Synthesis of Pyrazolo[1,5-*a*]pyridines and Pyrazolo[1,5-*c*]pyrimidines by Reaction of Heterocyclic Amidrazones with 1,3-Dicarbonyl Compounds

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1,3-Dicarbonyl compounds **2** react with 1-amino-2(1*H*)-pyridin-2-imines or 1-amino-2(1*H*)-pyrimidin-2-imines **1** giving new pyrazolo[1,5-*a*]pyridines or pyrazolo[1,5-*c*]pyrimidines **5** respectively by addition, oxidation and condensation. Isolation of an intermediate **3** shows that surprisingly the addition of the CH acidic 1,3-dicarbonyl compound to position 6 of the pyrimidine **1** is the initial step.

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Semicyclic amidrazones, such as 1,6-diamino-2(1*H*)-pyridin-2-ones [1] are known to react as N-C-N-N synthons with 1,3-dicarbonyl compounds as carboxyl equivalent (C-building block) by the formation of condensed 1,2,4-triazoles while the 1,3-dicarbonyl carbon skeleton is cleaved. Furthermore 1,2-diaminopyrimidinium iodide acts as N-C-N building block (elimination of the 1-amino group) in the reaction with 1,3-pentandione to form a 2,4-dimethylpyridopyrimidinium iodide [2]. We report now on reactions of 1-amino-2(1*H*)-pyridin-2-imines **1** (Y = CCN, R^1 = H) [3] and 1-amino-2(1*H*)-pyrimidin-2-imines **1** (Y = N, R^1 = aryl) [4] with 1,3-dicarbonyl compounds **2**.

It was found that these semicyclic amidrazones **1** preferably react as C-N-N building block forming condensed pyrazoles **5** (Y = CCN or N) (Methods A-D) while both the 1-amino nitrogen atom and the 1,3-dicarbonyl carbon skeleton are maintained. In case of the reaction of the 1-aminopyrimidine **1** (Y = N, $R^1 = C_6H_5$, $R^2 = 4\text{-}CH_3C_6H_4$) with dimedone a dihydropyrimidine **3** (tautomeric mixture) was obtained, which cyclized upon longer heating in hydrochloric acid/acetic acid solution (Method E). This result allows us to interpret the reaction mechanism as follows: In the first step an addition reaction of the acidic methylene group of the dicarbonyl compound **2** to position 6 of the pyrimidine ring of the starting *N*-aminoheterocycle **1**

Table 1

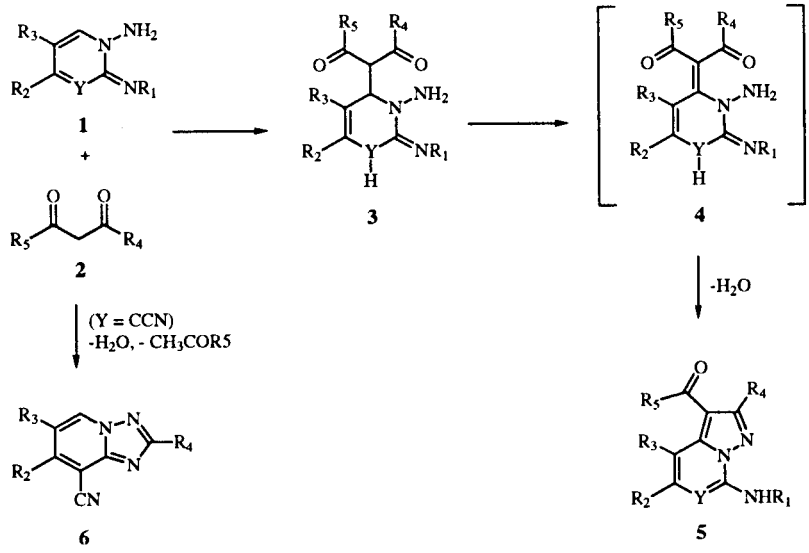
Intermediate **3r**, 7-Aminopyrazolo[1,5-*a*]pyridines **5** (Y = CCN), Pyrazolo[1,5-*c*]pyrimidines **5** (Y = N) and 7-Phenyl-1,2,4-triazolo[1,5-*a*]pyridine **6v**

