Synthesis of New Zwitterionic Pyridazino-*as*-triazines[1)]

Zsuzsanna Juhász-Riedl[a], György Hajós*[a], Eszter Gács-Baitz[a], Gert Kollenz[b], and András Messmer[a]

Central Research Institute of Chemistry[a],
P.O. Box 17, H-1525 Budapest, Hungary

Institute of Organic Chemistry, University of Graz[b],
Heinrichstraße 28, A- 8010 Graz, Austria

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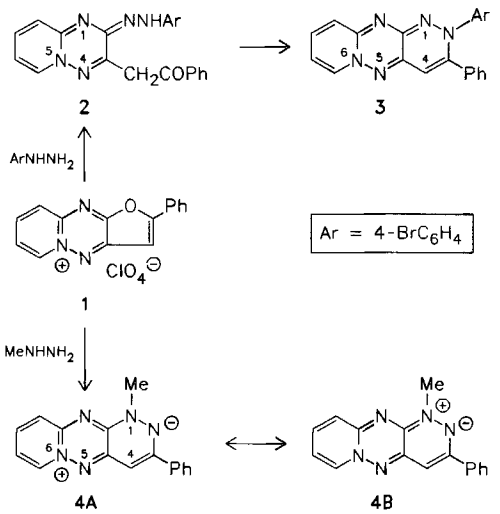
Reaction of the furo[2,3-*e*]pyrido[1,2-*b*]-*as*-triazinium salt **1** with methyl hydrazine gave the zwitterionic 1-substituted pyrido-pyridazino-*as*-triazine **4**. The neutral 2-substituted isomer **6** was formed when **1** was treated with 1-formyl-1-methylhydrazine. Reaction of **1** with 1-acyl-2-methylhydrazine gave rise to 1,3,4-trisubstituted zwitterionic derivatives of the same ring system. Efforts to synthesize aryl-substituted zwitterions led to simultaneous formation of the desired compound **12** and of a new ring transformation product, the pyrazolopyrido-*as*-triazine derivative **15**.

Recently, we reported that furo[2,3-*e*]pyrido[1,2-*b*]-*as*-triazinium salt **1** reacts with arylhydrazine to give the ring-opened hydrazone **2**, which can subsequently be cyclized to the fused pyridazine compound **3** of blue color[2)]. To prepare further derivatives on extension of this reaction seemed to be of interest, and **1** was therefore treated with methyl hydrazine. Unexpectedly, the reaction mixture rapidly changed color to deep green indicating a different course of the reaction compared to the earlier cases (i.e. to formation of the yellow hydrazone **2**).

Scheme 1



Spectroscopic analysis of the green crystals obtained from this reaction mixture revealed that, although the structure of the new compound is reminiscent of 2,3-diaryl-2*H*-pyrido[1,2-*b*]pyridazino[3,4-*e*]-*as*-triazine (**3**), the methyl group derived from the reagent is attached to N-1 instead of to N-2, and compound **4** was formed in one step.

Two important spectroscopic data proved to be decisive in the assignment of this zwitterionic structure: (i) no NOE was found between methyl and *ortho*-phenyl protons, while long-range (vicinal) heterocorrelation was observed between the methyl protons and the C-11a carbon, which rules out the 2-methyl structure analogous to **3**; (ii) the UV spectrum showed a significant "negative solvatochromy"[3)] typical for a zwitterionic structure like **4**. As resonance structures **4A** and **4B** demonstrate, there is extended delocalization of the positive charge over 5 centers, which renders both the bridge-head N-6 and N-1 partially positive. On the basis of NMR shifts and their comparison to the corresponding non-zwitterionic compound (**6**, see below) structure **4B** seems to make a greater contribution to the overall structure.

The formation of **4** requires that methylhydrazine reacts at the nitrogen atom bearing the methyl group, the basicity of which is obviously larger than that of the amino nitrogen[4)]. An appropriate modification of the reagent seemed therefore to be necessary to prepare the originally desired, *N*-2-substituted methyl compound. For this purpose, blocking of the more basic nitrogen of methylhydrazine proved to be suitable, and 1-formyl-1-methylhydrazine was prepared according to a text book procedure[5)].

