Synthesis and Ring Transformation of a New Fused *as*-Triazinium Salt

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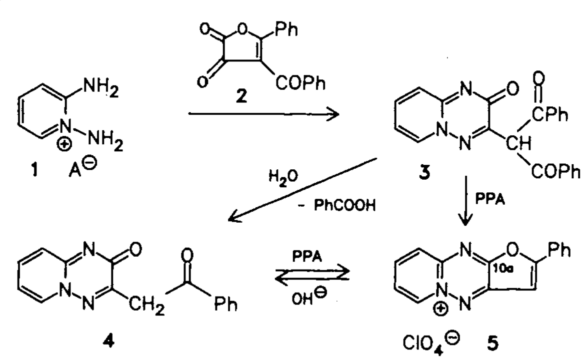
The 1,2-Diaminopyridinium salt **1** was treated with furandione **2** to give pyrido-*as*-triazinone **3**, which could be cyclized to the tricyclic furo[2,3-*e*]pyrido[1,2-*b*]-*as*-triazinium salt **5**. Reaction of **5** with nucleophiles resulted in different types of products. Thus, aqueous base afforded bicyclic triazinone **4**, methoxide ion or secondary amine led to stable zwitterions **7a, b**, whereas ammonia and hydrazines resulted in ring transformation of the furan moiety and gave new fused tricyclic pyrroles (**10, 11**) and pyridazines (**13, 14**), respectively.

Synthese und Ringtransformation von neuen kondensierten *as*-Triazinium-Salzen

Die Reaktion des 1,2-Diaminopyridinium-Salzes **1** mit dem Furandion **2** ergab ein Pyrido-*as*-triazinon **3**, das zum tricyclischen Furo[2,3-*e*]pyrido[1,2-*b*]-*as*-triazinium-Salz **5** cyclisiert wurde. Die Reaktion von **5** mit Nucleophilen führte zu unterschiedlichen Produkten: mit wäßriger Base entstand das bicyclische Triazinon **4**, mit dem Methoxid-Ion und sekundären Aminen wurden die stabilen Zwitter-Ionen **7a, b** erhalten, wohingegen Ammoniak und Hydrazine unter Transformation des Furanringes die neuen tricyclischen kondensierten Pyrrole **10, 11** bzw. Pyridazine **13, 14a, b** ergaben.

Earlier results have shown that both 4-benzoyl-5-phenyl-2,3-furandione (**2**) and its thiophene analogue readily react with *o*-phenylenediamine to give fused pyrazines[1,2]. As a continuation of our studies on fused *as*-triazinium salts[3,4] we were now interested in the reaction of this dioxo reagent **2** with a positively charged α-diamine. Earlier literature data[5], and our recent investigations[6], showed that 1,2-diaminopyridinium salt **1** is a suitable starting compound for the synthesis of bridgehead-nitrogen-containing fused systems.

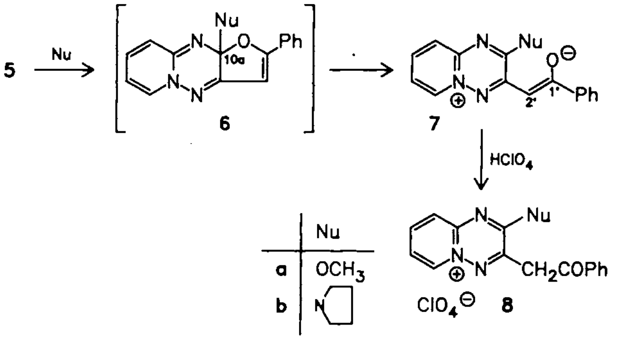
When the diamino salt **1** was treated with **2** under neutral conditions, the expected dibenzoyl compound **3** (cf. ref.[1]) was obtained. On treatment with polyphosphoric acid, ring closure and hydrolytic cleavage of one benzoyl group occurred, affording the desired new ring system: 2-phenylfuro[2,3-*e*]pyrido[1,2-*b*]-*as*-triazinium salt **5**, in poor yield.