	Yield/ Method	mp °C	Molecular Formula	Analysis Calcd./Found C	H	N	^{1}H-nmr (DMSO-d_6) δ, J (Hz)
3r	73/D	210-212	$C_{25}H_{28}N_4O_2$	72.09	6.78	13.45	0.98 (s, 4H, CH_3), 0.99 (s, 2H, CH_3), 2.13 (m, 4H, $2CH_2$), 2.33 (s, 2H,
[a]		(MeCN)	(416.5)	71.93	6.44	13.22	CH_3), 2.36 (s, 1H, CH_3), 3.39 (m, 1H, CH), 3.82 (m, 1H, CH), 5.64 (m, CHC=C), 6.35 (br, NH), 7.0-7.7 (m, 9H, aryl), 8.13 (s, 0.5H, NH), 11.3 (br, 0.5H, NH) (in $CDCl_3$)
5a	79/A	278-280	$C_{12}H_{12}N_4O$	63.14	5.30	24.55	2.63 (s, 3H, CH_3), 2.68 (s, 3H, CH_3) 2.86 (s, 3H, CH_3), 7.45
[b]		(AcOH)	(228.3)	63.66	5.42	24.45	(s, 1H, CH), 8.10 (s, 2H, NH_2)
5b	74/A	254-256	$C_{17}H_{14}N_4O$	70.33	4.86	19.30	2.44 (s, 3H, CH_3), 2.65 (s, 3H, CH_3), 7.19 (s, 1H, CH), 7.48
[c]		(*n*-BuOH)	(290.3)	68.94	4.93	19.46	(m, 5H, C_6H_5), 8.08 (s, 2H, NH_2)
5c	78/A	215-217	$C_{18}H_{16}N_4O$	71.04	5.30	18.41	2.18 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 2.84 (s, 3H, CH_3), 7.63-7.78
[d]		(*n*-BuOH)	(304.4)	71.28	5.28	18.61	(m, 5H, C_6H_5), 8.00 (s, 2H, NH_2)
5d	79/A	209-210	$C_{14}H_{16}N_4O$	65.61	6.29	21.86	1.38 (t, 3H, CH_3), 2.45 (s, 3H, CH_3), 2.80 (s, 6H, 2 CH_3), 3.05
		(*n*-BuOH)	(256.3)	65.32	6.51	21.51	(q, 2H, CH_2), 7.83 (s, 2H, NH_2)
5e	86/A	254-256	$C_{19}H_{16}N_4O$	72.13	5.10	17.71	2.73 (m, 4H, 2 CH_2), 2.79 (s, 3H, CH_3), 2.90 (s, 3H, CH_3), 7.55-7.60
		(*n*-BuOH)	(316.4)	72.59	5.45	15.62	(m, 3H, tetralone), 7.90 (s, 2H, NH_2), 8.08-8.30 (m, 1H, tetralone)
5f	87/A	268-270	$C_{15}H_{12}N_4O_2$	64.28	4.32	19.99	2.73 (s, 3H, CH_3), 2.98 (s, 3H, CH_3), 6.88-6.98 (m, 1H, fur-2-yl),
		(*n*-BuOH)	(280.3)	64.33	4.66	19.75	7.48-7.53 (m, 1H, fur-2-yl), 7.83 (s, 1H, CH), 8.12-8.20 (m, 1H, fur-2-yl), 8.23 (s, 2H, NH_2)
5g	57/A	266-268	$C_{15}H_{12}N_4OS$	60.80	4.08	18.91	2.75 (s, 3H, CH_3), 2.90 (s, 3H, CH_3), 7.49 (t, 1H, thien-2-yl), 7.58
		(*n*-BuOH)	(296.3)	60.59	4.37	18.84	(s, 1H, CH), 7.78-7.85 (m, 2H, thien-2-yl), 7.90-7.98 (m, 1H, thien-2-yl), 8.30 (2H, NH_2)

