Monatshefte für Chemie 120, 749—758 (1989)

Monatshefte für Chemie
Chemical Monthly

1-Amino-2-hydrazinopyrimidin-N-ylides. Unusual Tautomers of 1-Aminopyrimidin-2-hydrazones

Jürgen Liebscher[1,*], **Ahmed Hassoun**[1], and **Jürgen Fabian**[2]

[1] Sektion Chemie, Humboldt-Universität Berlin, DDR-1040 Berlin, German Democratic Republic
[2] Sektion Chemie, Technische Universität Dresden, DDR-8027 Dresden, German Democratic Republic

Summary. 1-Amino-2-methylthiopyrimidinium iodides **3** have been synthesized by reaction of 3-isothiocyanato-2-propeniminium perchlorates **1** with hydrazines and subsequent methylation of the resulting 1-amino-2(1*H*)-pyrimidinthiones **2**. Reaction of **3** with hydrazine causes substitution of the methylthio group and results in the formation of deeply coloured 1-amino-2-hydrazinopyrimidin-N-ylides **5** as unusual tautomers of the commonly expected 1-amino-2(1*H*)-pyrimidinhydrazones **4**. The structure of these N-ylides has been proved by spectroscopic methods as well as by subsequent transformation to 3-amino-1,2,4-triazolo[2,3-a]pyrimidinium salts **9** by dehydration or to pyrimidotriazinium salt **10c** by oxidation. Reaction of N,N-disubstituted 1-amino-2-methylthiopyrimidinium salt **7a** with hydrazine also causes substitution of methylthiol, the resulting orange N,N-disubstituted 1-amino-2(1*H*)-pyrimidinhydrazone **8a**, however, cannot tautomerize to N-ylides.

Keywords. 1-Amino-2-methylthiopyrimidinium salts; 1-Amino-2-hydrazinopyrimidin-N-ylides; 1,2,4-Triazolo[2,3-a]pyrimidinium salts; 1-Amino-2(1*H*)-pyrimidinhydrazones.

1-Amino-2-hydrazinopyrimidin-N-ylide. Ungewöhnliche Tautomere von 1-Aminopyrimidin-2-hydrazonen

Zusammenfassung. Es wurden 1-Amino-2-methylthiopyrimidiniumjodide **3** ausgehend von 3-Isothiocyanato-2-propeniminiumperchloraten **1** und Hydrazinen durch Methylierung der primär gebildeten 1-Amino-2(1*H*)-pyrimidinthione **2** hergestellt. Die Reaktion dieser Pyrimidiniumsalze **3** mit Hydrazin verläuft unter Substitution der Methylthiogruppe unter Bildung violett gefärbter 1-Amino-2-hydrazinopyrimidin-N-ylide **5** als ungewöhnliche Tautomere der allgemein erwarteten 1-Amino-2(1*H*)-pyrimidinhydrazone **4**. Die Struktur dieser Ylide **5** wird durch spektroskopische Methoden sowie durch nachfolgende Dehydratisierung zu 3-Amino-1,2,4-triazolo[2,3-a]pyrimidiniumsalzen **9** bzw. Oxydation zum Pyrimidotriaziniumsalz **10c** bewiesen. Die Reaktion des N,N-disubstituierten 1-Amino-2-methylthiopyrimidiniumsalzes **7a** mit Hydrazin verläuft ebenfalls unter Substitution der Methylthiogruppe. Jedoch kann das gebildete orange gefärbte, N,N-disubstituierte 1-Amino-2(1*H*)-pyrimidinhydrazon **8a** nicht zu einem N-Ylid tautomerisieren.

Introduction

Recently we reported the synthesis of some 1-aminopyrimidin-2-thiones **2** by reaction of 3-isothiocyanato-2-propeniminium salts **1** with hydrazines [1]. These

pyrimidine derivatives **2** represent semicyclic thiosemicarbazides and are hence of further synthetic interest, for example in the preparation of thiazolopyrimidinium salts [1]. They can also be easily S-methylated to afford 1-amino-2-methylthiopyrimidinium salts **3**.

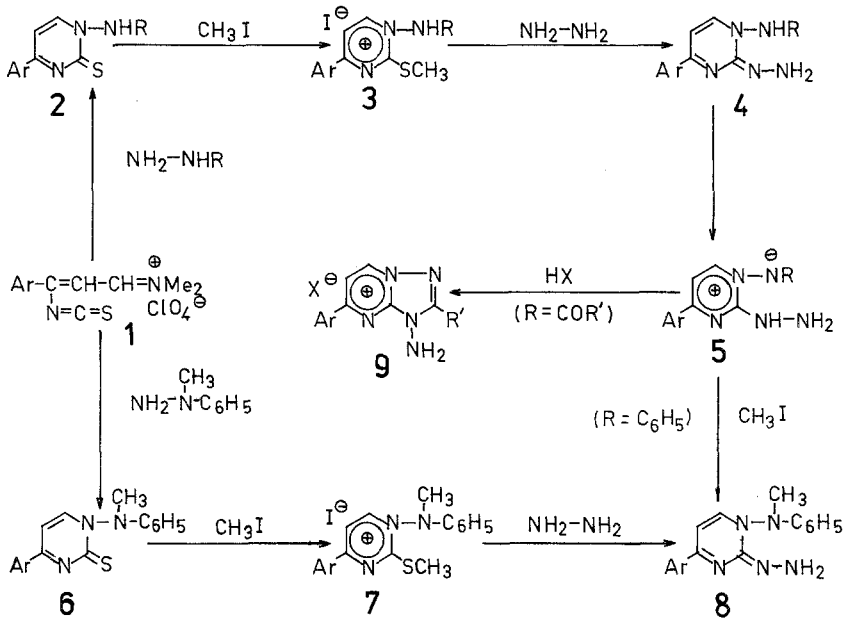
We now have synthesized a number of further 1-amino-2(1*H*)-pyrimidinthiones **2** and 1-amino-2-methylthiopyrimidinium iodides **3** ($X^- = I^-$) and report on reactions of these pyrimidinium salts **3** with hydrazine.

Results and Discussion

If a solution of the reactants **3** and hydrazine is heated, methylmercaptan evolution occurs. Therefore 1-amino-2(1*H*)-pyrimidinhydrazones **4** were expected as condensation products by analogy with known reactions of other 2-methylthio-pyrimidine compounds with hydrazines [2–6]. The results of elemental analysis as well as MS, IR and ^{1}H-NMR spectroscopy are in agreement with structure **4** except the violet or deep red colour. It is noteworthy that this colour is not very much affected by the substituent *R*. UV-vis investigations, ^{13}C-NMR spectroscopy and chemical results revealed that the products obtained are no 1-aminopyrimidin-2-hydrazones **4** but tautomeric 1-amino-2-hydrazinopyrimidin-N-ylides **5**. Studies of the solvent dependence of the UV-vis absorption have shown a negative solvatochromism as is known for 1-aminopyridin-N-ylides which also exhibit a violet colour [7, 8]. The hypsochromic shift in the case of **4a** (*R* = *Ar* = phenyl) amounts to 57 nm and 61 nm on passing from cyclohexane to acetonitrile or ethanol, respectively.