However, a much more convenient preparation of **5**, in a yield of 70%, was achieved by the following modification: **3** was carefully hydrolyzed to the monobenzoyl derivative **4**, and this compound **4** was then treated with polyphosphoric acid. The ring-closed structure of **5** was unambiguously proved by the microanalytical, IR (absence of $C=O$ bands), and NMR data (aromatic protons only; characteristic downfield shift at $\delta = 9.43$ of 6-H adjacent to the positive nitrogen; cf. ref.[4]).

This new fused *as*-triazinium salt **5** – like other related bridgehead-nitrogen-containing heteroaromatic cations in our hands[7] – showed a fairly high reactivity towards nucleophiles. Thus, **5** reacted easily with aqueous base, and the starting compound **4** of the ring-closure procedure could be recovered in good yield. In this reaction the hydroxide ion evidently attacked the C-10a atom, with subsequent ring opening of the furan moiety.

It is interesting to note that both compound **4** and the dibenzoyl derivative **3** could exist, in principle, in several tautomeric forms which could not be distinguished clearly by simple spectroscopic methods in any case. Nevertheless, on the basis of its ^{1}H-NMR spectrum, compound **4** has predominantly the depicted structure, i.e. the spectrum implies a benzoylmethylene group as substituent (see Experimental).



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However, when **5** was treated with other nucleophiles such as methoxide or secondary amines (e.g. pyrrolidine), the zwitterions **7a, b** were formed in good yield. The structures of these relatively stable salts were supported both by the downfield shift of 6-H protons adjacent to the positively charged nitrogen (at δ = 8.85 and 8.50, resp.) and by the significant negative solvatochromy found in the UV spectrum of **7a** (Figure 1)[8]. Treatment of **7** with mineral acid afforded pyrido[1,2-*b*]-*as*-triazinium salts bearing the functional group provided by the nucleophilic reagent **8a, b**.

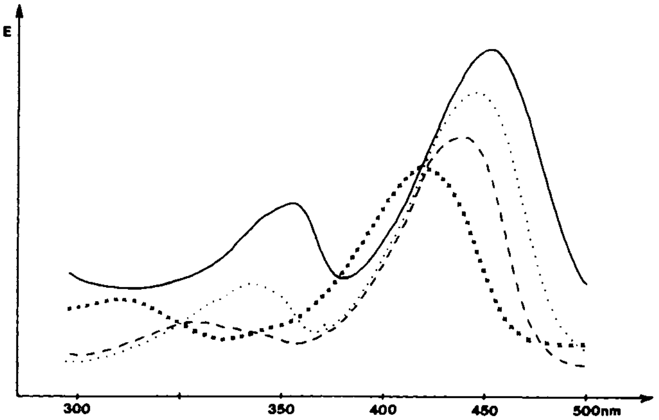
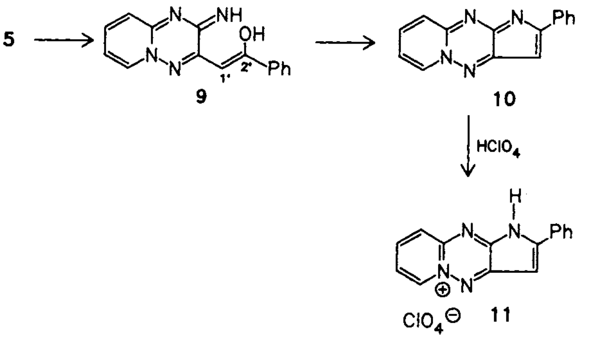


Figure 1.
Comparison of the UV spectra of **7a** in solvents of different polarity — carbon tetrachloride; ... chloroform; — — — ethanol; xxx water

