Tetrahedron Vol. 41, No. 22, pp. 5371 to 5376, 1985
Printed in Great Britain.

0040-4020/85 $3.00 + .00
Pergamon Press Ltd.

REACTION OF N-ACYLTHIOUREAS WITH ELECTROPHILIC REAGENTS

SYNTHESIS OF 1,3,5-OXADIAZINIUM SALTS, 1,3,5-THIADIAZINIUM SALTS, 1,2,4-DITHIAZOLIUM SALTS AND BENZOTHIAZOLES[1]

HORST HARTMANN,*† JÜRGEN LIEBSCHER‡ and PETER CZERNEY
Sektion Chemie, Technische Universität, Mommsenstrasse 13, 8027 Dresden, DDR

(*Received in Germany* 20 *January* 1984)

Abstract—N-Acylthioureas **1** can be easily transformed into 2,4-diamino-6-aryl-1,3,5-oxadiazinium salts **12**, 2,4-diamino-6-aryl-1,3,5-thiadiazinium salts **13**, 3-amino-5-aryl-1,2,4-dithiazolium salts **19** and 2-acyliminobenzothiazolines **22**, respectively by reaction with different electrophiles. The structure of the compounds prepared is confirmed by analytical data as well as by chemical transformations.

Owing to their availability and their high reactivity thioureas attract a wide interest in analytical[2] and synthetic chemistry, especially as starting materials in heterocyclic chemistry.[3] The same applies to several derivatives of thioureas. N-Acylthioureas **1**, for example, which can be easily prepared from acyl chlorides, alkalirhodanides and amines,[4] gain interest in coordination chemistry[5] and as versatile building blocks in synthetic organic chemistry.[6] Thus, the reaction of **1** with alkylating reagents gives rise to the formation of relatively stable N-acyl-S-alkylisothiouronium salts **2**[7] useful for many changes of the acylthiourea moiety into various kind of prodcuts.

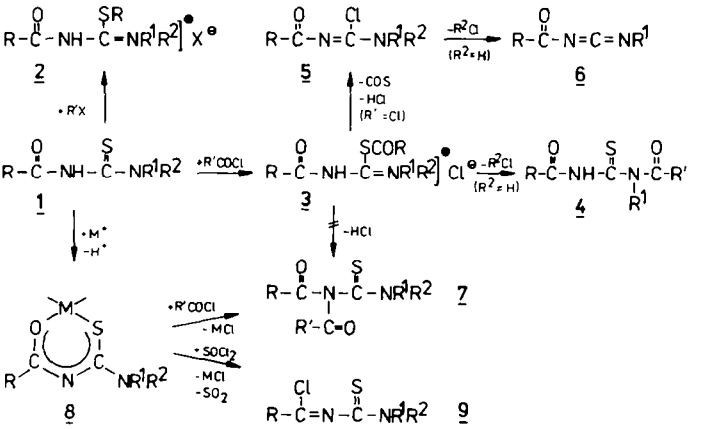
Similar to the alkylation reaction, the acylation of N-acylthioureas **1** takes place at the thiocarbonyl sulfur. The resulting S,N-diacylisothiouronium salts **3**, however, are not stable in most cases but undergo further transformation in the course of their preparation. Usually a rearrangement to N,N'-diacylthioureas **4**[8] occurs. With $COCl_2$, however, the S-chlorocarbonyl-N-acylisothiouronium salts **3** (R' = Cl) primarily formed eliminate COS instead of rearranging it. The resulting N-acylcarbamide chlorides **5** were further transformed into N-acylcarbodiimides **6** by base catalysed HCl-elimination.[9]

N,N-Diacyl isomers **7** of **4** which have been assumed in the early lit.[10] do not appear in acylation reactions of the N-acylthioureas **1**, but they have recently become available by treating metal complexes **8** of **1** with organic acyl chlorides.[11] On the other hand, these complexes **8** react with inorganic acid chlorides, e.g. $SOCl_2$, in quite a different manner giving rise to the hitherto unknown N-aminothiocarbonylimidochlorides **9**.[12]