On reaction with **1** this reagent led to formation of a yellow product, which proved to be a mixture of two different crystalline compounds; these could be separated by column chromatography. The major product was the substituted hydrazone **5** (analogous to **2**) which, on treatment with acid and subsequently with base, gave the expected 2-methylpyridazine **6**, an isomer of **4**. This compound, similarly to the aryl analogue **3**, has a blue color; NMR analysis showed a significant NOE between the methyl and *ortho*-phenyl protons: long-range (vicinal) heterocorrelation was found between the methyl protons and C-3, and, moreover, no negative solvatochromy could be observed in its UV spectrum. All these spectroscopic findings fit nicely with the structural differences between **4** and **6**.

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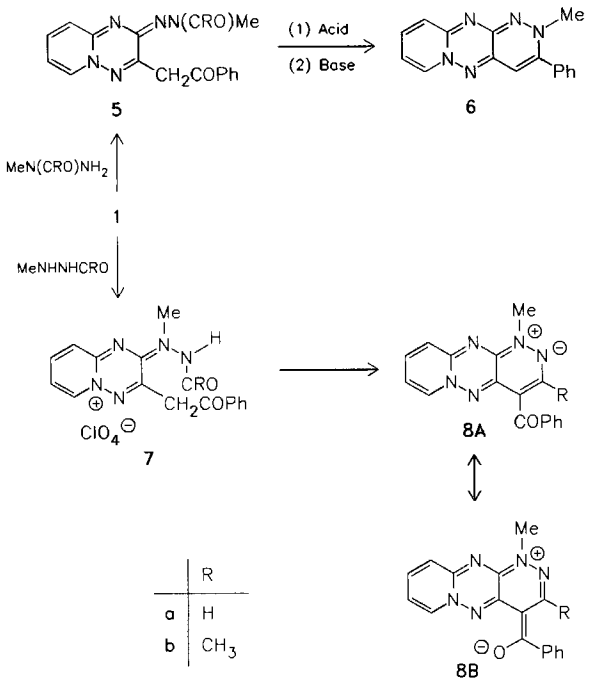
Scheme 2



Chromatographic separation of the minor product led to isolation of a new red crystalline compound in a yield of approximately 15 per cent. Its NMR spectrum revealed that a 4-benzoyl-1-methyl-substituted derivative of the same ring system was formed, shown here by the two resonance structures **8aA** and **8aB**. Formation of this product can be explained by supposing the presence of 1-formyl-2-methylhydrazine in the reagent. Like methylhydrazine, this compound is also able to react at the nitrogen atom attached to the methyl group, and formation of intermediate **7a** can be postulated. This intermediate has, however, the structural feature that the phenacyl methylene group can attack the formyl carbonyl group under basic conditions; water elimination results in formation of the fused pyridazine ring bearing the benzoyl group at C-4 as well as the methyl group at N-1.

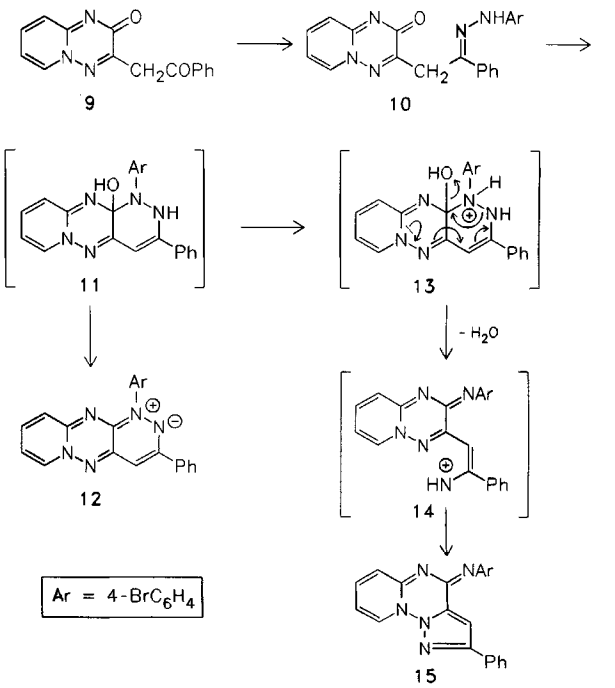
The structure of **8a** was further corroborated by two NOE measurements: (i) between 3-H and the *ortho*-phenyl protons there is a significant NOE, (ii) no NOE effect can, however, be found between the methyl protons and 3-H. Moreover, the methyl protons gave long-range heterocorrelation with C-11a, while no such correlation was found with C-3; the 2-methyl structure can thus safely be excluded. Furthermore, a definite negative solvatochromy was found in the UV spectrum, supporting the zwitterionic structure of **8a**; the yellow color of the product (first UV maximum at $\lambda = 446$ nm in chloroform) seems to reveal a greater contribution of resonance structure **8B** than **8A**, because structure **8A** having an electronic system analogous to that of **4**, would be expected to be green.