Table 1 (continued)

	Yield/ Method	mp °C	Molecular Formula	Analysis Calcd./Found C	H	N	^{1}H-nmr (DMSO-d_6) δ, J (Hz)
5h [e]	56/A	297-299 (AcOH)	$C_{14}H_{14}N_4O$ (254.3)	66.13 66.35	5.55 5.63	22.03 21.79	2.05 (m, 2H, CH_2), 2.43 (s, 3H, CH_3), 2.55 (s, 3H, CH_3), 2.85 (m, 2H, CH_2), 3.10 (m, 2H, CH_2), 7.75 (s, 2H, NH_2)
5i	58/A	246-247 (AcOH)	$C_{15}H_{16}N_4O$ (268.3)	67.15 66.88	6.01 6.19	20.88 21.04	1.88-2.05 (m, 4H, 2 CH_2), 2.75 (m, 10H, 2 CH_2, 2 CH_3), 7.78 (s, 2H, NH_2)
5j	92/A	195-197 (AcOH)	$C_{16}H_{18}N_4O$ (282.3)	68.06 67.87	6.43 6.36	19.84 20.19	1.80-2.05 (m, 6H, 3 CH_2), 2.73 (m, 6H, 2 CH_3), 2.88-3.25 (m, 4H, 2 CH_2), 7.75 (s, 2H, NH_2)
5k	38/B	267 dec (*n*-BuOH)	$C_{20}H_{18}N_4O$ (330.4)	72.71 72.42	5.50 5.66	16.96 16.75	1.08 (s, 6H, 2 CH_3), 2.40 (s, 2H, CH_2), 2.87 (s, 2H, CH_2), 7.14 (s, 1H, CH), 7.53 (m, 5H, C_6H_5), 8.25 (s, 2H, NH_2)
5l	36/B	265 dec (*n*-BuOH)	$C_{21}H_{20}N_4O$ (344.4)	73.23 73.17	5.85 6.11	16.27 16.55	1.07 (s, 6H, 2 CH_3), 2.40-2.56 (m, 5H, CH_2, CH_3), 2.88 (s, 2H, CH_2), 7.26 -7.56 (m, 5H, C_6H_5), 7.90 (s, 2H, NH_2)
5m	24/B 56/C	236-240 (*n*-BuOH)	$C_{22}H_{20}N_4O$ (356.4)	74.14 74.45	5.66 6.08	15.72 16.08	1.07 (s, 6H, 2 CH_3), 2.43-2.53 (m, 4H, 2 CH_2), 2.85 (m, 2H, CH_2), 3.33-3.44 (m, 2H, CH_2), 7.27-7.38 (m, 3H, tetralone), 7.92-8.11 (m, 3H, NH_2, tetralone)
5n	71/B 56/C	240 dec (*n*-BuOH)	$C_{18}H_{16}N_4OS$ (336.4)	64.27 63.87	4.79 4.90	16.65 16.22	1.08 (s, 6H, 2 CH_3), 2.40 (s, 2H, CH_2), 2.86 (s, 2H, CH_2), 7.21-7.32 (m, 2H, CH, thien-2-yl), 7.65-7.84(m, 2H, thien-2-yl), 8.23 (s, 2H, NH_2)
5o [f]	33/D	195-197 (EtOH)	$C_{22}H_{20}N_4O$ (356.5)	74.14 74.13	5.66 5.66	15.72 15.72	2.34 (s, 3H, CH_3), 2.55 (s, 3H CH_3), 2.65 (s, 3H, CH_3), 7.00-7.45 (m, 5H, C_6H_5, C_6H_4), 7.72 (s, 1H, CH), 7.90 (m, 4H, C_6H_5, C_6H_4), 9.74 (s, 1H, NH)
5p [g]	34/D	184-185 (EtOH)	$C_{22}H_{20}N_4O_2$ (372.4)	70.95 71.18	5.41 5.51	15.04 15.39	2.48 (s, 3H, CH_3), 2.49 (s, 3H, CH_3), 3.77 (s, 3H, CH_3O), 7.00 (m, 2H, C_6H_4), 7.48 (m, 3H, C_6H_5), 7.77 (s, 1H, CH), 7.81 (m, 2H, C_6H_5), 8.06 (m, 2H, C_6H_4), 9.80 (s, 1H, NH)
5q	42/D	176-178 (EtOH)	$C_{23}H_{22}N_4O_2$ (386.5)	71.49 71.36	5.74 6.02	14.50 14.35	2.34 (s, 3H, CH_3), 2.55 (s, 3H, CH_3), 2.64 (s, 3H, CH_3), 3.76 (s, 3H, CH_3O), 6.92 (d, 2H, J = 9.2), 7.23 (d, 2H, J = 8.0), 7.68 (s, 1H, CH), 7.77 (d, 2H, J = 9.2), 7.88 (d, 2H, J = 8.0), 9.69 (s, 1H, NH)
5r	44/E	218-219 (MeCN)	$C_{25}H_{24}N_4O$ (396.5)	75.73 76.02	6.10 6.38	14.13 14.33	1.08 (d, 4H, 2 CH_2), 2.08 (m, 6H, 2 CH_3), 2.47 (s, 3H, $CH_3C_6H_4$), 7.26 (m, 4H, C_6H_4), 7.69 (m, 1H, CH), 7.77 (m, 5H, C_6H_5)
5s [h]	33/D	238-240 (MeCN)	$C_{27}H_{22}N_4O$ (418.5)	77.49 77.25	5.30 5.26	13.39 12.98	2.44 (s, 3H, $CH_3C_6H_4$), 2.46 (s, 3H, CH_3), 7.14-7.70 (m, 10H, C_6H_5, C_6H_4, C_6H_5), 7.89 (s, 1H, CH), 7.97 (m, 2H, C_6H_4), 8.07 (m, 2H, C_6H_5), 9.65 (s, 1H, NH)
5t	36/D	160-162 (EtOH)	$C_{23}H_{22}N_4O_2$ (386.5)	71.48 71.63	5.74 5.72	14.50 14.48	1.45 (s, 3H, CH_3CH_2), 2.42 (s, 3H, $CH_3C_6H_4$), 2.69 (s, 3H, CH_3CO), 4.40 (q, 2H, CH_2), 7.19 (m, 2H, C_6H_4), 7.43 (m, 3H, C_6H_s), 7.80 (s, 1H, CH), 7.87 (m, 2H, C_6H_4), 7.98 (m, 2H, C_6H_5), 10.12 (s, 1H, NH)
5u	34/D	190-192 (EtOH)	$C_{28}H_{23}N_5O_4$ (493.6)	68.14 68.31	4.70 4.58	14.19 13.97	2.39 (s, 6H, 2 CH_3), 3.40 (s, 2H, CH_2), 7.08 (m, 2H, C_6H_4), 7.31 (m, 3H, C_6H_5), 7.53 (m, 2H, C_6H_4), 7.67 (m, 2H, C_6H_4), 7.83 (s, 1H, CH), 8.04 (m, 2H, C_6H_4), 8.74 (m, 2H, C_6H_4), 10.66 (s, 1H, NH)
6v [i]	30	229-231 (AcOH)	$C_{13}H_8N_4$ (220.2)	70.90 70.95	3.66 3.42	25.44 25.21	7.38 (d, 1H, J = 7.5, H-6), 7.40-7.80 (m, 5H, C_6H_5), 8.70 (s, 1H, NH), 9.30 (d, 1H, J = 7.5, H-5)