We would like to report on our results from reactions of the free N-acylthioureas **1** with inorganic acid chlorides and with oxidising reagents. In contrast to the masked N-acylthioureas **8** the interaction of the free N-acylthioureas **1** with $SOCl_2$ results neither in the formation of N-acylcarbamidoylchlorides **5** nor in the formation of N-aminothiocarbonylimidoyl chlorides **9** but leads to the stable 2,4 - diamino - 6 - aryl - 1,3,5 - oxadiazinium salts **12**.[13,14] The same products **12** appear in the reaction of **1** with PCl_5. These syntheses of the oxadiazinium salts **12**, however, can only be achieved when N',N'-disubstituted N-acylthioureas **1** are used. Otherwise the reaction fails (see below). The

† Present address: Sektion Chemie, Technische Hochschule "Carl Schorlemmer", DDR-4200 Merseburg, DDR.

‡ Present address: Sektion Chemie, Humboldt-Universität, Hessesche Strasse 2, DDR-1040 Berlin, DDR.



Scheme 1.

best yields of **12** are obtained at a slightly elevated temperature in haloalkane solutions.

As can be seen from the structure of the 2,4 - diamino - 6 - aryl - 1,3,5 - oxadiazinium salts **12**, two molecules of the N-acylthiourea used as reactant are incorporated in the product whereas one amino group (NR^1R^2), one acyl moiety and two S-atoms (as H_2S) have been split off.

To our surprise no 1,3,5-oxadiazinium salts **12** but their sulfur analogous 2,4 - diamino - 6 - aryl - 1,3,5 - thiadiazinium salts **13** arise when the same N-acylthioureas **1** are allowed to react with $POCl_3$ under similar conditions.[14,15] These salts **13** are composed again by two molecules of the reactant **1** but only one S-atom is kept in the molecule.

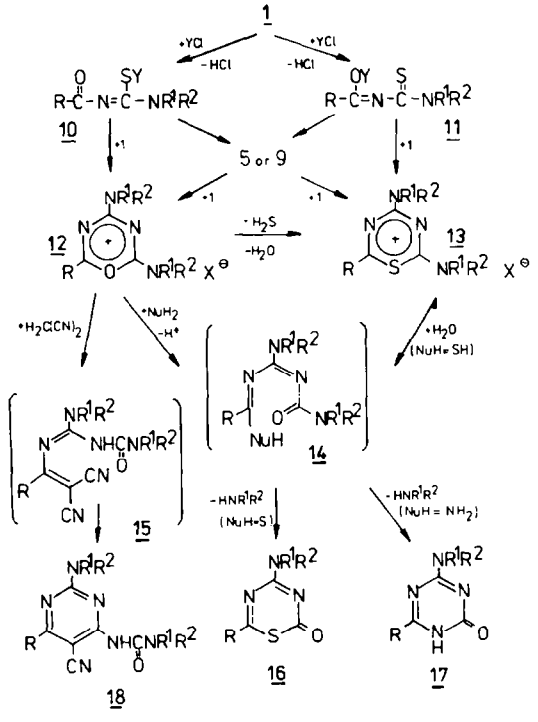
This difference in the behaviour of the N-acylthioureas **1** against similar inorganic acid chlorides can be understood by a primary attack of $SOCl_2$ or PCl_5 on the S-atom of **1** giving rise to the intermediates **10** while $POCl_3$ primarily interacts with the O-atom leading to compounds **11**. The intermediates **10** may be further transformed into N-acylcarbamoyl chlorides **5**. Finally, the 1,3,5-oxadiazinium salts **12** could be formed by the cyclocondensation of either **10** or **5** with the still unchanged N-acylthioureas **1** or with substituted cyanamides R^1R^2NCN evolved by the elimination of RCOCl from the intermediates **5**. Similarly the intermediates **11** may be transformed into N - aminothiocarbonylimidoyl chlorides **9**. The subsequent reaction of **11** or **9** with starting material **1** could produce **13** analogously.