This proposed mechanism implies the action of 1-formyl-2-methylhydrazine, the presence of which, besides the 1,1-isomer, has not been reported in the literature. To check this, we carried out a 400-MHz NMR study to clarify the composition of the reagent prepared according to the known procedure. When compared with recent literature data[6] concerning the NMR assignment of the rotamers of 1-formyl-1-methylhydrazine the observed signals revealed that, as supposed, 1-formyl-2-methylhydrazine was also present in 10 per cent. The restricted rotation about the amide bond allowed to distinguish between the protons belonging to *E* (major) and *Z* (minor) isomers (NCH_3: $\delta = 2.67$ and 2.70, respectively; CHO: $\delta = 8.08$ and 8.06, respectively).

The above assumption that formation of **8a** was due to the presence of minor amounts of the 1,2-isomer in the reagent could nicely be proved by treating pure 1-formyl-2-methylhydrazine with **1** under the above conditions. Because of lack of any feasible preparation of this isomeric hydrazine[7], this was carried out with its acetyl analogue as follows. Reaction of **1** with pure 1-acetyl-2-methylhydrazine[8] gave the colorless crystalline salt **7b** in 80% yield, which proved to have a structure analogous to the intermediate supposed for the corresponding reaction with the formyl reagent. Treatment of the compound **7b** with base afforded the desired **8b** in acceptable yield. Both NMR and IR data of **8b** could be correlated with those of its demethyl analogue **8a**. It is interesting to note that 1-acetyl-1-methylhydrazine, which is also easily available in pure form, gives rise to the same blue-colored **6** which was obtained with the formyl reagent (obviously, however, through the different intermediate **5b**).

Observation of the above regioselective reactions prompted us to prepare 1-aryl-substituted analogues of the zwitterion **4** as well. For this purpose, phenacyl-pyridotriazinone **9** described by us recently[2] was treated with arylhydrazine. In **9** a higher reactivity of the phenacyl carbonyl

Scheme 3



group can be presumed compared to the lactam-type carbonyl function, and formation of the hydrazone **10** can be expected. The reaction afforded product **10** indeed, which proved to be different from the isomeric compound **2** and, in accordance with the C—N bond formation, the NMR signal of the carbonyl carbon atom underwent a marked upfield shift.

Treatment of hydrazone **10** with acid, however, showed an unexpected result. Depending on the type of acid used in this conversion, two products were formed in different ratios. One of these (green spot on TLC) proved to be the desired zwitterionic 1-arylpyridazine **12**. This new, green, crystalline compound was compared with **3** and showed the same differences in NMR- and UV-spectroscopic behavior as expected on the basis of two differently substituted (i.e., zwitterionic and neutral) methyl compounds **4** and **6**.

Besides this, however, a colorless compound could be isolated in considerable yield varying from 28 to 44 per cent, showing an MS molecular ion peak and elemental analysis identical to that of **12**. From NMR decoupling experiments we concluded that a ring transformation had occured and a derivative of a new tricyclic ring system [4-(4-bromophenylimino)-2-phenyl-4*H*-pyrazolo[2,3-*f*]pyrido[1,2-*b*]-*as*-triazine (**15**)] was formed. Since the two isolated products **12** and **15** could not be interconverted by treatment with acid we must suppose that formation of **15** is due to protonation of the common intermediate **11** at the N-1 atom bearing the aryl group. The protonated form **13** can then undergo fragmentation involving cleavage of the N-1—N-2 bond and water elimination as shown by the arrows in the formula, and the attack of the resulting nitrenium cation **14** on the *as*-triazine nitrogen yields the considerably stable five-membered ring in **15**.