[a] ^{13}C-nmr (62.5 Hz, deuteriochloroform): δ 21.5 (*C*H_3phenyl), 28.5 (2 CH_3), 31.3 (CH_2), 31.5 (CH_2), 38.7 (CH_2), 38.9 (CH_2), 50.3 (*C*Me_2), 54.2 (CH), 54.7 (CH), 107.8 (C quart), 108.8 (C quart), 124.0 (CH), 125.6 (CH), 126.4 (CH),127.0 (CH), 127.6 (CH), 128.1 (C quart), 128.3 (C quart), 129.2 (CH), 129.4 (CH), 129.7 (CH), 130.0 (CH), 134.3 (C quart), 135.5 (C quart), 141.0 (C quart), 149.3 (C quart), 160.2 (C quart), 160.9 (C quart), 192.7 (C=O). [b] ms: m/z (%) 228 (M^+, 100), 214 (97), 199 (8), 185 (98), 159 (60); ir (potassium bromide): ν 3400-3200 (NH), 2220 (CN), 1680-1580 cm^{-1}. [c] ms: m/z (%) 290 (M^+, 290), 275 (98), 258 (5), 247 (60), 221 (50); ir (potassium bromide): ν 3430-3310 (NH), 2220 (C≡N), 1660, 1640 cm^{-1}; ^{13}C-nmr (62.5 Hz, DMSO-d_6): δ 15.4 (CH_3), 30.5 (*C*H_3CO), 75.5 (*CC*≡N), 104.4 (CH pyridine), 112.1 (OC*C* pyrazole), 116.4 (CN), 128.4 (CH phenyl), 128.6 (CH phenyl), 129.3 (CH phenyl), 137.5 (*C* phenylipso), 142.0 (HC*C*N pyridine), 143.7 (phenyl *C* pyridine), 147.7 (*C*NH_2), 155.2 (CH_3*C* pyrazole), 191.7 (C=O). [d] ms: m/z (%) 304 (M^+, 76), 289 (100), 261 (10), 244 (10), 220 (13); ir (potassium bromide): ν 3550-3400 (NH), 2200 (C≡N), 1660, 1630 cm^{-1}. [e] ms: m/z (%) 254 (M^+, 51), 239 (100), 211 (10), 184 (9); ir (potassium bromide): ν 3400-3320 (NH), 2220 (C≡N), 1650, 1625 cm^{-1}. [f] ms: m/z (%) 356 (M^+, 37), 341 (32), 222 (25), 152 (18), 118 (36), 115 (37), 91 (43), 77 (75), 51 (37), 43 (100); ir (potassium bromide): ν 3394, 1658, 1630, 1608, 1605 cm^{-1}; uv (dichloromethane): λ max 259 (4.53), 284.5 (4.28), 355 nm (1g ε 4.37); ^{13}C-nmr (62.5 Hz, deuteriochloroform): δ 15.6 (*C*H_3CN), 21.3 (*C*H_3 phenyl), 30.5 (*C*H_3CO), 99.1 (CH), 112.7 (*C*COCH$_3$), 119.7 (CH), 123.7 (CH phenyl), 126.9 (CH phenyl), 129.0 (CH phenyl), 129.4 (CH phenyl), 134.7 (C quart), 137.6 (C quart), 139.9 (C quart), 141.8 (C quart) 144.5 (C quart), 151.9 (C quart), 155.2 (N=*C*CH_3), 192.1 (C=O). [g] ms: m/z (%) 372 (M^+, 100), 357 (70), 225 (31), 208 (50), 152 (27), 140 (34), 133 (31), 115 (27), 77 (53), 65 (15), 51 (24), 43 (86), 42 (39), 15 (39); ir (potassium bromide): ν 3390, 1750, 1605, 1575, 1500 cm^{-1}; ^{13}C-nmr (62.5 Hz, DMSO-d_6): δ 15.2 (*C*H_3CN), 30.6 (*C*H_3CO), 55.2 (CH_3O), 99.0 (CH), 112.0 (*C*COCH$_3$), 113.6 (CH), 123.3 (CH), 123.4 (CH), 126.6 (CH), 128.7 (CH),129.6 (CH), 130.9 (C quart), 137.1 (NC*N*C), 142.9 (C quart), 144.2 (C quart), 150.5 (C quart), 154.8 (C quart), 155.7 (N=*C*CH_3), 191.8 (C=O). [h] ms: m/z (%) 418 (M^+, 1), 416 (22), 415 (73), 298 (23), 180 (18), 118 (15), 115 (19), 105 (100), 91 (25), 77 (92), 65 (16), 18 (34); the intensive fragment peak at 105 proves the benzoyl substituent thus ruling out an acetyl isomer. [i] ms: m/z (%) 220 (M^+, 100), 193 (12), 165 (20), 139 (23); ir (potassium bromide): ν 3100, 3080, 2940, 2230 (C≡N), 1630-1610 (C=N) cm^{-1}.