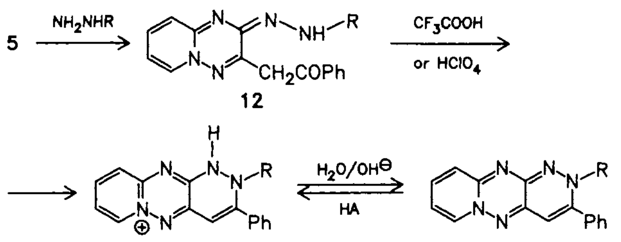
Among nucleophilic reagents, those which were suitable for internal nucleophilic attack in structure **7** form an additional fused ring were of particular synthetic interest[9]. Thus, we found that reaction of **5** with ammonia afforded a ring-opened imine **9** (an analogue of products obtained with other nucleophiles; e.g. **7**) which, on prolonged heating underwent cyclization to give the neutral, tricyclic, new pyrido[1,2-*b*]pyrrolo[2,3-*e*]-*as*-triazine **10** as brilliant red crystals.



9 **10** **11**

The structure of this novel fused heteroaromatic ring system was verified both by its mass spectrum, which showed the expected molecular mass, and by its ^{1}H- and ^{1}H-coupled ^{13}C-NMR spectra, which contained only characteristic aromatic resonances. For the complete assignment of the proton and carbon shifts, a COSY spectrum was recorded and analyzed.

Treatment of this new compound **10** with acid gave rise to the stable, yellow, fused triazinium salt **11**.



12 **13** **14**

$A^{\ominus} = CF_3COO^{\ominus}$ or $ClO_4^{\ominus}$

	R
a	4-Br—C_6H_4
b	H

Reaction of **5** with *p*-bromophenyl hydrazine showed similar nucleophilic attack, and afforded the hydrazone **12a** in the first step, the structure of which is based on IR- and ^{1}H-NMR-spectroscopic data. When **12a** was dissolved in trifluoroacetic acid at room temperature, the initial yellow color of the solution changed to deep red, and red crystals containing trifluoroacetate ion separated from the reaction mixture in acceptable yield. When added to water or to aqueous base this salt underwent facile deprotonation to afford a new deep blue crystalline compound.

Structure elucidation of the colored products was basically accomplished by NMR spectroscopy and mass spectrometry. The ^{1}H-NMR spectrum showed that the red trifluoroacetate salt contains a positively charged pyridine moiety, while the signals of these protons are strongly upfield-shifted in the spectrum of the blue compound. Consideration of the MS molecular mass and fragmentations led to the conclusion that the red compound represents the first derivative of a new ring system: pyrido-[1,2-*b*]pyridazino[3,4-*e*]-*as*-triazinium salt **13**, partially implying a heteroaromatic bicyclic moiety. The blue, neutral deprotonation product seems to have the interesting nonaromatic structure **14**.

Compound **5** was also found to react in an analogous manner with unsubstituted hydrazine hydrate. The hydrazone **12b** formed initially again cyclizes to give the triazinium salt **13b**, subsequently yielding the deep green unsubstituted deprotonation product **14b**. This could, however, only be isolated with difficulty. The spectral behaviour of **13b** and **14b** was found to be reminiscent of the aryl compounds **13a** and **14a**, respectively.

Studies on these interesting new fused triazines are in progress.

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Experimental

Melting points were determined with a Büchi apparatus and are uncorrected. NMR spectra were measured with Varian EMX-360, XL-100, XL-200, and XL-400 spectrometers, infra red spectra were recorded with Specord 75 equipment, and UV spectra were recorded with a Unicam SP 800 spectrometer. Mass spectra were determined with an AEI MS-902 spectrometer.

3-(Dibenzoylmethyl)-2H-pyrido[1,2-b]-as-triazin-2-one (**3**): To a mixture of 1,2-diaminopyridinium perchlorate (4.4 g; 20 mmol), acetonitrile (30 ml), and aqueous sodium hydroxide (1.6 g in 3 ml of water), a solution of 4-benzoyl-5-phenyl-2,3-furandione (**2**, 5.56 g; 20 mmol) in benzene (100 ml) was added at room temperature. The mixture was stirred for 30 min, then evaporated, and the residue was treated with a 5% sodium hydroxide solution (300 ml). This mixture was filtered and the filtrate neutralized with acetic acid, whereupon the product precipitated. Recrystallization from a mixture of acetonitrile and glacial acetic acid afforded 4.8 g (65%) of product; mp 228–229°C. The product was found to crystallize with 1 mol of acetonitrile. – IR (KBr): $\tilde{\nu}$ = 3050, 2235 (C≡N), 1670, 1650, 1600, 1480, 1380, 1280, 1200, 1000, 760, 690 cm^{-1}.