It has to be mentioned that the N,N-dimethyl-N'(*p*-nitrobenzoyl)-thiourea **1** ($R = p\text{-}NO_2C_6H_4$; $R^1 = R^2 = CH_3$) whose corresponding N-acylimidoyl chloride **5** is known to be relatively stable[16] does not react with PCl_5 but remains unchanged under the conditons used for the synthesis of 2,4-diamino-1,3,5-oxadiazinium salts **12**. Both the 1,3,5-oxadiazinium salts **12** and the 1,3,5-thiadiazinium salts **13** form stable crystalline perchlorates ($X = ClO_4$). The structures of these compounds could be proved by elemental analysis (Table 4) and by spectroscopic data. As expected, the 1,3,5-thiadiazinium salts **13** absorb at longer wavelength in the UV region than the corresponding oxa-analogues **12**. The structure of the heterocyclic salts **12** and **13** is further confirmed by the comparison of the IR spectrum and the m.p. of **12a** with those obtained from an authentic sample[17] and by the transformation of the 1,3,5-oxadiazinium salts **12** into the corresponding 1,3,5-thiadiazinium salts **13** by means of H_2S in acetonitrile in the presence of triethylamine (method B in Table 1). If the reaction of 1,3,5-oxadiazinium salts **12** with H_2S is carried out in an acidic medium, however, no thiadiazinium salts **13** appear but 1,3,5 - thiadiazin - 2 - ones **16** are formed by the elimination of R^1R^2NH (Table 2).

The 1,3,5-oxadiazinium salts **12** can also react with other nucleophiles such as malodinitrile or ammonia by ring rearrangement. Similarly to the reaction of 2,4,6 - triphenyl - 1,3,5 - oxadiazinium perchlorate with acetonitrile derivatives[18] the 2,4-diamino-1,3,5-oxadiazinium salts **12** form 2 - amino - 4 - carbamido - 6-arylpyrimidines **18** by reaction with malonitrile. The interaction of NH_3 on the oxadiazinium salts **12** yields 2(1H)-triazinones **17** but not 2,4 - diamino - 6 - aryl - 1,3,5 - triazines, which were observed in similar reactions.[17] All these ring transformations can be understood by the primary attack of the nucleophile (NuH_2) on the aryl substituted ring C-atom (position 6) of **12** resulting in ring opened products **14** or **15**. Each of these intermediates **14** or **15** recycles either by further interaction of the nucleophilic substituent NuH (SH or NH_2) with the carbonyl C-atom followed by the elimination of H_2O or HNR^1R^2, respectively, or by the addition of the N-atom (position 3 of the starting material **13**) to one of the cyanosubstituents of **15** with subsequent rearrangements when malonitrile is used.

Furthermore, we studied the reactions of N-acylthioureas **1** with the electrophiles bromine as well as H_2O_2 in an acidic medium. In these cases no 6-membered heterocycles were obtained but substituted 3-amino-1,2,4-dithiazolium salts **19** (Table 3).[19] The mechanism of this reaction may be interpreted via an intermediate disulfide **20** that cyclises by the subsequent elimination of a corresponding N-acylurea moiety and HNR^1R^2. The structure of the 1,2,4-dithiazolium salts **19** is confirmed by the results of the elemental analysis and the spectral data obtained. Furthermore, compound **19a** shows identical properties (IR spectrum and m.p.) of an authentic sample prepared by the known reaction of 3 - methylmercapto - 5 - phenyl - 1,2,4 - dithiazolium perchlorate[20] with dimethyl amine. For a further characterisation of **19** it is worth mentioning the formation of the *p*-nitrophenylhydrazon derivatives **21** which occur if the salts of **19** are allowed to react with *p*-nitrophenylhydrazine in acetonitrile as is shown for **19d**. The starting N-acylthioureas **1** occur again when the 1,2,4-dithiazolium salts **19** are hydrolysed in alkaline solution.

Additional investigations of the behaviour of the N-acylthioureas **1** have shown that the course of the reactions with inorganic acid chlorides as well as with



Scheme 2.

