, and recrystallized from dilute ethanol. Compounds XII (Table III) were obtained in quantitative yields.

Procedure 2.

2-Amino-4-methylthiazole XI was treated with the appropriate diazonium salt solution, prepared from 0.011 mole of the aromatic amine and buffered with sodium acetate. The isolated products XII proved to be identical with those prepared by procedure 1.

REFERENCES AND NOTES

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