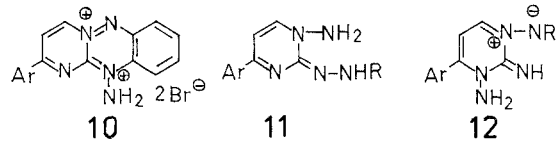
In the ^{13}C-NMR spectra of compounds **5c** (*Ar* = *p*-tolyl: *R* = phenyl) an unusual signal at 92.5 ppm (one CH-carbon atom according to *J*-modulated spin echo experiment) is found belonging to an aromatic ring: This signal is assigned to the *p*-position of the N-phenyl ring. In comparison to anilines, such derivatives possessing a high electron density at the nitrogen atom, like in N-lithiated anilines, disclose two effects in the ^{13}C-NMR: First a remarkable upfield shift of the *ortho* and *para* C-signals and secondly the reversal of the sequence of these signals (*para* at lower field than *ortho*) [9]. The same is found for compound **5c**. The effect is even stronger than in N-lithiated anilines.

Such a negatively charged N-atom adjacent to the phenyl ring (*R* = phenyl) cannot exist in Dimroth rearranged isomeric structures **11** (*R* = phenyl). Since the tautomerization of **4** to **5** requires shifting of the proton at the 1-amino group, corresponding N,N-disubstituted derivatives as for example compounds **8**, should not be subjected to tautomerization and, hence, should exhibit the usual orange colour. This was proved by the synthesis of compounds **8a** (*Ar* = *p*-tolyl) which was obtained via the pyrimidin-2-thione **6a** and the corresponding 2-methyl-mercaptopyrimidinium salt **7a**; it is indeed orange red coloured rather than violet. The same 1-methylphenylamino-2(1H)-pyrimidinhydrazone **8a** (*Ar* = 4-tolyl) is obtained when the pyrimidin-N-ylide **5c** is methylated with methyl iodide (method B). These results again rule out alternative Dimroth-rearranged structures **11** for the compounds yielded by the reaction of **3** with hydrazine. The pyrimidin-N-ylides **5** are stable crystalline compounds. They lose their colour in acidic medium probably due to protonation of the negatively charged N-atom. Corresponding salts can be isolated (see **5c**). Heating of the acyl substituted pyrimidin-N-ylides **5** (*R* = *R'*CO) in



1	2	3	5	9	*Ar*	*R*
a	**a**	**a**	**a**		C_6H_5	C_6H_5
b	**b**	**b**	**b**	**b**	C_6H_5	COC_6H_5
c	**c**	**c**	**c**		4-$CH_3C_6H_4$	C_6H_5
d	**d**	**d**	**d**		4-$CH_3C_6H_4$	4-$NO_2C_6H_4$
e	**e**	**e**	**e**		4-$CH_3C_6H_4$	2,4-$(NO_2)_2C_6H_3$
f	**f**	**f**	**f***	**f**	4-$CH_3C_6H_4$	$COCH_3$
g	**g**	**g**	**g**	**g**	4-$CH_3C_6H_4$	COC_6H_5
h	**h**	**h**	**h**		4-ClC_6H_4	C_6H_5
i	**i**	**i**	**i***	**i**	4-ClC_6H_4	COC_6H_5
j	**j**	**j**	**j**	**j**	4-$CH_3OC_6H_4$	COC_6H_5

acidic acid leads to dehydration giving rise to the 1,2,4-triazolo-[2,3-a]-pyrimidinium salts **9**. Their N-amino structure can be easily proved by MS cleavage of NH_2 as the major fragmentation process in the case of their iodides (X = I). Hence alternative formation of 6-membered pyrimidotetrazine isomers is unprobable. The transformation of **5** to **9** excludes Dimroth-rearrangements of **5** resulting in products such as **12**, where the two hydrazino units are not found on adjacent positions of the pyrimidin ring. Oxidation of **5c** by bromine giving the



* Only obtained as corresponding hydroperchlorate

pyrimidotriazinium salt **10 c** also rules out Dimroth-rearranged structures **12**. The salt **10 c** forms a red coloured azomethine (m.p. 141–145°C; 61% yield) upon heating with 4-dimethylaminobenzaldehyde in acetic acid.

Formation of the 2-hydrazinopyrimidin-N-ylides rather than the commonly observed [2–4, 10–16] tautomeric 1-aminopyrimidin-2-hydrazone structures is considered as unusual: This phenomenon seems to be restricted to a limited number of cases. For some acyl substituted compounds ylides **5** could only be obtained as mixtures with their corresponding hydroiodides or as salts at all (see **5 f** and **5 i**). If furthermore the NH_2 group is replaced by aryl or hydroxy radicals, the corresponding pyrimidines do not exist as ylides but as 1-substituted pyridin-2-aniles or oximes **4** (aryl or OH instead of NH_2) and are hence yellow or colourless, respectively. These results as well as a detailed report on the solvent dependence of the UV-vis absorption and on the reaction of 1-amino-2-methylmercapto-pyrimidinium salts **3** with substituted hydrazines giving unusual N—N-bond fission will be reported elsewhere.

Acknowledgement

We greatfully acknowledge the assistance in structure elucidation given by Dr. A. Mehlhorn, Technische Universität Dresden, and Prof. E. Kleinpeter of the Martin-Luther-Universität Halle-Wittenberg.

Experimental Part

Melting points: Heating block Boetius. IR-Spectra: Specord IR 72 Carl-Zeiss Jena. ^{1}H-NMR-Spectra: BS 487C (80 MHz) Tesla, Brno. ^{13}C-NMR: Bruker 200 MHz. MS: HP 5995 A, Hewlett Packard. UV-vis: Specord, Carl-Zeiss Jena.

3-Isothiocyanato-propen-(2)-dimethyliminium Perchlorates **1** [1]

A suspension of 0.1 mol 3-chloro-propen-(2)-dimethyliminium perchlorate [17], 9.7 g (0.1 mol) KSCN and 3.5 g benzyltriethylammonium bromide or 2 g tetrabutylammonium iodide was stirred for 20 min. After the inorganic byproducts have been filtered off by suction the product is precipitated by diluting the filtrate with diethyl ether. It is filtered by suction, washed with some diethyl ether and can be used without recrystallization for further syntheses.

1-Amino-2(1H)pyrimidinthiones **2** *and* **6 a**

Method A. A stirred solution of 15 mmol 3-isothiocyanato-propen-(2)-dimethyliminium perchlorate **1** and 20 mmol of the corresponding hydrazine in 100 ml ethanol is shortly heated to boiling. After 30 min of standing at room temperature the product was filtered by suction, washed with some ethanol and recrystallized.

Method B. A stirred solution of 10 mmol 3-isothiocyanato-propen-(2)-dimethyliminium perchlorate **1** and 12 mmol of the corresponding hydrazine in 20 ml ethanol is allowed to stand at room temperature for 20 min. The product is filtered by suction, washed with some ethanol and recrystallized.