In summary this work indicated that the reaction of **1** with various substituted hydrazines yield a range of ring transformation products (**3**, **4**, **6**, **8**, **12**, and **15**) in a regioselective manner and with acceptable yields. The electronic distribution of the new zwitterions (**4**, **8**, and **12**) will be subject to further studies.

Thanks are due to Dr. *J. Tamás* for the MS measurements. Gy. H. thanks the *Alexander-von-Humboldt-Stiftung* (Bonn, FRG) for the generous gift of a KRONWALD SEPACHROM preparative MPLC system.

Experimental

Melting points were determined on a Büchi apparatus and are uncorrected. — IR: Specord 75 IR. — NMR: Varian XL-400, TMS as internal standard. — ^{1}H assignments, if necessary, were performed with the aid of homonuclear spin decoupling experiments. Connectivities between identified protons and protonated carbons were obtained by two-dimensional (HETCOR) experiments. Assignment of quaternary carbon atoms was obtained by observing their correlations with identified protons (by long-range HETCOR and one- and two-dimensional INEPT long-range experiments). ^{1}H- and ^{13}C-NMR data of the bicyclic derivatives **2**, **5a**, **5b**, **7b**, **9**, and **10** are summarized in Table 1 and 2, respectively, and those of the tricyclic fused pyridazines **3**, **12**, **6**, **4**, **8a**, and **8b** are collected in Table 3 and 4, respectively. — MS: AEI-902. — Chromatographic separations: KRONWALD SEPACHROM preparative MPLC system using a liquid pressure of 6 bar.

Table 1. ^{1}H-NMR data (δ values, *J* values [Hz] in parentheses) of bicyclic derivatives measured in $CDCl_3$ solutions at ambient temperature

	2	5a	5b	7b[a]	9	10
6-H	7.44 (6.5,1.5)	7.73 (7,1.6,0.5)	7.78 (7,1.5,0.7)	8.81 (7,1.5,0.7)	8.10 (7,1.8,0.5)	8.14 (7,1.6)
7-H	6.24 (7,6.5,1)	6.56 (7,6.8,1.3)	6.61 (7,7,1.5)	7.72 (7,7,1.5)	6.95 (7,7,2)	6.98 (7,7,1.8)
8-H	7.19 (8.5,7,1.5)	7.42 (8.5,6.8,1.6)	7.46 (9,7,12.5)	8.39 (9,7,1.5)	7.70 (8.5,7,1.8)	7.70 (8.5,7,1.6)
9-H	6.70 (8.5,1)	6.93 (8.5,1.3,0.5)	7.00 (9,1.5,0.7)	7.94 (9,1.5,0.7)	7.37 (8.5,2,0.5)	7.35 (8.5,1.8)
1'-H	4.20	4.33	4.38	4.82,5.02 (18)	4.54	4.35
4'-,8'-H	8.05	8.03	8.02	8.09	8.04	8.04
5'-,7'-H	7.51	7.51	7.51	7.61	7.50	7.40
6'-H	7.62	7.61	7.62	7.74	7.60	7.33
2''-,6''-H	6.64	-	-	-	-	7.34
3''-,5''-H	7.11	-	-	-	-	7.19
NCH_3	-	3.28	3.26	3.56	-	-
NCHO	-	8.26	-	-	-	-
NH	8.40	-	-	10.79	-	8.01
$COCH_3$	-	-	1.84	1.64	-	-

[a] In $CDCl_3$ + [D_6]DMSO solution.