3	5	6	Y	R^1	R^2	R^3	R^4	R^5
	a		CCN	H	CH_3	H	CH_3	CH_3
	b		CCN	H	C_6H_5	H	CH_3	CH_3
	c		CCN	H	C_6H_5	CH_3	CH_3	CH_3
	d		CCN	H	CH_2CH_3	CH_3	CH_3	CH_3
	e		CCN	H		$(CH_2)_2$	CH_3	CH_3
	f		CCN	H		H	CH_3	CH_3
	g		CCN	H		H	CH_3	CH_3
	h		CCN	H		$(CH_2)_3$	CH_3	CH_3
	i		CCN	H		$(CH_2)_4$	CH_3	CH_3
	j		CCN	H		$(CH_2)_5$	CH_3	CH_3
	k		CCN	H	C_6H_5	H	$CH_2C(CH_3)_2CH_2$	
	l		CCN	H	C_6H_5	CH_3	$CH_2C(CH_3)_2CH_2$	
	m		CCN	H		$(CH_2)_2$	$CH_2C(CH_3)_2CH_2$	
	n		CCN	H		H	$CH_2C(CH_3)_2CH_2$	
	o		N	C_6H_5	4-$CH_3C_6H_4$	H	CH_3	CH_3
	p		N	4-$CH_3OC_6H_4$	C_6H_5	H	CH_3	CH3
	q		N	4-$CH_3OC_6H_4$	4-$CH_3C_6H_4$	H	CH_3	CH_3
r	r		N	C_6H_5	4-$CH_3C_6H_4$	H	$CH_2C(CH_3)_2CH_2$	
	s		N	C_6H_5	4-$CH_3C_6H_4$	H	CH_3	C_6H_5
	t		N	C_6H_5	4-$CH_3C_6H_4$	H	CH_3	OCH_2CH_3
	u		N	C_6H_5	4-$CH_3C_6H_4$	H	4-NO_2-C_6H_4	OCH_2CH_3
		v	CCN	H	C_6H_5	H	H	