2 a: m.p. 210–212°C (*Ac*OH); 87%/B. ^{1}H-NMR (*DMSO-d_6*: δ = 7.0 (d, 2 H, J = 8.0, NHC_6H_5), 7.35 (d, 1 H, J = 7.0, NC_6H_5), 7.52 (t, 2 H, J = 7.5, NC_6H_5), 7.83 (d, 1 H, J = 7, CH=CH), 7.85 (s, 3 H, C_6H_5), 8.42—8.55 (m, 2 H, C_6H_5), 8.9 (d, 1 H, J = 7, CH=CH), 9.65 (s, 1 H, NH). MS (70 eV): m/e = 279 (M^+, 17%), 187 (18), 128 (20), 115 (21), 102 (32), 92 (39), 77 (78), 65 (100), 39 (94). UV (CH_2Cl_2): λ_{max} = 298 (5.51), 409 (3.29) nm. $C_{16}H_{13}N_3S$ (279.4).

2b: m.p. 162–165°C (*Me*CN); 86%/A; ^{1}H-NMR (*DMSO-d*$_6$): δ = 7.58–7.77 (m, 6H, C_6H_5), 8.02–8.3 (m, 4H, C_6H_5), 8.13 (d, 1H, J = 7.1, CH=CH), 8.63 (d, 1H, J = 7.1, CH=CH); 12.17 (br, 1H, NH). MS (70 eV): m/e = 307 (M^+, 0.5%), 171 (24), 118 (29), 105 (61), 103 (68), 77 (100), 51 (89). IR (KBr): 1692 (C=O). $C_{17}H_{13}N_3OS$ (307.4).

2c: m.p. 217–219°C (*Me*CN); 78%/B. ^{1}H-NMR (*DMSO-d*$_6$): δ = 2.67 (s, 3H, CH_3), 6.97 (d, 2H, J = 8, C_6H_4), 7.2 (d, 1H, J = 7, C_6H_5), 7.51 (d, 2H, J = 8, C_6H_5), 7.64 (d, 2H, J = 8, C_6H_5), 7.81 (d, 1H, J = 7, CH=CH), 8.4 (d, 2H, J = 8, C_6H_4), 8.87 (d, 1H, J = 7, CH=CH), 9.65 (s, 1H, NH). MS (70 eV): m/e = 293 (M^+, 58%), 277 (20), 260 (100), 201 (23), 143 (11), 129 (8), 115 (50), 92 (30), 91 (42), 77 (29). UV (CH_2Cl_2): λ_{max} = 304 (4.59), 407 (3.44) nm. $C_{17}H_{15}N_3S$ (293.4).

2d: m.p. 206–208°C (*Ac*OH); 82%/B. ^{1}H-NMR (*DMSO-d*$_6$): δ = 2.4 (s, 3H, CH_3), 6.77 (d, 2H, J = 9.18, C_6H_4), 7.35 (d, 2H, J = 8.2, C_6H_4), 7.55 (d, 1H, J = 7.03, CH=CH), 8.07 (d, 2H, J = 9.18, C_6H_4), 8.1 (d, 2H, J = 8.2, C_6H_4), 8.57 (d, 1H, J = 7.03, CH=CH), 10.44 (s, 1H, NH). MS (70 eV): m/e = 338 (M^+, 16%), 201 (57), 187 (10), 169 (21), 142 (16), 128 (16), 115 (80), 91 (42), 77 (12), 65 (48), 63 (64), 39 (47), 30 (100). UV (CH_2Cl_2): λ_{max} = 305 (4.60), 394 sh (3.51) nm. $C_{17}H_{14}N_4O_2S$ (338.4).

2e: m.p. 220–223°C (*Me*CN); 76%/B. ^{1}H-NMR (*DMSO-d*$_6$): δ = 2.63 (s, 3H, CH_3), 7.14 (d, 1H, J = 10, C_6H_3), 7.61 (d, 2H, J = 8, C_6H_4), 7.86 (d, 1H, J = 7, CH = CH), 8.37 (d, 2H, J = 8, C_6H_4), 8.42 (d, J = 3) and 8.55 (d, J = 3, C_6H_3) (1H), 8.87 (d, 1H, J = 7, CH=CH), 9.14 (d, 1H, J = 3, C_6H_3), 11.52 (s, 1H, NH). MS [m/e]: 383 (M^+, 14%), 305 (41), 337 (36), 201 (67), 117 (35), 115 (100), 91 (70), 77 (35), 65 (43), 39 (38). UV (CH_2Cl_2): λ_{max} = 299 (4.56), 318 (4.56) nm. $C_{17}H_{13}N_5O_4S$ (383.4).

2f: m.p. 164–166°C (*Ac*OH); 74%/A. ^{1}H-NMR (*DMSO-d*$_6$): δ = 2.06 (s, 3H, CH_3CO), 2.32 (s, 3H, C_6H_4), 7.3 (d, 2H, J = 8.3, C_6H_4), 7.43 (d, 1H, J = 6.8, CH=CH), 8.03 (d, 2H, J = 8.3, C_6H_4), 8.33 (d, 1H, J = 6.8, CH=CH), 11.56 (s, 1H, NH). MS (70 eV): m/e = 259 (M^+, 71%), 242 (16), 216 (67), 200 (100), 185 (20), 159 (50), 142 (85), 115 (29), 91 (21), 43 (46). UV (CH_2Cl_2): λ_{max} = 297 (4.20), 314 sh (4.18), 361 (4.1) nm. IR (KBr): 1720 (C=O). $C_{13}H_{13}N_3OS$ (259.3).

2g: m.p. 199–201°C (*Me*CN); 92%/A). ^{1}H-NMR (*DMSO-d*$_6$): δ = 2.6 (s, 3H, CH_3), 7.57 (d, 2H, J = 8, C_6H_4), 7.7–8.0 (m, 4H, C_6H_5, CH=CH), 8.12–8.3 (m, 2H, C_6H_5), 8.35 (d, 2H, J = 8, C_6H_4), 8.8 (d, 1H, J = 7, CH=CH), 12.42 (s, 1H). MS (70 eV): m/e = 321 (M^+, 9%), 201 (16), 200 (25), 142 (12), 105 (100), 77 (42), 51 (14). UV (CH_2Cl_2): λ_{max} = 296 (4.53), 311 s (4.48), 386 (3.60) nm. IR (KBr): 1690 (C=O). $C_{18}H_{15}N_3OS$ (321.4).

2h: m.p. 211–214°C (*Ac*OH); 86%/B. ^{1}H-NMR (*DMSO-d*$_6$): δ = 6.69 (d, 2H, J = 7.42, C_6H_5), 6.92 (d, 1H, J = 6.6, C_6H_5), 7.17 (d, 2H, J = 7.4, C_6H_5), 7.55 (d, 1H, J = 7.03, CH=CH), 7.59 (d, 2H, J = 8.6, C_6H_4), 8.20 (d, 2H, J = 8.6, C_6H_4), 8.63 (d, 1H, J = 7.03, CH=CH), 9.34 (s, 1H, NH). MS (70 eV): m/e = 315 (15), 313 (M^+, 39%), 282 (23), 280 (64), 221 (23), 189 (11), 136 (23), 123 (21), 111 (18), 101 (26), 92 (50), 91 (28), 77 (38), 75 (39), 65 (100), 51 (34), 39 (64). UV (CH_2Cl_2): λ_{max} = 301 (4.52), 411 (3.41) nm. $C_{16}H_{12}ClN_3S$ (313.8).