Table 1. 2,4-Diamino-1,3,5-oxadiazinium perchlorates **12** (X = ClO_4) and 2,4-diamino-1,3,5-thiadiazinium perchlorates **13** (X = ClO_4)

	R	R^1	R^2	% Yield/method	M.p.	UV (acetonitrile) λ_{max} (nm) (log ε)
12a	C_6H_5	CH_3	CH_3	36/A 75/B	283[a] (acetic acid)	239(4.46) 284(4.29)
12b	C_6H_5	$(CH_2)_5$		39/A 71/B	207 (acetic acid)	244(4.53) 286(4.28)
12c	C_6H_5	$(CH_2)_2O(CH_2)_2$		38/A 90/B	295 (acetic acid)	248(4.53) 289(4.26)
12d	p-$CH_3C_6H_4$	$(CH_2)_4$		94/B	259–260 (acetic acid)	222s(4.16) 226(4.16) 246(4.29) 299(4.43)
12e	p-$CH_3C_6H_4$	$(CH_2)_5$		80/B	232–233 (acetic acid)	221s(4.22) 226(4.25) 243(4.46) 296(4.43) 381s(2.36)
12f	p-$CH_3C_6H_5$	$(CH_2)_2O(CH_2)_2$		31/B	264–266 (acetic acid)	222s(4.16) 226(4.16) 246(4.39) 299(4.43)
12g	p-ClC_6H_4	$(CH_2)_5$		68/B	215–217 (acetic acid)	227s(4.16) 242(4.26) 310(4.20) 364s(3.47)
13a	C_6H_5	CH_3	CH_3	50/A	363 (acetonitrile)	225(4.22) 301(4.36) 358(3.96)
13b	C_6H_5	$(CH_2)_5$		53/A	204 (acetonitrile)	230(4.18) 273(4.38) 360(3.75)
13c	C_6H_5	$(CH_2)_2O(CH_2)_2$		60/A	284 (acetonitrile)	239(4.15) 293(4.33) 360(3.77)
13d	p-$CH_3C_6H_4$	$(CH_2)_4$		98/A	224–226 (acetic acid)	227(4.22) 323(4.37) 396s(3.82)

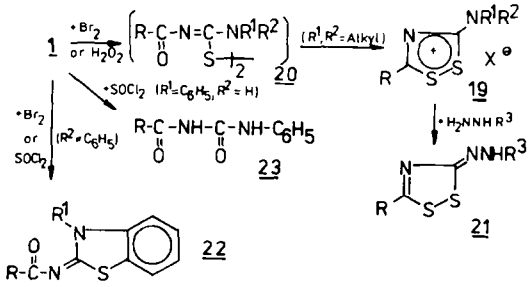
[a] Ref. 13 m.p. 280°.

Table 2. 4-Morpholino-1,3,5-thiadiazin-2-one **16**, 2(1H)-4-amino-1,3,5-triazinones **17** and 2-amino-4-carbamido-5-cyano-6-aryl-pyrimidines **18**

	R	R^1	R^2	% Yield	M.p.	UV (acetonitrile) λ_{max} (nm) (log ε)	IR (KBr) (cm^{-1}) C=O	CN
16	C_6H_5	$(CH_2)_2O(CH_2)_2$		97	169[a] (acetonitrile)	252(4.21) 289(4.03) 318(4.16)	1675	—
17a	C_6H_5	CH_3	CH_3	88	282[b] (DMF/water)	223(4.46) 237(4.34) 267(4.00)	1675	—
17b	C_6H_5	$(CH_2)_5$		90	291 (DMF/water)	228(4.48) 239(4.42) 273(4.01)	1680	—
17c	C_6H_5	$(CH_2)_2O(CH_2)_2$		90	308 (DMF/water)	226(4.45) 240(4.37) 273(4.02)	1670	—
18a	C_6H_5	CH_3	CH_3	83	185 (acetonitrile)	244(4.54) 278(4.44) 327(3.74)	1695	2220
18b	C_6H_5	$(CH_2)_5$		75	158 (acetonitrile)	245(4.56) 280(4.45) 331(3.78)	1690	2210
18c	C_6H_5	$(CH_2)_2O(CH_2)_2$		65	227	224(4.53) 277(4.41) 327(3.62)	1705	2205

[a] Corresponding hydroperchlorate m.p. 300° (acetonitrile), UV (acetonitrile) λ_{max} in nm (log ε): 237(4.09), 249(4.01), 294(4.19); IR (in KBr) C=O: 1730 cm^{-1}.