occurs. The resulting dihydroheterocycle **3** suffers further oxidation to a conjugated system **4** which finally cyclizes by intramolecular hydrazone formation. Most probably, depending on the nature of substituents Y, R^1-R^5, different mechanisms can conduct the dehydrogenation step from **3** to **4**. A number of the aromatic pyrazolo products **5** (*eg*, **5a-f, 5j, 5n**) were obtained in high yields suggesting the oxygen of the air acts as an oxidizing reagent. In other cases yields were below 50% and can not be increased by the addition of an external oxidizing reagent such as bromine or hydroperoxide. The effect of excluding air in one of the latter cases **5o** did not effect the yield at all. These results suggests that most probably a redox disproportionation takes place giving both, the aromatic **5** and a reduction product,

which however could not be isolated from the complex reaction mixture. Such a disproportionation reaction could also explain, the yields being at maximum 50% in such cases. Suitable 1,3-dicarbonyl compounds **2** for the synthesis of condensed pyrazoles **5** are especially 1,3-pentandione, dimedone, benzoylacetone (only for Y = N) and β-ketoacetates. Dibenzoylmethane gave no reaction with pyridines **1** (Y = CCN) while formylacetone **2** (R^4 = H, R^5 = CH_3) reacts as acetic acid derivative to give triazolopyridines **6.**

These results demonstrate that the formation of condensed triazoles which is documented in literature for other semicyclic amidrazones plays a minor role in reactions of 1-aminopyridines and pyrimidines **1**. So far formation of pyrazolo[1,5-*a*]pyridines in reactions with 1,3-diketones [2] or 1,3-dicarbonyl derivatives [5,6,7] under dehydrogenation was only found in 1-aminopyridines, lacking an amino or imino group in position 2. Furthermore 1-amino-2-methylthiopyridinium salts are known to form pyrazolo[1,5-*a*]pyridines too in reactions with 1,3-dicarbonyl compounds without a dehydrogenation process being involved [8].