2i: m.p. 212–213°C (*Me*CN); 95%/A. ^{1}H-NMR (*DMSO-d*$_6$): δ = 7.75–7.96 (m, 3H, C_6H_5), 7.82 (d, 1H, J = 7, CH=CH), 7.85 (d, 2H, J = 8, C_6H_4), 8.12–8.37 (m, 2H, C_6H_5), 8.47 (d, 2H, J = 8, C_6H_4), 8.87 (d, 1H, J = 7, CH=CH), 12.5 (br, 1H, NH). MS (70 eV): m/e = 341 (M^+, 4%), 223 (7), 221 (14), 105 (100), 103 (46), 77 (46), 51 (18). UV (*Me*CN): λ_{max} = 234 (4.16), 259 (3.97), 293 (4.01), 338 (4.27), 380 (4.23) nm. IR (KBr): 1688 (C=O). $C_{17}H_{12}ClN_3OS$ (341.8).

2j: m.p. 185–187°C (*Me*CN); 82%/A. ^{1}H-NMR (*DMSO-d*$_6$): δ = 3.8 (s, 3H, CH_3), 7.03 (d, 2H, J = 9, C_6H_4), 7.5 (d, 1H, J = 7, CH=CH), 7.5–7.6 (m, 3H, C_6H_5), 7.7–8.03 (m, 2H, C_6H_5), 8.15 (d, 2H, J = 9, C_6H_4), 8.45 (d, 1H, J = 7, CH=CH), 12.06, s, 1H, NH). MS (70 eV): m/e = 337 (M^+, 11%), 304 (13), 216 (23), 201 (20), 158 (17), 105 (100), 103 (43), 77 (33). IR (KBr): 1680 (C=O). $C_{18}H_{15}N_3O_2S$ (337.4).

1-Methylphenylamino-4-(p-tolyl)-2(1H)pyrimidinthione **6a** (*Ar* = *p*-tolyl)

M.p. 201–203 (CH_3CN); orange; 86%. ^{1}H-NMR (*DMSO-d*$_6$): δ = 2.42 (s, 3 H, CCH_3), 3.45 (s, 3 H, NCH_3), 6.52 (d, 2 H, J = 7.8, C_6H_4), 6.89 (d, 1 H, J = 7.1, CH=CH), 7.21 (d, 2 H, J = 8.06, C_6H_5), 7.4 (d, 2 H, J = 8.1, C_6H_5), 7.58 (d, 1 H, J = 7.3, C_6H_5), 8.15 (d, 2 H, J = 8.3, C_6H_4), 8.55, d, 1 H, J = 7.1, CH=CH). MS (70 eV): *m*/e = 307 (M^+, 4%), 201 (13), 115 (16), 105 (100), 77 (39), 65 (9), 51 (15). UV (CH_2Cl_2): λ_{max} = 240 (4.20), 306 (4.60), 406 (3.48). $C_{18}H_{17}N_3S$ (307.4).

1-Amino-2-methylthiopyrimidinium Iodides **3** *and* **7**

Method A. 1.7 g (0.012 mol) methyl iodide are added to a solution of 0.01 mol 1-amino-2(1*H*)-pyrimidinthione **2** or **6** in 50 ml acetonitril. The mixture is heated until a clear solution is obtained. In order to complete precipitation of the product the cold reaction mixture is diluted with some diethyl ether. The product is filtered by suction, washed with some diethyl ether and recrystallized.

3a: m.p. 119–121°C (CH_3CN); 95%. ^{1}H-NMR (*DMSO-d*$_6$): δ = 3.12 (s, 3 H, CH_3), 7.17–7.5 (m, 5 H, C_6H_5), 7.97–8.1 (m, 3 H, C_6H_5), 8.77–8.87 (m, 2 H, C_6H_5), 8.82 (d, 1 H, J = 7, CH=CH), 9.63 (d, 1 H, J = 7, CH=CH), 10.85 (s, 1 H, NH). MS (70 eV): *m*/e = 247 (M^+-*Me*S-I, 13%), 202 (10), 105 (12), 103 (10), 102 (32), 77 (100), 51 (52), 39 (17). $C_{17}H_{16}IN_3S$ (421.3).

3b: m.p. 234–236°C (*Ac*OH); 88%. ^{1}H-NMR (*DMSO-d*$_6$): δ = 2.8 (s, 3 H, CH_3), 7.11 (d, 1 H, J = 7.03, CH=CH), 7.48–7.69 (m, 6 H, C_6H_5), 7.86–8.13 (m, 2 H, C_6H_5), 8.27–8.52 (m, 2 H, C_6H_5), 9.42 (d, 1 H, J = 7.03, CH=CH), 12.26 (s, 1 H, HN). MS (70 eV): *m*/e = 321 (M^+-HI, 0.7%), 274 (22), 171 (11), 142 (23), 128 (100), 105 (16), 103 (18), 77 (18), 47 (55). IR (KBr): 1 705 (C=O). $C_{18}H_{16}IN_3OS$ (449.3).

3c: m.p. 125–126°C (*Me*CN); 82%. ^{1}H-NMR (*DMSO-d*$_6$): δ = 2.46 (s, 3 H, CCH_3), 2.79 (s, 3 H, SCH_3), 6.82–7.31 (m, 5 H, C_6H_5), 7.48 (d, 2 H, J = 8.4, C_6H_4), 8.39 (d, 2 H, J = 8.4, C_6H_4), 8.40 (d, 1 H, J = 7.03, CH=CH), 9.23 (d, 1 H, J = 7.03, CH=CH), 10.46 (s, 1 H, NH). MS (70 eV): *m*/e = 254 (23%), 216 (98), 215 (36), 170 (64), 169 (55), 155 (47), 127 (100), 115 (81), 93 (90), 77 (46), 66 (47). UV (*Me*CN): λ_{max} = 254 (4.17), 337 (4.47), 416 sh (3.55) nm. $C_{18}H_{18}IN_3S$ (435.3).

3d: m.p. 148–151°C (*Me*CN); 84%. ^{1}H-NMR (*DMSO-d*$_6$): δ = 2.68 (s, 3 H, CH_3), 3.03 (s, 3 H, SCH_3), 4.35 (br, 1 H, NH), 7.27 (d, 2 H, J = 9, C_6H_4), 7.72 (d, 2 H, J = 8, C_6H_4), 8.36 (d, 2 H, J = 9, C_6H_4), 8.65 (d, 2 H, J = 8, C_6H_4), 8.72 (d, 1 H, J = 7, CH=CH), 9.56 (d, 1 H, J = 7, CH=CH). MS (70 eV): *m*/e = 338 (M^+-*Me*I, 17%), 305 (50), 254 (100), 216 (69), 201 (46), 169 (39), 142 (42), 127 (88), 115 (87), 91 (39), 65 (73). $C_{18}H_{17}IN_4O_2S$ (480.3).