[b] Ref. 13 m.p. 280–281°.



Scheme 3.

Table 3. 3-Amino-1,2,4-dithiazolium perchlorates **19** (X = ClO_4), 2-acyliminobenzothiazolines **22** and N-acylureas **23**

	R	R^1	R^2	% Yield	M.p.	UV (CH_2Cl_2) λ_{max} (nm) (log ε)
19a	C_6H_5	CH_3	CH_3	43	192–193[a] (acetic acid)	320(4.35) 365s(3.67)
19b	C_6H_5	C_2H_5	C_2H_5		147–148 (acetic acid)	312(4.40) 360s(3.79)
19c	C_6H_5	$(CH_2)_4$		40	196–197 (acetic acid)	319(4.37) 360s(3.75)
19d	C_6H_5	$(CH_2)_2O(CH_2)_2$		72	210–211 (nitromethane/ether)	325(4.38) 368s(3.77)
19e	p-$CH_3OC_6H_4$	$(CH_2)_2O(CH_2)_2$		71	243–245 (acetic acid)	368(4.53) 380(4.54)
22a	C_6H_5	CH_3	—	91/A 88/B	154[b] (ethanol)	
22b	p-$NO_2C_6H_4$	CH_3	—	93/A 95/B	302 (ethanol)	
23a	C_6H_5	C_6H_5	H	68	207[c]	
23b	p-ClC_6H_4	C_6H_5	H	75	243	

[a] Ref. 20 m.p. 189–190°.
[b] Ref. 21 m.p. 155°.
[c] Ref. 22 m.p. 210°.

oxidising reagents does not only depend on the kind of the electrophile but also on the substituents in the substrate molecules **1**. Heterocyclic salts **12**, **13** and **19** are only obtained when both the substituents R^1 and R^2 in the N-acylthioureas **1** are alkyl groups or join together to form a saturated ring. On the other hand, if one of these substituents is phenyl, the interaction of the corresponding N-acylthiourea **1** (R^1 = phenyl, R^2 = alkyl) with thionyl chloride gives rise to the formation of 2 - acyliminobenzothiazolines **22** (Table 3, method A). This oxidation can also be accomplished by bromine in dichloromethane (method B).

In contrast to this, the reaction of N-monophenyl substituted acylthiourea **1** (R^1 = phenyl, R^2 = H) with $SOCl_2$ results neither in heterocyclic salts **12**, **13** or **19** nor in benzothiazolines **22** but leads to corresponding N-acylureas **23**. In accordance with the above mentioned results obtained with $COCl_2$[9] we assume that after the attack of the thionyl chloride at the thiocarbonyl sulfur atom of **1** N-acylcarbodiimides **6** are formed which hydrolyse with water added to the reaction mixture.

EXPERIMENTAL

2,4-Diamino-1,3,5-oxadiazinium perchlorates **12** (Table 1)—*General procedure*

Method A. 0.05 mol **1** were slowly added to a stirred suspension of 14.6 g (0.07 mol) PCl_5 in 50 ml 1,2-dichloroethane. The mixture was allowed to stand at room temp for 1 day and was then combined with 4 g 70% $HClO_4$. After diluting the resultant soln with diethyl ether, the product precipitates, it was then filtered by suction and recrystallised.

Method B. 0.05 mol **1** were slowly added to a stirred soln of 8.3 g (0.07 mol) $SOCl_2$ in 50 ml 1,2-dichloroethane. The mixture was then refluxed for 15 min while a turbidity of S was formed. After the mixture had cooled down to room temp 4 g 70% $HClO_4$ was added. Dilution of the resultant soln with diethyl ether afforded a ppt of the product. This was then filtered by suction and recrystallised.