Table 2. ^{13}C-NMR data (δ values) of bicyclic derivatives

	2[a]	5a[b]	5b[b]	7b[a]	9[b]	10[b]
C-2	154.49	154.10	154.06	152.65	160.18	161.47
C-3	143.88	146.55	147.33	147.08	156.37	155.90
C-6	136.66	136.32	136.34	137.86	136.38	136.43
C-7	109.00	110.85	111.04	120.13	113.55	114.44
C-8	137.56	137.70	137.71	143.07	137.64	138.08
C-9	122.14	123.30	123.51	124.41	124.35	124.20
C-9a	150.07	148.95	149.13	146.54	152.22	151.56
C-1'	40.48	41.53	41.76	46.09	40.96	29.04
C-2'	195.16	194.93	194.63	193.47	194.50	144.89
C-3'	136.73	136.58	136.60	134.65	136.82	136.93
C-4',C-8'	128.48	128.36	128.33	128.45	128.54	125.90
C-5',C-7'	128.77	128.74	128.77	129.00	128.77	128.31
C-6'	133.51	133.60	133.65	134.50	133.76	127.98
C-1''	135.70	--	--	--	--	137.56
C-2'',C-6''	113.93	--	--	--	--	115.18
C-3'',C-5''	131.55	--	--	--	--	131.75
C-4''	109.94	--	--	--	--	111.79
NCH_3	--	33.24	34.05	40.61	40.96	--
NCO	--	163.69	171.28	170.77	--	--
$COCH_3$	--	--	21.33	20.41	--	--

[a] In $CDCl_3$ + [D_6]DMSO solution. — [b] In $CDCl_3$ solution.

Table 3. ^{1}H-NMR data (δ values, *J* values [Hz] in parentheses) of tricyclic fused pyridazines measured in $CDCl_3$ solution at ambient temperature

	3	12	6	4	8a	8b
3-H	-	-	-	-	6.99	-
4-H	4.80	5.09	4.41	4.78	-	-
7-H	6.75 (7,1.5,1)	7.10 (7,1.5)	6.59 (7,2,0.6)	6.81 (7,1.5,0.6)	7.37 (7,1.8,0.5)	6.61 (7,1.5)
8-H	5.91 (7,7,2)	6.29 (7,7,1.5)	5.83 (7,7,1.5)	6.12 (7,7,1,6)	6.47 (7,7,1.5)	6.17 (7,7,1.5)
9-H	6.85 (8.5,7,1.5)	6.90 (8.5,7,1.5)	6.75 (8.5,7,2)	6.79 (8.5,7.5,1.5)	7.20 (8.5,7,1.8)	6.95 (8.5,7,1.5)
10-H	6.17 (8.5,2,1)	6.04 (8.5,1.5)	6.01 (8.5,1.5,0.6)	6.03 (8.5,1.6,0.6)	6.49 (8.5,1.5,0.5)	6.27 (8.5,1.5)
2'-,6'-H	7.01	7.53	7.20	7.48	7.55	8.00
3'-,5'-H	7.20	7.33	7.40	7.30	7.37	7.42
4'-H	7.28	7.33	7.40	7.30	7.37	7.49
2''-,6''-H	6.85	7.40	-	-	-	-
3''-,5''-H	7.20	7.52	-	-	-	-
NCH_3	-	-	2.88	3.08	3.14	3.10
CH_3	-	-	-	-	-	1.66

Table 4. ^{13}C-NMR data (δ values) of tricyclic fused pyridazines in $CDCl_3$

	3	12	6	4	8a	8b
C-3	153.71*)	157.22	155.48	157.22	151.51	155.74
C-4	101.36	88.48	97.93	89.46	100.61	101.68
C-4a	151.20*)	155.14	152.68	153.56	150.39	150.57
C-7	135.99	134.73	135.68	134.73	137.11	135.76
C-8	109.70	116.23	109.51	115.18	115.87	115.16
C-9	137.76	135.93	137.46	136.25	138.41	136.76
C-10	121.09	120.73	120.76	120.15	121.41	120.62
C-10a	156.43*)	155.05	157.23	155.95	153.31	154.14*)
C-11a	154.69*)	153.90	156.37	154.77	153.21	153.25*)
C-1'	134.17	135.93	133.95	135.95	140.24	138.73
C-2',C-6'	128.53	125.22	128.89	125.02	128.01	128.36
C-3',C-5'	127.58	128.18	127.29	128.15	128.09	128.63
C-4'	129.45	129.25	129.68	129.06	130.38	132.08
C-1''	141.91	140.19	-	-	-	-
C-2'',C-6''	131.12	131.52	-	-	-	-
C-3'',C-5''	126.65	127.40	-	-	-	-
C-4''	119.46	121.27	-	-	-	-
NCH_3	-	-	42.54	39.46	39.47	38.97
CO	-	-	-	-	190.31	194.14

*) The values marked with asterisks are interchangeable within the column.