3e: m.p. 188–190°C (*Me*CN); 85%. ^{1}H-NMR (*DMSO-d*$_6$: δ = 2.68 (s, 3 H, CH_3), 3.1 (s, 3 H, SCH_3), 6.44 (br, 1 H, NH), 7.51 (d, 1 H, J = 10, C_6H_3), 7.73 (d, 2 H, J = 9, C_6H_4), 8.42 (d, J = 3) and 8.53 (d, J = 3, C_6H_3) (1 H), 8.67 (d, 2 H, J = 9, C_6H_4), 8.85 (d, 1 H, J = 7, CH=CH), 9.11 (d, 1 H, J = 2, C_6H_3), 9.63 (d, 1 H, J = 7, CH=CH). MS (70 eV): *m*/e = 383 (M^+-*Me*I, 3%), 254 (69), 216 (100), 215 (34), 201 (21), 183 (31), 170 (55), 169 (36), 155 (33), 142 (91), 128 (60), 127 (69), 115 (33), 91 (26). $C_{18}H_{16}IN_5O_4S$ (525.3).

3f: m.p. 153–155°C (*Me*CN); 81%. ^{1}H-NMR (*DMSO-d*$_6$): δ = 2.17 (s, 3 H, $COCH_3$), 2.45 (s, 3 H, CH_3-phenyl), 2.8 (s, 3 H, CH_3S), 7.4 (d, 2 H, J = 9, C_6H_4), 8.3 (d, 2 H, J = 9, C_6H_4), 8.5 (d, 1 H, J = 7, CH=CH), 9.3 (d, 1 H, J = 7, CH=CH), 10.25 (br, NH). MS (70 eV): *m*/e = 273 (M^+-HI, 1.5%), 259 (7), 226 (50), 185 (21), 142 (100), 91 (4), 48 (56). IR (KBr): 1 718 (C=O). $C_{14}H_{16}IN_3OS$ (401.3).

3g: m.p. 228–230°C (*Ac*OH); 86%. ^{1}H-NMR (*DMSO-d*$_6$): δ = 2.45 (s, 3 H, CH_3C), 2.77 (s, 3 H, CH_3S), 7.35 (d, 2 H, J = 8, C_6H_4), 7.41–7.6 (m, 3 H, C_6H_5), 7.95–8.1 (m, 2 H, C_6H_5), 8.21 (d, 2 H, J = 8, C_6H_4), 8.31 (d, 1 H, J = 7, CH=CH), 9.21 (d, 1 H, J = 7, CH=CH). MS (70 eV): *m*/e = 321 (M^+-*Me*I, 3%), 288 (60), 185 (21), 142 (56), 128 (48), 115 (30), 105 (94), 103 (37), 77 (100), 47 (97). IR (KBr): 1 692 (C=O). $C_{19}H_{18}IN_3OS$ (463.3).

3h: m.p. 120–121°C (*Me*CN); 82%. ^{1}H-NMR (*DMSO-d*$_6$): δ = 2.80 (s, 3 H, SCH_3), 6.82–7.39 (m, 5 H, C_6H_5), 7.74 (d, 2 H, J = 8.6, C_6H_4), 8.48 (d, 1 H, J = 7, CH=CH), 8.49 (d, 2 H, J = 8.6, C_6H_4), 9.34 (d, 1 H, J = 7, CH=CH), 10.49 (s, 1 H, NH). MS (70 eV): m/e = 254 (28%), 236 (73), 190 (55), 155 (100), 136 (26), 127 (62), 101 (44), 93 (98), 77 (52), 75 (70). $C_{17}H_{15}ClIN_3S$ (455.7).

3i: m.p. 180–192°C decomposition (*Me*CN); 84%. ^{1}H-NMR (CF_3COOH): δ = 2.77 (s, 3 H, CH_3), 7.47 (d, 2 H, J = 9, C_6H_4), 7.42–7.67 (m, 3 H, C_6H_5), 7.91 (d, 1 H, J = 7, CH=CH), 7.95 (d, 2 H, J = 9, C_6H_4), 8.12–8.25 (m, 2 H, C_6H_5), 8.68 (d, 1 H, J = 7, CH=CH). MS (70 eV): m/e = 342 (M^+-*Me*I, 2%), 308 (18), 150 (13), 127 (39), 105 (100), 77 (73), 47 (79). IR (KBr): 1 712 (C=O). $C_{18}H_{15}ClIN_3OS$ (483.7).

3j: m.p. 175–181°C decomposition (*Me*CN); 79%. ^{1}H-NMR (*DMSO-d*$_6$): δ = 2.82 (s, 3 H, SCH_3), 3.92 (s, 3 H, OCH_3), 7.17 (d, 2 H, J = 9.0, C_6H_4), 7.56–7.64 (m, 3 H, C_6H_5), 7.92–8.04 (m, 2 H, C_6H_5), 8.42 (d, 1 H, J = 7.03, CH=CH), 8.45 (d, 2 H, J = 3.0, C_6H_4), 9.3 (d, 1 H, J = 7.03, CH=CH), 9.82 (br, 1 H, NH). MS (70 eV): m/e = 304 (M^+-*Me*I, SH, 4%), 142 (42), 105 (18), 103 (16), 77 (22), 51 (16), 47 (100), 45 (91), 44 (19). IR (KBr): 1 700 (C=O). $C_{19}H_{18}IN_3O_2S$ (479.3).

1-(Methylphenylamino)-2-methylthio-4-(p-tolyl)-pyrimidinium Iodide (**7a**) (*Ar* = *p*-tolyl)

M.p. 166–168°C (CH_3CN); 76%. ^{1}H-NMR (*DMSO-d*$_6$): δ = 2.49 (s, 3 H, CCH_3), 2.84 (s, 3 H, SCH_3), 3.57 (s, 3 H, NCH_3), 6.97–7.28 (m, 3 H, C_6H_5), 7.36 (d, 2 H, J = 7.8, C_6H_5), 7.54 (d, 2 H, J = 8.3, C_6H_4), 8.49 (d, 2 H, J = 8.3, C_6H_4), 8.61 (d, 1 H, J = 7.3, CH=CH), 9.57 (d, 1 H, J = 7.3, CH=CH). MS (70 eV): m/e = 274 (M^+-*Me*I, —SH, 0.8%), 216 (100), 170 (61), 169 (50), 155 (46), 143 (22), 142 (20), 120 (18), 115 (68), 106 (63), 91 (29), 77 (52), 51 (54), 45 (51), 39 (56). UV (CH_2Cl_2): λ_{max} = 239 (4.41), 346 (4.46), 450 sh (3.17) nm. $C_{19}H_{20}IN_3S$ (449.3).

1-Amino-2-hydrazinopyrimidin-N-ylides **5** *and 1-(Methylphenylamino)-4-(p-tolyl)-2(1H)pyrimidinhydrazone* **8a**

Method A. 0.8 g (0.012 mol) 50% Hydrazine hydrate are added to a mixture of 0.01 mol 2-alkylthio-1-aminopyrimidinium iodide **3** or **7**. The mixture is stirred for 10 min and then shortly heated to boiling. After cooling to room temperature the product is filtered by suction and recrystallized.