$C_{22}H_{15}N_3O_3CH_3CN$ (410.4) Calcd. C 70.24 H 4.38 N 13.65
Found C 70.42 H 4.52 N 13.60

3-(Benzoylmethyl)-2H-pyrido[1,2-b]-as-triazin-2-one (**4**): Compound **3** (3.7 g; 10 mmol), ethanol (50 ml), and 10% hydrochloric acid (20 ml) were heated for 2 h at reflux. Ice/water (100 ml) was then added, and the reaction mixture was neutralized with 10% sodium hydroxide solution. The precipitated product was filtered off, washed with ethanol, and recrystallized from acetonitrile to give 2.1 g (80%) of monobenzoyl compound **4**; mp 204–205°C. – IR (KBr): $\tilde{\nu}$ = 3050, 1670, 1650, 1600, 1480, 1390, 1370, 1310, 1200, 1190, 1000, 780, 740 cm^{-1}. – ^{1}H NMR (CDCl$_3$/[D$_6$]DMSO, 60 MHz): δ = 8.4–6.9 (m, 9H), 4.6 (s, 2H, CH$_2$).

$C_{15}H_{11}N_3O_2$ (265.3) Calcd. C 67.91 H 4.18 N 15.84
Found C 67.88 H 4.39 N 15.73

2-Phenylfuro[2,3-e]pyrido[1,2-b]-as-triazinium Perchlorate (**5**): A mixture of **4** (5.3 g ; 20 mmol) and polyphosphoric acid (50 g) was stirred at 150–160°C for two hours. The cooled slurry was diluted with ice/water (200 ml) and was then treated with 70% perchloric acid (5 ml), yielding a yellow precipitate. Filtration, washing with ethyl acetate, and recrystallization from nitromethane/ethyl acetate gave 4.9 g (70%) of perchlorate **5**; mp 320°C. – IR (KBr): $\tilde{\nu}$ = 3100, 1630, 1620, 1580, 1490, 1400, 1250, 1100, 780, 690, 620 cm^{-1}. – ^{1}H NMR (trifluoroacetic acid, 60 MHz): δ = 9.43 (d, 1H, 6-H), 8.9–8.6 (m, 2H, 8,9-H), 8.56–8.1 (m, 3H, 7-H, phenyl H), 8.1–7.7 (m, 3H, phenyl H), 7.66 (s, 1H, 3-H).

$C_{15}H_{10}N_3ClO_5$ (347.7) Calcd. C 51.81 H 2.90 N 12.08
Found C 51.97 H 2.98 N 12.11

2-(2-Methoxypyrido[1,2-b]-as-triazin-3-io)-1-phenyl-1-ethenolate (**7a**): To a suspension of **5** (0.35 g; 1 mmol) in methanol (5 ml), a methanolic solution of sodium methoxide (2 mmol) was added dropwise. A clear solution formed initially, followed by precipitation of an orange solid. Recrystallization of the filtered product from acetonitrile yielded 0.18 g (64%) of methoxy compound **7a**; mp 162–164°C. – IR (KBr): $\tilde{\nu}$ = 3050, 1500, 1470, 1400, 1350, 1260, 1220, 1170, 1150, 1060, 980, 840, 770, 710, 700 cm^{-1}. – ^{1}H NMR (CDCl$_3$, 60 MHz): δ = 8.85 (d, 1H, 6-H), 8.3–7.2 (m, 8H, phenyl and pyridyl-H), 6.20 (s, 1H, 2′-H), 4.2 (s, 3H, OCH$_3$). The product proved to be unsuitable for elementary analysis.