The proposed structure of the new compounds **3**, **5** and **6** is in good agreement with the spectroscopic data obtained. It is clearly seen from the ^{1}H-nmr that the heterocyclic proton adjacent to the ring nitrogen atom of the reactant **1** is missing in the product proofing a substitution at this position. The structure of the dihydropyrimidine derivatives **3** is supported by the observation of an ABX-signal system in the ^{1}H-nmr spectrum also ruling out other possible tautomeric structures.

EXPERIMENTAL

Melting points are determined on a "Boetius" hot-stage apparatus and are uncorrected. The ^{1}H nmr spectra were recorded on a Tesla BS 587 (80 MHz) FT or a Bruker AC 300 spectrometer. The ^{13}C nmr spectra were measured on a Bruker AC 300. Tetramethylsilane was used as the internal reference in deuterated dimethyl sulfoxide unless specified otherwise. Mass spectra (ms) were taken with a Hewlett Packard 599 SA spectrometer (electron impact). Infrared spectra were taken with a Perkin Elmer 580 B in potassium bromide. Elemental analyses were determined by the microanalytical laboratory of Humboldt-University Berlin.

The ^{1}H nmr spectral abbreviations are: d = doublet, m = multiplet, s = singlet.

Condensed Pyrazoles **5** and Intermediate **3** .

General Procedures.

Method A.

A mixture of 1-amino-2(1*H*)-pyridin-2-imine **1** (Y = CCN) (0.01 mole), 1,3-dicarbonyl compound **2** (0.02 mole) and 20 ml of methanol was refluxed for 30 minutes. After cooling to room temperature the product is filtered by suction, washed with a few ml of ethanol and recrystallized.

Method B.

A mixture of 1-amino-2(1*H*)-pyridin-2-imine **1** (Y = CCN) (0.01 mole), 1,3-dicarbonyl compound **2** (0.02 mole) and 10 ml mesitylene is refluxed for 15 minutes. After diluting with 10 ml of ethanol the solution is kept in a refrigerator for 12 hours. The product is isolated according to method A.

Method C.

Analogous to method B but using diphenyl ether instead of mesitylene. The mixture is heated to 200° for 5 minutes.

Method D.

A mixture of 1-amino-2(1*H*)-pyrimidin-2-imine **1** (Y = N) hydroiodide (0.01 mole), 1,3-dicarbonyl compound **2** (0.01 mole), 20 ml of acetonitrile and 2 ml of triethylamine is refluxed for 15 minutes. If the product does not precipitate after cooling to room temperature the solvent is evaporated. The product is filtered by suction and recrystallized.

Method E.

A mixture of the dihydropyrimidine intermediate **3** (3.6 mmoles) and 15 ml acetic acid is combined with hydrochloric acid (0.13 g, 3.6 mmoles) and subsequently refluxed for 1 hour. After cooling to room temperature the crystallization of the product is completed by the addition of about 7 ml of water. The product is filtrated and recrystallized.

7-Phenyl-1,2,4-triazolo[1,5-*a*]pyridine **6v.**

A mixture of 1-amino-2(1*H*)-pyridin-2-imine **1** (Y = CCN) (0.01 mole), formylacetone **2** (R^4 = H, R^5 = CH_3, as the Na-salt) (1.62 g, 0.015 mole) and 30 ml of acetic acid is refluxed for 30 minutes. The resulting solution is diluted with 30 ml of water and kept in a refrigerator for 12 hours. The product is filtered by suction and recrystallized.

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