5a: m.p. 162–166°C (*Et*OH); black crystals; 89%. ^{1}H-NMR (*DMSO-d*$_6$): δ = 5.9 (s, 2 H, NH_2), 6.36 (d, 1 H, J = 7, CH=CH), 6.76 (q, 1 H, J = 5, NC_6H_5), 7.31 (d, 4 H, J = 4, NC_6H_5), 7.65–7.77 (m, 3 H, C_6H_5), 7.95 (d, 1 H, J = 7, CH=CH), 8.3–8.4 (m, 2 H, C_6H_5), 8.42 (s, 1 H, NH). MS (70 eV): m/e = 277 (M^+, 11%), 261 (12), 157 (20), 155 (11), 104 (19), 103 (24), 77 (100), 65 (25), 51 (43), 39 (22). UV (CH_3CN): λ_{max} = 291 (4.44), 312 (4.35), 518 (2.90) nm. UV (*Et*OH): λ_{max} = 230 sh (4.10), 287 (4.43), 318 sh (4.26), 514 (2.85) nm. UV (dioxane): λ_{max} = 292 (4.45), 310 s (4.32), 553 (2.89) nm. UV ($CHCl_3$): λ_{max} = 289 (4.42), 319 sh (4.26), 541 (287) nm. UV (cyclohexane): λ_{max} = 224 sh, 287, 320 sh, 575 nm (qualitative). $C_{16}H_{15}N_5$ (277.3).

5b: m.p. 195–198°C (*Et*OH); purple crystals; 96%. ^{1}H-NMR (*TFA*): δ = 7.25–7.52 (m, 7 H, C_6H_5, CH=CH), 7.72–8.0 (m, 4 H, C_6H_5), 8.35 (d, 1 H, J = 7, CH=CH), 10 (br, NH). MS (70 eV): m/e = 305 (M^+, 14%), 290 (15), 172 (17), 157 (13), 105 (100), 103 (14), 77 (58), 51 (20), 28 (72). UV (CH_3CN): λ_{max} = 223 (4.24), 281 (4.32), 451 (3.13). IR (KBr): 1 670 (C=O). $C_{17}H_{15}N_5O$ (305.3).

5c: m.p. 144–146°C (*Et*OH); black crystals; 91%). ^{1}H-NMR (*DMSO-d*$_6$): δ = 2.57 (s, 3 H, CH_3), 5.85 (s, 2 H, NH_2), 6.35 (d, 1 H, J = 7, CH=CH), 6.75 (q, 1 H, J = 5, C_6H_5), 7.29 (d, 4 H, J = 4, C_6H_5), 7.5 (d, 2 H, J = 8, C_6H_4), 7.92 (d, 1 H, J = 7, CH=CH), 8.27 (d, 2 H, J = 8, C_6H_4), 8.4 (s, 1 H, NH). ^{13}C-NMR (*DMSO-d*$_6$): δ = 20.96 (CH), 92.50 (CH), 111.79 (CH), 127.42 (CH), 128.46 (CH), 129.10 (CH), 133.16 (C), 141.31 (C), 144.01 (C), 147.2 (C), 148.08 (CH), 163.53 (C). MS (70 eV): m/e = 291 (M^+, 15%), 275 (17), 117 (31), 91 (21), 77 (100), 43 (12), 39 (25). UV (CH_2Cl_2): λ_{max} = 300 (4.43), 515 (2.84) nm. $C_{17}H_{17}N_5$ (291.4).

Corresponding hydroperchlorate: m.p. 178–179°C (*Me*CN); yellow crystals.

5d: m.p. 208–210°C (*Ac*OH); violett-black crystals; 86%. ^{1}H-NMR (*DMSO-d*$_6$): δ = 2.40 (s, 3 H, CH_3), 5.9 (s, 2 H, NH_2), 6.43 (d, 1 H, J = 6.8, CH=CH), 7.22 (d, 2 H, J = 9.27, C_6H_4), 7.34 (d, 2 H, J = 8.05, CC_6H_4), 7.9 (d, 1 H, J = 6.8, CH=CH), 8.01 (d, 2 H, J = 8.27, C_6H_4), 8.2 (d, 2 H, J = 8.05, CC_6H_4), 9.81 (s, 1 H, NH). MS (70 eV): m/e = 336 (M^+, 7%), 201 (23), 169 (17), 155 (10), 142 (15), 128 (19), 122 (31), 115 (72), 91 (45), 76 (29), 65 (57), 39 (61), 30 (100). UV (*Me*CN): λ_{max} = 223 (4.25), 292 (4.45), 470 (4.45) nm. $C_{17}H_{16}N_6O_2$ (336.4).

5e: m.p. 269–271°C (*DMF*); violet-brown crystals; 80%. ^{1}H-NMR (*DMSO-d*$_6$): δ = 2.5 (s, 3 H, CH_3), 6.27 (s, 2 H, NH_2), 6.8 (d, 1 H, J = 7.1, CH=CH), 7.4 (d, 2 H, J = 8.3, C_6H_4), 7.96 (d, 1 H, J = 9.8, C_6H_3), 8.08 (d, 2 H, J = 8.3, C_6H_4), 8.18 (d, J = 3.76) and 8.22 (d, J = 3.17) (1 H, C_6H_3), 8.20 (d, 1 H, J = 7.1, CH=CH), 8.88 (d, 1 H, J = 2.44, C_6H_3), 12.42 (s, 1 H, NH). MS (70 eV): m/e = 381 (M^+, 100%), 365 (35), 227 (22), 200 (25), 184 (26), 169 (69), 155 (19), 142 (23), 128 (19), 117 (40), 115 (69), 91 (52), 77 (25), 75 (40), 63 (28), 43 (24), 39 (19), 30 (55). UV (CH_2Cl_2): λ_{max} = 278, 306, 435 (not sufficiently soluble). $C_{17}H_{15}N_7O_4$ (381.4).

5f·$HClO_4$: m.p. 170–185°C decomp. (*Me*CN); light yellow crystals; 91%. ^{1}H-NMR (*DMSO-d*$_6$): δ = 2.02 (s, 3 H, CH_3), 2.35 (s, 3 H, $COCH_3$), 6.94 (br, 2 H, NH_2), 7.37 (d, 2 H, J = 8.3, C_6H_4), 7.74 (d, 1 H, J = 6.8, CH=CH), 8.08 (d, 2 H, J = 8.3, C_6H_4), 8.61 (d, 1 H, J = 6.8, CH=CH), 10.34 (s, 1 H, NH). MS (70 eV): m/e = 257 (M^+-$HClO_4$, 9.5%), 242 (20), 200 (37), 171 (32), 158 (92), 130 (19), 43 (16), 32 (100). IR (KBr): 1 690 (C=O). $C_{13}H_{16}ClN_5O_5$ (357.8).

5g: m.p. 209–211°C (*Et*OH); red-violet crystals; 73%. ^{1}H-NMR (*TFA*): δ = 2.22 (s, 3 H, CH_3), 7.12 (d, 2 H, J = 8, C_6H_4), 7.47 (d, 1 H, J = 7, CH=CH), 7.40–7.50 (m, 3 H, C_6H_5), 7.75–7.92 (m, 2 H, C_6H_5), 7.85 (d, 2 H, J = 8, C_6H_4), 8.26 (d, 1 H, J = 7, CH=CH). MS (70 eV): m/e = 319 (M^+, 36%), 304 (24), 288 (11), 118 (43), 115 (19), 105 (100), 91 (17), 77 (74). UV (*Me*CN): λ_{max} = 301 (4.47), 446 (3.16) nm. IR (KBr): 1 670 (C=O). $C_{18}H_{17}N_5O$ (319.4).