1-Methyl-3-phenylpyrido[1,2-b]pyridazino[3,4-e]-as-triazinium-2-ide (**4**): A suspension of 2-phenylfuro[2,3-*e*]pyrido[1,2-*b*]-*as*-triazinium perchlorate (**1**, 0.70 g; 2.0 mmol) in acetonitrile (5 ml) was treated with methylhydrazine (0.5 ml), whereupon a dark solution was formed and green crystals commenced to precipitate. Water (5 ml) was added, and the crystalline product was filtered off to give 0.40 g (72%) of product; mp 191°C. – IR (KBr): ν = 3010 cm^{-1}, 1610, 1460, 1300, 1210, 1140, 1100, 920, 880, 840, 740, 690, 670. – UV (acetonitril): λ_{max} (lg ε) = 251 nm, (4.233), 302 (4.732), 377 (3.931), 426 (4.419), 585 (2.736). – MS (70 eV): *m/z* = 275 [M^+].

$C_{16}H_{13}N_5$ (275.3) Calcd. C 69.80 H 4.76 N 25.43
Found C 69.46 H 4.75 N 25.44

3-(Benzoylmethyl)-2-(2-formyl-2-methylhydrazono)-2H-pyrido[1,2-b]-as-triazine (**5a**): A mixture of perchorate salt **1** (0.35 g; 1 mmol), acetonitrile (3 ml), and 1-formyl-1-methylhydrazine (0.15 g; 2 mmol) was stirred at room temperature for one day. Triethylamine (0.2 ml) was then added, the solution was evaporated, and the residue was chromatographed on alumina with chloroform. The first (i.e., less polar) red fraction was put aside for other purposes (see preparation of **8a**), and the subsequent yellow main fraction was collected and recrystallized from ethanol to give 0.11 g (34%) of yellow crystals; mp 185–188°C. – IR (KBr): ν = 3030 cm^{-1}, 1690, 1630, 1600, 1580, 1510, 1380, 1320, 1210, 1180, 1050, 1100, 860, 760, 710.

$C_{17}H_{15}N_5O_2$ (321.3) Calcd. C 63.55 H 4.67 N 21.80
Found C 63.52 H 4.67 N 21.94

2-(2-Acetyl-2-methylhydrazono)-3-benzoylmethyl-2H-pyrido[1,2-b]-as-triazine (**5b**): To a suspension of perchlorate salt **1** (0.35 g, 1 mmol) in acetonitrile (3 ml), 1-acetyl-1-methylhydrazine (0.18 g, 2 mmol) was added dropwise during 30 min. The resulting clear solution was then stirred for 24 h, it was diluted with water (20 ml) and extracted with dichloromethane (3 × 20 ml). After evaporation of the organic solvent the residue was recrystallized from ethyl acetate to afford 0.25 g (74%) of orange crystals; mp 137 to 139°C. – IR (KBr): ν = 2900 cm^{-1}, 1680, 1650, 1640, 1580, 1500, 1450, 1370, 1350, 1310, 1280, 1120, 1010, 990, 760.

$C_{18}H_{17}N_5O_2$ (335.4) Calcd. C 64.46 H 5.11 N 20.88
Found C 64.68 H 5.14 N 20.97

2-Methyl-3-phenyl-2H-pyrido[1,2-b]pyridazino[3,4-e]-as-triazine (**6**): A suspension of perchlorate salt **1** (0.35 g, 1 mmol) in acetonitrile (3 ml) was treated with 1-formyl-1-methylhydrazine (0.15 g; 2 mmol) and was then stirred at room temperature for 24 h. The resulting solution was evaporated, methanol (3 ml) and aqueous hydrogen bromide (40%, 0.5 ml) were added, the solution was allowed to stand for an additional 24 h, and was then diluted with water (10 ml) and neutralized with 10% sodium hydroxide solution to pH = 8–9. The mixture was extracted with three portions of chloroform (3 × 30 ml), the organic solvent was evaporated, and the residue was recrystallized from acetonitrile to give 0.15 g (55%) of blue crystals; mp 140–141°C. (The same product was obtained when **5a** was treated with acid as described here for **1**.) – IR (KBr): ν = 3020 cm^{-1}, 2910, 1620, 1560, 1540, 1490, 1440, 1370, 1320, 1290, 1260, 750, 700. – UV (acetonitrile): λ_{max} (lg ε) = 287 nm (4.553), 375 (4.121), 396 (4.072), 575 (2.613), 631 (2.559). – MS (70 eV): *m/z* = 275 [M^+].