2,4-Diamino-1,3,5-thiadiazinium perchlorates **13** (Table 1)—*General procedure*

Method A. 0.05 mol **1** were added to a stirred soln of 30.7 g (0.2 mol) $POCl_3$ in 50 ml 1,2-dichloroethane. The mixture was refluxed for 15 min. After it had cooled down to room temp the resulting soln was combined with 4 ml 70% $HClO_4$. Dilution with diethyl ether gave rise to the separation of the product which usually appeared oily at the beginning. When it was crystallised it was filtered by suction and recrystallised.

Method B. 0.01 mol **10** (X = ClO_4) was added to a stirred soln of H_2S in 40 ml acetonitrile which had been saturated at 0°. After the dropwise addition of 1.01 g (0.01 mol) Et_3N the resultant mixture was allowed to stand at room temp for 15 min. Later on when the soln was acidified by means of AcOH the product precipitated. After 1 hr it was filtered by suction and recrystallised.

4-Morpholino-6-phenyl-1,3,5-thiadiazin-2-one **16** (Table 2)

4.3 g (0.01 mol) **12e** were added to a stirred soln of H_2S in 40 ml acetonitrile which had been saturated at 0°. After the dropwise addition of 1.01 g (0.01 mol) Et_3N the resultant mixture was allowed to stand at room temp for 15 min. Then it was cooled to 0° and combined with 1.2 ml 70% $HClO_4$. The product precipitated as the corresponding hydroperchlorate. It was filtered by suction. The free base can be generated from the hydroperchlorate by further treatment with water.

2(1H)-3-Amino-1,3,5-triazinones **17** (Table 2)—*General procedure*

A mixture of 0.01 mol **12** with 10 ml conc NH_4OH was gently heated until an oil was formed. The oil was separated and then combined with some EtOH resulting in the crystalline product. This was filtered by suction and recrystallised.

2(1H)-6-Amino-1-carbamido-3-cyanopyrimidines **18** (Table 2)—*General procedure*

To the mixture of 0.01 mol **12**, 0.7 g (0.01 mol) malonic dinitrile and 40 ml acetonitrile 2 g (0.02 mol) Et_3N were added dropwise. After 15 min reflux the product precipitated when the resultant soln had cooled down to room temp. The product was filtered by suction and recrystallised.