5h: m.p. 162–165°C (*Et*OH); black-brown crystals, 88%. ^{1}H-NMR (*DMSO-d*$_6$): δ = 5.72 (s, 2 H, NH_2), 6.18 (d, 1 H, J = 6.8, CH=CH), 6.57 (q, 1 H, J = 4.4, C_6H_5), 7.12 (d, 4 H, J = 4.1, C_6H_5), 7.55 (d, 2 H, J = 8.5, C_6H_4), 7.79 (d, 1 H, J = 6.8, CH=CH), 8.24 (s, 1 H, NH), 8.25 (d, 2 H, J = 8.5, C_6H_4). MS (70 eV): m/e = 311 (M^+, 4%), 191 (13), 137 (11), 105 (20), 93 (20), 77 (100), 51 (40). UV (CH_2Cl_2): λ_{max} = 293 (4.45), 521 (3.83) nm. $C_{16}H_{14}ClN_5$ (311.8).

5i·$HClO_4$: m.p. 172–182°C decomp. (*Me*CN); light yellow crystals; 89%. ^{1}H-NMR (*DMSO-d*$_6$): δ = 7.23 (br, 2 H, NH_2), 7.59–7.69 (m, 5 H, C_6H_5, C_6H_4), 7.84–8.03 (m, 3 H, C_6H_5, CH=CH), 8.17 (d, 2 H, J = 8.5, C_6H_4), 8.81 (d, 1 H, J = 7, CH=CH), 11.06 (s, 1 H, NH). MS (70 eV): m/e = 339 (M^+-$HClO_4$, 6%), 206 (18), 138 (36), 105 (100), 77 (93). IR (KBr): 1 685 (C=O). UV (*Me*CN): λ_{max} = 228 (4.43), 265 (4.34), 333 sh (4.13) nm. $C_{17}H_{15}ClN_5O_5$ (440.2).

5j: m.p. 211–213°C (*Et*OH); red-brown crystals; 72%. ^{1}H-NMR (*DMSO-d*$_6$): δ = 3.81 (s, 3 H, CH_3), 5.85 (s, 2 H, NH_2), 6.44 (d, 1 H, J = 7, CH=CH), 7.03 (d, 2 H, J = 8.6, C_6H_4), 7.45–7.50 (m, 3 H, C_6H_5), 7.74–7.84 (m, 2 H, C_6H_5), 7.9 (d, 1 H, J = 7, CH=CH), 8.08 (d, 2 H, J = 8.6, C_6H_4). MS (70 eV): m/e = 335 (M^+, 36%), 320 (24), 218 (18), 202 (26), 187 (19), 186 (14), 134 (36), 105 (100), 77 (59). IR (KBr): 1 675 (C=O). $C_{18}H_{17}N_5O_2$ (335.4).

8a: m.p. 195–197°C (*Et*OH); orange-red; 80%. ^{1}H-NMR (*DMSO-d*$_6$): δ = 2.35 (s, 3 H, CCH_3), 3.13 (s, 3 H, NCH_3), 6.1 (s, 2 H, NH_2), 6.5 (d, 2 H, J = 7.08, CH=CH), 6.55–6.67 (m, 1 H, C_6H_5), 6.9–7.15 (m, 4 H, C_6H_5), 7.29 (d, 2 H, J = 8.05, C_6H_4), 7.96 (d, 2 H, J = 8.05, C_6H_4), 7.97 (d, 1 H, J = 7.08, CH=CH). MS (70 eV): m/e = 305 (M^+, 20%), 200 (29), 186 (39), 159 (36), 130 (14), 128 (13), 117 (17), 115 (25), 106 (23), 105 (25), 104 (30), 91 (26), 77 (100), 65 (18), 51 (31), 43 (20), 39 (20). UV (CH_2Cl_2): λ_{max} = 292 (4.48), 468 (2.89) nm. $C_{18}H_{19}N_5$ (305.4).

Method B. The mixture of 2.9 g (0.01 mol) **5c**, 20 ml acetonitrile and 1.6 g (0.011 mol) methyl iodide is heated to boiling. After one hour of standing at room temperature the corresponding 1-anilino-2-hydrazino-4-(4-tolyl)-pyrimidinium iodide (m.p. 180–183°C, yield 56%) is precipitated by the addition

of water. It is filtered by suction and deprotonated to the N-ylide **8 a** by treatment with triethylamine in ethanol.

3-Amino-1,3,4-triazolo[3,2-a]pyrimidinium Salts **9**

Method A. A solution of 0.01 mol 1-acylamino-2-hydrazinopyrimidin-N-ylide **5** (R = acyl) in 20 ml acetic acid is refluxed for 90 min. After cooling to room temperature 0.5 ml 70% perchloric acid or 1 ml concentrated aqueous HI is added. The product is filtered by suction, washed with some diethyl ether and recrystallized with ethanol.

Method B. A solution of 0.01 mol 1-acylamino-2-methylthiopyrimidinium iodide and 0.05 mol 50% hydrazine hydrate in 20 ml acidic acid is refluxed for 1 h. After cooling to room temperature the product may be converted to the corresponding hydro perchlorate by adding 2 ml 70% $HClO_4$. The product is filtered by suction, washed with some ethanol and recrystallized.

9 b ($X = ClO_4$): m.p. 245–255°C (decomp.) (*Et*OH); 64%/A. ^{1}H-NMR (*DMSO-d*$_6$): δ = 6.88 (s, 2 H, NH_2), 5.59–7.72 (m, 6 H, C_6H_5), 8.14–8.55 (m, 5 H, C_6H_5, CH=CH), 8.77 (d, 1 H, J = 7, CH=CH). MS (70 eV): m/e = 301 (1%), 272 (63), 155 (16), 115 (10), 105 (100), 103 (22), 77 (84), 63 (10), 51 (32). UV (CH_3CN): λ_{max} = 245 (4.36), 338 (4.54), 4.80 sh (1.63) nm. $C_{17}H_{14}ClN_5O_4$ (387.8).

9 f ($X = ClO_4$): m.p. 228–240°C (decomp.) (*Et*OH); 66%/A. ^{1}H-NMR (*DMSO-d*$_6$): δ = 2.40 (s, 3 H, CH_3), 3.26 (s, 3 H, CCH_3), 6.61 (s, 2 H, NH_2), 7.45 (d, 2 H, J = 7.8, C_6H_4), 8.34 (d, 2 H, J = 7.8, C_6H_4), 8.44 (d, 1 H, J = 7.3, CH=CH), 9.65 (d, 1 H, J = 7.3, CH=CH). MS (70 eV): m/e = 254 (40%), 224 (100), 127 (12), 91 (9). UV (CH_3CN): λ_{max} = 246 (4.01), 327 (4.42) nm. $C_{13}H_{14}ClN_5O_4$ (339.7).