$C_{16}H_{13}N_3O_2$ (279.3) Mol. mass 279 (MS)

1-Phenyl-2-(2-pyrrolidinopyrido[1,2-b]-as-triazin-3-io)-1-ethenolate (**7b**): To a suspension of **5** (0.35 g; 1 mmol) in acetonitrile (5 ml), pyrrolidine (0.2 ml) was added, and the mixture was stirred at room temperature for 1 h. Upon addition of the reagent, a clear solution was formed. After stirring, the mixture was treated with ice/water (15 ml), and the precipitated orange solid was recrystallized from acetonitrile to give 0.25 g (79%) of product; mp 176–180°C. – IR (KBr): $\tilde{\nu}$ = 3050, 2950, 2850, 1620, 1580, 1420, 1450, 1380, 1350, 1320, 1210, 760, 700 cm^{-1}. – ^{1}H NMR (CDCl$_3$, 100 MHz): δ = 8.52 (d, 1H, 6-H; J_o = 6 Hz, J_m = 1.2 Hz), 7.90 (m, 2H, phenyl H), 7.75–7.55 (m, 3H, phenyl H), 7.4 (t, 1H, 8-H), 7.20 (d, 1H, 9-H; J_o = 8.5 Hz, J_p = 0.5 Hz), 6.97 (t, 1H, 7-H; J_o = 6.0; 7.0), 5.82 (s, 1H, 2′-H), 3.98 (m, 4H, 1″-H), 2.02 (m, 4H, 2″-H). The product proved to be unsuitable for elementary analysis.

$C_{19}H_{18}N_4O$ (318.4) Mol. mass 318 (MS)

3-(Benzoylmethyl)-2-methoxypyrido[1,2-b]-as-triazinium Perchlorate (**8a**): Following the procedure given for preparation of **8b**, **7a** (0.14 g, 0.5 mmol) afforded 0.14 g (73%) of bright yellow crystals; mp 170–171°C. – IR (KBr): $\tilde{\nu}$ = 3080, 1600, 1520, 1460, 1390, 1330, 1280, 1220, 1100, 970, 780, 710, 680, 610 cm^{-1}. – ^{1}H NMR (trifluoroacetic acid, 60 MHz): δ = 9.15 (d, 1H, 6-H), 8.75 (m, 1H, 8-H), 8.5–7.5 (m, 7H, 7,9-H, phenyl H), 5.2 (s, 2H, CH$_2$), 4.5 (s, 3H, OCH$_3$).

$C_{16}H_{14}N_3ClO_6$ (379.8) Calcd. N 11.06 Found N 10.89

3-(Benzoylmethyl)-2-pyrrolidinopyrido[1,2-b]-as-triazinium Perchlorate (**8b**): Upon addition of 70% perchloric acid (0.1 ml) to a solution of **7b** (0.16 g; 0.5 mmol) in acetonitrile (4 ml) a yellow solid precipitated immediately. Ether was added to the mixture, and the precipitate was filtered off. Recrystallization from acetonitrile/ether afforded 0.16 g (76%) of product, mp 148–150°C. – IR (KBr): $\tilde{\nu}$ = 3050, 2950, 2850, 1610, 1560, 1520, 1480, 1450, 1320, 1100, 760, 730, 720, 610 cm^{-1}. – ^{1}H NMR (trifluoroacetic acid, 60 MHz): δ = 8.6 (d, 1H, 6-H), 8.4–7.3 (m, 8H, 7, 8, 9-H, phenyl H), 5.3 (s, 2H, CH$_2$), 4.1 (m, 4H, pyrrolidine H), 2.2 (m, 4H, pyrrolidine H).