Table 4. Elemental analytical data of the compounds prepared

		Calc/found				
		C	H	Cl	N	S
12a	$C_{13}H_{17}ClN_4O_5$	45.29	4.97	10.28	16.25	—
	(344.7)	44.83	4.93	10.42	15.31	—
12b	$C_{19}H_{25}ClN_4O_5$	53.71	5.93	8.34	13.18	—
	(424.9)	53.01	5.86	9.88	13.49	—
12c	$C_{17}H_{21}ClN_4O_7$	47.61	4.94	8.27	13.07	—
	(428.81)	47.64	4.90	8.59	13.08	—
12d	$C_{18}H_{23}ClN_4O_5$	52.62	5.64	8.63	13.64	—
	(410.9)	52.24	5.73	8.79	13.08	—
12e	$C_{20}H_{27}ClN_4O_5$	54.73	6.20	8.08	12.77	—
	(438.9)	54.94	6.18	8.06	11.30	—
12f	$C_{18}H_{23}ClN_4O_7$	48.82	5.24	8.01	12.65	—
	(442.9)	48.84	5.16	8.63	12.43	—
12g	$C_{19}H_{24}Cl_2N_4O_5$	49.68	5.23	15.47	12.20	—
	(459.3)	47.13	4.93	14.85	10.57	—
13a	$C_{13}H_{17}ClN_4O_4S$	43.27	4.74	9.82	15.52	8.88
	(360.8)	42.94	4.62	9.81	15.26	8.50
13b	$C_{19}H_{25}ClN_4O_4S$	51.75	5.71	8.04	12.70	7.27
	(440.9)	51.79	5.70	8.41	12.32	6.77
13c	$C_{17}H_{21}ClN_4O_6S$	45.89	4.75	7.96	12.59	7.20
	(444.9)	45.50	4.72	8.22	12.28	7.42
13d	$C_{18}H_{23}ClN_4O_4S$	50.64	5.43	8.30	13.12	7.51
	(426.9)	50.30	5.39	8.53	13.35	8.34
16	$C_{13}H_{13}N_3O_2S$	56.71	4.76	—	15.26	11.64
	(275.3)	57.00	4.81	—	15.29	11.95
17a	$C_{11}H_{22}N_4O$	61.09	5.59	–	25.91	—
	(216.2)	61.17	5.59	—	25.91	—
17b	$C_{14}H_{16}N_4O$	65.60	6.29	—	21.86	—
	(256.3)	65.57	6.31	—	21.87	—
17c	$C_{13}H_{14}N_4O_2$	60.45	5.46	—	21.69	—
	(258.3)	60.74	5.41	—	21.69	—
18a	$C_{16}H_{18}N_6O$	61.91	5.84	—	27.08	—
	(310.3)	62.00	5.90	—	27.13	—
18b	$C_{22}H_{26}N_6O$	67.66	6.71	—	21.52	—
	(390.5)	67.76	6.69	—	21.59	—
18c	$C_{20}H_{22}N_6O_3$	60.90	5.62	—	21.30	—
	(394.4)	60.90	5.63	—	21.29	—
19a	$C_{10}H_{11}ClN_2O_4S_2$	37.21	3.44		8.68	
	(322.5)	37.91	3.41		9.12	
19b	$C_{12}H_{15}ClN_2O_4S_2$	41.08	4.31	10.11	7.99	18.28
	(359.5)	41.04	4.31	10.45	7.82	17.78
19c	$C_{12}H_{13}ClN_2O_2S_2$	41.32	3.76	10.16	8.03	18.38
	(348.8)	41.16	3.72	10.13	8.04	17.87
19d	$C_{12}H_{13}N_2O_5S_2$	39.50	3.59	9.72	7.68	17.58
	(364.8)	39.60	7.72	9.50	7.66	16.81
19e	$C_{13}H_{15}ClN_2O_6S_2$	38.66	3.74	8.78	6.94	
	(403.9)	39.28	3.89	8.99	7.09	
22a	$C_{15}H_{12}N_2OS$	67.14	4.50	–	10.44	11.94
	(268.3)	66.25	4.35	—	10.29	12.43
22b	$C_{15}H_{11}N_3O_3S$	57.49	3.53	- -	13.41	10.23
	(313.3)	57.52	3.47	- -	13.39	10.10
23a	$C_{14}H_{12}N_2O_2$	69.98	5.03	—	11.66	—
	(240.2)	69.59	5.06	—	11.56	—
23b	$C_{14}H_{11}ClN_2O_2$	61.21	4.03	12.90	10.19	–
	(274.7)	61.48	3.86	13.87	10.19	—

3-Amino-1,2-dithiazolium perchlorates **19** (Table 3)—*General procedure*

0.02 mol of **1** were suspended in a mixture of 10 ml formic acid or AcOH and 4 ml 70% $HClO_4$. While the mixture was stirred 1 ml 30% H_2O_2 was added, and an exothermic reaction took place. The resultant mixture was then heated to b.p. When it had cooled down to room temp it was diluted with ether. The ppt was filtered by suction and recrystallized.

5 - Phenyl - 1,2,4 - dithiazolin - 3 - (p - nitrophenylhydrazones) **21**

The mixture of 3.6 g (0.01) of **19d**, 1.5 g (0.01 mol) *p*-nitrophenylhydrazine and 20 ml acetonitrile was heated to b.p. When the mixture had cooled down to room temp the product precipitated. It was filtered by suction and recrystallised from acetonitrile, yield: 2.48 g (71%), m.p. 281–283°.