9 g ($X = ClO_4$): m.p. 226–235°C (decomp.) (*Et*OH); 79%/A. ^{1}H-NMR (*DMSO-d*$_6$): δ = 2.64 (s, 3 H, CH_3), 6.48 (br, 2 H, NH_2), 7.67 (d, 2 H, J = 9, C_6H_4), 7.81–8.0 (m, 3 H, C_6H_5), 8.47 (d, 1 H, J = 7, CH=CH), 8.37–8.62 (m, 2 H, C_6H_5), 8.72 (d, 2 H, J = 9, C_6H_4), 9.98 (d, 1 H, J = 7, CH=CH). ^{13}C-NMR (*DMSO-d*$_6$): δ = 21.14 (CH), 112.37 (CH), 122.89 (CH), 128.78 (CH), 129.08 (CH), 129.54 (CH), 130.17 (CH), 131.02 (CH), 132.93 (C), 139.97 (C), 144.64 (CH), 147.71 (C), 155.47 (C), 165.54 (C). MS (70 eV): m/e = 316 (3%), 286 (100), 169 (8), 143 (9), 115 (11), 103 (11), 91 (7), 77 (13). UV (*Me*CN): λ_{max} = 245 (4.36), 338 (4.54), 480 sh (1.63) nm. $C_{18}H_{16}ClN_5O_4$ (401.8).

9 i ($X = ClO_4$): m.p. 240–246°C (*Ac*OH); 58%/B. ^{1}H-NMR (*DMSO-d*$_6$): δ = 6.97 (br, 2 H, NH_2), 7.71–7.87 (m, 5 H, C_6H_5, C_6H_4), 8.27–8.39 (m, 2 H, C_6H_5), 8.57 (d, 2 H, J = 8.8, C_6H_4), 8.64 (d, 1 H, J = 7.08, CH=CH), 9.94 (d, 1 H, J = 7.08, CH=CH). MS (70 eV): m/e = 308 (31%), 306 (M^+-ClO_4—NH_2, 100), 189 (31), 140 (42), 114 (24), 111 (14), 103 (17), 77 (32), 76 (23), 51 (29). $C_{17}H_{13}Cl_2N_5O_4$ (422.2).

9 j (X = I): m.p. 245–247°C (*Et*OH); 85%/A. ^{1}H-NMR (*DMSO-d*$_6$): δ = 4.14 (s, 3 H, CH_3), 7.14 (s, 2 H, NH_2), 7.44 (d, 2 H, J = 9, C_6H_4), 7.81–8.65 (m, 3 H, C_6H_5), 8.45 (m, 2 H, C_6H_5), 8.74 (d, 2 H, J = 9 Hz, C_6H_4), 8.75 (d, 1 H, J = 7, CH=CH), 9.97 (d, 1 H, J = 7, CH=CH). MS (70 eV): m/e = 317 (M^+-I, 8%), 302 (100), 259 (16), 156 (20), 129 (14), 103 (14), 77 (22), 51 (13). UV (CH_3CN): λ_{max} = 346 (4.53), 365 (4.58) nm. $C_{18}H_{16}IN_5O$ (445.3).

Pyrimidotriazinium Bromide **10 c** (*Ar* = *p-tolyl*)

1.6 g (0.01 mol) Br_2 is added to a solution of 0.005 mol of the 1-anilino-2-hydrazinopyrimidin-N-ylide (**5 d**). After short boiling the mixture is allowed to stand at room temperature for 30 min. The product is filtered by suction, washed with a small amount of ethanol and recrystallized. M.p. 188–190°C (*Me*CN); yellow crystals; 87%. ^{1}H-NMR (*DMSO-d*$_6$): δ = 2.6 (s, 3 H, CH_3), 7.1 (d, 1 H, J = 8, C_6H_4), 7.5 (d, 2 H, J = 8, *Me*C_6H_4), 7.52 (d, 1 H, J = 8, C_6H_4), 7.89 (d, 1 H, J = 7, CH=CH), 7.8–7.95 (m, 1 H, C_6H_4), 8.16 (d, 3 H, J = 8, *Me*C_6H_4, C_6H_4), 8.82 (d, 1 H, J = 7, CH=CH). ^{13}C-NMR (*DMSO-d*$_6$): δ = 21.07 (CH), 106.85 (CH), 107.79 (C), 110.72 (C), 115.57 (CH), 128.38 (CH), 129.81 (CH), 130.81 (CH), 131.02 (CH), 133.92 (CH), 144.47 (CH), 144.78 (C), 151.59 (CH), 154.40 (C), 167.12 (C). MS (70 eV): m/e = 451 (M^+-2, 51%), 449 (M^+, 100), 447 (50), 415 (21), 352 (58), 235 (28), 115 (38), 91 (31). $C_{17}H_{15}Br_2N_5$ (449.1). M.p. of the corresponding diperchlorate (*Me*CN): 190–195°C (decomp.).

References

[1] Liebscher J., Hartmann H. (1982) J. prakt. Chem. **324**: 942
[2] Liu K. C., Hu M. K. (1986) J. Taiwan. Pharm. Assoc. **38**: 85
[3] Kottke K., Kühmstedt H. (1982) Pharmazie **37**: 635
[4] Liu K. C., Hsu S. W., Hu M. K. (1986) J. Taiwan. Pharm. Assoc. **38**: 242
[5] Brown D. J. (1962) Pyrimidines. In: Weissberger A. (ed.) Chemistry of Heterocyclic Compounds, Vol. 16. Wiley, New York London, p. 291
[6] Brown D. J. (1970) Pyrimidines Supplement 1. In: Weissberger A. (ed.) Chemistry of Heterocyclic Compounds, Vol. 16, Suppl. 1. Wiley, New York London, p. 219
[7] Dimroth K., Arnoldy G., von Eicken S., Schiffler G. (1957) Liebigs Ann. Chem. **604**: 221
[8] Dimroth K. (1961) Chimia **15**: 80
[9] Kalinowski H. O., Berger S., Braun S. (1984) Chemische Verschiebung einzelner Verbindungsklassen: ^{13}C-NMR-Spektroskopie. Thieme, Stuttgart New York, p. 285
[10] Dickinson R. G., Jacobsen N. W., Gillis R. G. (1975) Aust. J. Chem. **28**: 895
[11] Dickinson R. G., Jacobsen N. W., Pitman I. H. (1978) Aust. J. Chem. **31**: 2023
[12] Gupta C. M., Bhaduri A. P., Khanna N. M. (1968) J. Med. Chem. **11**: 392
[13] Bitha P., Hlavka J. J., Lin Yi (1987) J. Org. Chem. **52**: 2220
[14] Hlavka J. J., Bitha P., Lin Yi, Strohmeyer T. (1984) J. Heterocycl. Chem. **21**: 1537
[15] Hlavka J. J., Bitha P., Lin Yi, Strohmeyer T. (1985) J. Heterocycl. Chem. **22**: 1317
[16] Murdoch R., Tully W. R., Westwood R. (1986) J. Heterocycl. Chem. **23**: 833
[17] Liebscher J., Hartmann H. (1976) J. prakt. Chem. **318**: 731

Received October 24, 1988. Accepted December 12, 1988