$C_{16}H_{13}N_5$ (275.2) Calcd. C 69.80 H 4.76 N 25.44
Found C 69.65 H 4.77 N 25.35

2-(2-Acetyl-1-methylhydrazino)-3-(benzoylmethyl)pyrido[1,2-b]-as-triazinium Perchlorate (**7b**): A suspension of perchlorate salt **1** in acetonitrile (3 ml) was treated with 1-acetyl-2-methylhydrazine (0.18 g, 2 mmol) during 30 min and was then stirred for 24 h. Ether was added, and the separated colorless crystals were filtered off to give 0.38 g (87%) of product; mp 196–198°C. – IR (KBr): ν = 3230 cm^{-1}, 3060, 2930, 1710, 1650, 1580, 1560, 1450, 1390, 1320, 1280, 1250, 1200, 1100, 760, 750, 680, 600.

$C_{18}H_{18}ClN_5O_6$ (435.8) Calcd. C 49.60 H 4.16 N 16.07
Found C 49.77 H 4.25 N 16.27

4-Benzoyl-1-methylpyrido[1,2-b]pyridazino[3,4-e]-as-triazinium-2-ide (**8a**): In the course of the preparation of **5a**, the red minor fraction obtained by column chromatography was collected and recrystallized from methanol to give 0.05 g of red crystals; mp 197–198°C. – IR (KBr): ν = 3070 cm^{-1}, 2920, 1620, 1560, 1550, 1480, 1400, 1350, 1330, 1280, 900, 750, 710. – MS (70 eV): *m/z* = 303 [M^+], 226 [$M - C_6H_5^+$].

$C_{17}H_{13}N_5O$ (303.3) Calcd. C 67.32 H 4.32 N 23.09
Found C 67.22 H 4.32 N 22.87

4-Benzoyl-1,3-dimethylpyrido[1,2-b]pyridazino[3,4-e]-as-triazinium-2-ide (**8b**): A mixture of compound **7b** (0.3 g, 0.7 mmol), acetonitrile (5 ml), and triethylamine (0.3 mol) was allowed to stand at room temperature for 2 d. The separated red crystals were filtered off, the mother liquor was chromatographed on alumina using chloroform as eluent, and the red fraction was collected and added to the filtered product. Recrystallization from methanol gave 0.14 g (64%) or product; mp 196–205°C. – IR (KBr): ν = 3050 cm^{-1}, 2900, 1620, 1520, 1480, 1420, 1360, 1350, 1200, 880, 750.

$C_{18}H_{15}N_5O$ (317.4) Calcd. C 68.12 H 4.76 N 22.07
Found C 68.18 H 4.79 N 22.07

3-[2-(4-Bromophenylhydrazono)-2-phenylethyl]-2H-pyrido[1,2-b]-as-triazin-2-one (**10**): A mixture of 3-(benzoylmethyl)-2*H*-pyrido-[1,2-*b*]-*as*-triazin-2-one (**9**; 1.32 g, 5 mmol), dry ethanol (40 ml), 4-bromophenylhydrazine hydrochloride (1.3 g), sodium acetate (0.5 g), and chloroform (50 ml) was heated at reflux for 2 h. Water (100 ml) was then added, the mixture was extracted with chloroform (5 × 50 ml), and the extracts were evaporated. Recrystallization of the residue from dimethylformamide gave 1.8 g (83%) of product; mp 225–226°C. – IR (KBr): ν = 3220 cm^{-1}, 3080, 1640, 1610, 1590, 1570, 1480, 1430, 1270, 1240, 800, 750. – MS (70 eV): *m/z* = 434 [M^+].