2-Acyliminobenzothiazolines **22** (Table 3)—*General procedure*

Method A. 0.05 mol of **1** ($R^1 = CH_3$, $R^2 = C_6H_5$) were added to a soln of 8.3 g (0.07 mol) $SOCl_2$ in 50 ml 1,2-dichloroethane at 0°. After the addition was completed the mixture was refluxed for 10 min. When the mixture cooled down the product precipitated. It was filtered by suction and recrystallised.

Method B. The soln of 8 g (0.05 mol) Br_2 in 20 ml CH_2Cl was added dropwise to a soln of 0.05 mol of **1** ($R^1 = CH_3$, R^2

= C_6H_5). A yellow ppt was formed. The methylene chloride was distilled from the mixture and the remaining product recrystallised.

N-*Acylureas* **23** (Table 3)

0.05 mol of **1** ($R^1 = C_6H_5$, $R^2 = H$) were slowly added to a soln of 8.3 g (0.07 mol) $SOCl_2$ in 50 ml 1,2-dichloroethane. The mixture was refluxed for 10 min. A turbidness consisting of elemental S appeared. The mixture was filtered while still hot. After addition of water (2 ml) the product crystallized from the cold filtrate. It was filtered by suction and recrystallised.

REFERENCES AND NOTES

[1] Presented in part to the Symposium *Chemiedozententagung der DDR*, Berlin (1976).
[2] J. H. Yoe and L. G. Overholser, *Ind. Eng. Chem. Analyt.* **14**, 435 (1942).
[3] T. S. Griffin, T. S. Woods and D. L. Klayman, *Advances in Heterocyclic Chemistry* (Edited by A. R. Katritzky and A. J. Boulton), Vol. 18, p. 99. Academic Press, New York (1975).
[4] R. Esmail and F. Kurzer, *Synthesis* 301 (1975).
[5] L. Beyer, E. Hoyer, H. Hartmann and J. Liebscher, *Z. Chem.* **21**, 81 (1981).
[6] I. B. Douglas and F. B. Dains, *J. Am. Chem. Soc.* **56**, 719 (1934); L. L. Whitfield Jr. and E. P. Papandopoulos, *J. Heterocycl. Chem.* **18**, 1197 (1981).
[7] D. Klayman, S. Shine and J. D. Boweer, *J. Org. Chem.* **37**, 1532 (1972); W. Haede, *J. Heterocycl. Chem.* **18**, 1417 (1981).
[8] M. J. Janseen and J. Spoelstram, *Z. Chem.* **10**, 391 (1970).
[9] R. Neidlein and E. Heukelbach, *Arch. Pharm.* **289**, 709 (1966); *Tetrahedron Letters* 149 (1965).
[10] E. F. Kohman, *J. Am. Chem. Soc.* **37**, 2132 (1915).
[11] L. Beyer, J. Hartung and R. Widers, *Tetrahedron* **40**, 405 (1984).
[12] L. Beyer and R. Widera, *Tetrahedron Letters* **23**, 1881 (1982).
[13] H. Hartmann, J. Liebscher and P. Czerney, *DDR-Pat.* 138206, *Chem. Abstr.* **92**, 128947 (1980).
[14] P. Czerney, Diplomarbeit, TU, Dresden (1975).
[15] H. Hartmann, J. Liebscher and P. Czerney, *DDR-Pat.* 138206, *Chem. Abstr.* **92**, 128973 (1980).
[16] J. Herrmann, Thesis, Martin-Luther University, Halle (1973).
[17] K. Bredereck and R. Richter, *Chem. Ber.* **99**, 1454 (1966).
[18] I. Shibaya, *Kagakes Nyusu Kagaku Kogyo Shira* **17**, 44 (1982).
[19] J. Liebscher and H. Hartmann, *DDR-Pat.* 126401 (1977), *Chem. Abstr.* **88**, 62394 (1978).
[20] J. E. Oliver, *J. Org. Chem.* **36**, 3465 (1971).
[21] J. B. Douglass and F. B. Daine, *J. Am. Chem. Soc.* **56**, 1408 (1934).
[22] C. C. Billeter, *Ber. Dtsch. Chem. Ges.* **36**, 3218 (1983).