$C_{21}H_{16}BrN_5O$ (434.3) Calcd. C 58.06 H 3.68 N 16.12
Found C 58.27 H 3.90 N 16.03

1-(4-Bromophenyl)-3-phenylpyrido[1,2-b]pyridazino[3,4-e]-as-triazinium-2-ide (**12**): A mixture of hydrazone **10** (0.43 g, 1 mmol), ethanol (5 ml), and concd. hydrochloric acid (0.5 ml) was heated at reflux for 4 h to give a red solution. Water (10 ml) was then added, the mixture was neutralized with sodium hydroxide and extracted with chloroform (3 × 20 ml). TLC of the crude product obtained upon evaporation of the organic solvent showed two components: a more polar colorless and a less polar green spot. Separation of this latter by column chromatography using chloroform afforded 0.15 g (36%) of green crystals; mp 231–232°C. – IR (KBr): ν = 3050 cm^{-1}, 2900, 1610, 1520, 1510, 1480, 1430, 1400, 1290, 810, 740. – UV (ethanol): λ_{max} (lg ε) = 254 nm (4.364), 306 (4.711), 428 (4.152), 575 (2.831). – MS (70 eV): *m/z* = 416 [M^+].

$C_{21}H_{14}BrN_5$ (416.3) Calcd. C 60.59 H 3.39 N 16.82
Found C 60.60 H 3.43 N 16.71

4-(4-Bromophenylimino)-2-phenyl-4H-pyrazolo[2,3-f]pyrido[1,2-b]-as-triazine (**15**): The colorless fractions in the chromatographic separation described with compound **10** were collected and recrystallized from toluene to give 0.11 g (26%) of product; mp 232–234°C. – IR (KBr): ν = 3000 cm^{-1}, 1630, 1590, 1490, 1450, 1370, 1350, 1325, 1300, 1260, 1060, 1000, 830, 760, 740, 690. – ^1H NMR (400 MHz, $CDCl_3$): δ = 8.51 (dd, 1H, 9-H, J_o = 7.0 Hz, J_m = 1.5 Hz), 7.94 (m, 2H, 2′-, 6′-H), 7.74 (d, 1H, 11-H, J_o = 8.5 Hz, J_m = 1.5 Hz), 7.56, 7.46 (m, 4H, 2″-, 3″-, 5″-, 6″-H), 7.54 (m, 1H, 7-H, J_o = 8.5 and 7.0 Hz, J_m = 1.5 Hz), 7.45, 7.36 (m, 3H, 3′-, 4′-, 5′-H), 7.41 (s, 1H, 3-H), 7.05 (m, 1H, 8-H, J_o = 7.0 and 7.0 Hz, J_m = 1.5 Hz). – ^{13}C NMR ($CDCl_3$): δ = 156.16 (C-4), 152.49 (C-2), 150.95 (C-5a), 139.51 (C-1″), 135.49 (C-1′), 132.44 (C-3a), 131.74 (C-2″, -6″), 130.06 (C-7), 128.72 (C-3′, -5′), 128.48 (C-9), 128.29 (C-4′), 127.42 (C-3″, -5″), 125.84 (C-2′, -6′), 121.75 (C-4″), 116.73 (C-6), 114.24 (C-8), 107.69 (C-3). – UV (ethanol): λ_{max} (lg ε) = 248 nm (4.630). – MS (70 eV): *m/z* = 416 [M^+].

$C_{21}H_{14}BrN_5$ (416.3) Calcd. C 60.59 H 3.39 N 16.82
Found C 60.30 H 3.44 N 16.71

CAS Registry Numbers

1: 121232-63-1 / **2**: 121232-71-1 / **3**: 121232-72-2 / **4**: 126134-46-1 / **5a**: 126134-47-2 / **5b**: 126134-48-3 / **6**: 126134-49-4 / **7b**: 126134-51-8 / **8a**: 126134-52-9 / **8b**: 126134-53-0 / **9**: 121232-61-9 / **10**: 126134-54-1 / **12**: 126134-55-2 / **15**: 126134-56-3 / methylhydrazine: 60-34-4 / 1-formyl-1-methylhydrazine: 758-17-8 / 1-acetyl-1-methylhydrazine: 3530-13-0 / 1-acetyl-2-methylhydrazine: 29817-35-4 / 4-bromophenylhydrazine hydrochloride: 622-88-8

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