$C_{19}H_{19}N_4ClO_5$ (418.9) Calcd. C 54.48 H 4.57 N 13.38
Found C 54.05 H 4.81 N 13.76

3-(2-Hydroxy-2-phenylethenyl)-2-imino-2H-pyrido[1,2-b]-as-triazine (**9**): To a suspension of **5** (0.70 g, 2 mmol) in acetonitrile (6 ml), concd. ammonium hydroxide (1 ml) was added, whereupon a yellow solid immediately precipitated. Recrystallization from dimethylformamide afforded 0.47 g (89%) of product; mp 235–240°C. – IR (KBr): $\tilde{\nu}$ = 3280, 3030, 1620, 1590, 1540, 1470, 1400, 1270, 1220, 920, 900, 750, 720, 700 cm^{-1}. – ^{1}H NMR ([D$_6$]DMSO, 100 MHz): δ = 8.7 (s, 1H, NH), 8.39 (d, 1H, 6-H, J_o = 6.5 Hz), 7.90 (m, 2H, 2″,6″-H), 7.83 (t, 1H, 8-H, J_o = 7.9 Hz), 7.45 (m, 3H, 3″,4″,5″-H), 7.34 (d, 1H, 9-H, J_o = 9 Hz), 7.24 (d, 1H, 7-H, J_o = 6.5 Hz), 5.96 (s, 1H, 1′-H).

$C_{15}H_{12}N_4O$ (264.3) Calcd. C 68.16 H 4.58 N 21.20
Found C 68.13 H 4.59 N 21.28

2-Phenylpyrrolo[2,3-e]pyrido[1,2-b]-as-triazine (**10**): A mixture of **9** (0.53 g; 2 mmol), pyridine (10 ml), and a few crystals of *p*-toluenesulphonic acid were heated for 30 min at reflux. The resulting red mixture was then poured onto 50 ml of ice/water. The precipitated solid was filtered off and recrystallized from dimethylformamide to give 0.35 g (71%) of product; mp 241–243°C. – ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 8.67 (d, 1H, 6-H, J_o = 6.5 Hz), 8.39 (m, 2H, 2′,6′-H), 7.98 (d, 1H, 9-H, J_o = 8.5 Hz), 7.74 (t, 1H, 8-H, J_o = 7.5; 8.5 Hz), 7.50–7.51 (m, 3H, 3′,4′,5′-H), 7.26 (t, 1H, 7-H, J_o = 6.5; 7.5 Hz), 7.10 (s, 1H, 3-H). – ^{13}C NMR (CDCl$_3$): δ = 175.60 (C-9a, m), 151.21 (C-10a, d, $^4J_{C\text{-}10a,H\text{-}3}$), 149.15 (C-3a, d, $^2J_{C\text{-}3a,H\text{-}3}$), 144.5 (C-2, m), 136.27 (C-6), 135.1 (C-1′), 131.82 (C-8), 131.08 (C-4′), 128.77 (C-2′), 128.67 (C-3′), 127.12 (C-9), 116.21 (C-7), 92.41 (C-3). – IR (KBr): $\tilde{\nu}$ = 3110, 1640, 1575, 1510, 1490, 1460, 1450, 1440, 1400, 1240, 1060, 780, 720, 700, 680 cm^{-1}.

$C_{15}H_{10}N_4$ (246.3) Calcd. C 73.15 H 4.09 N 22.87
Found C 73.15 H 4.15 N 22.73
Mol. mass 246 (MS)

2-Phenyl-1H-pyrrolo[2,3-e]pyrido[1,2-b]-as-triazinium Perchlorate (**11**): A mixture of **10** (0.12 g; 0.5 mmol) and acetonitrile (2 ml) was treated with 70% perchloric acid (0.1 ml) resulting in rapid precipitation of yellow crystals. The product was filtered off and washed with ether; yield 0.13 g (75%); mp 299 – 310°C. – IR (KBr): $\tilde{\nu}$ = 3300, 3060, 1610, 1550, 1520, 1480, 1420, 1260, 1100, 760, 690, 620 cm^{-1}. – ^1H NMR (trifluoroacetic acid, 60 MHz): δ = 9.35 (d, 1H, 6-H), 8.7 – 8.5 (m, 2H, phenyl H), 8.3 – 8.1 (m, 3H, 7,8,9-H), 8.0 – 7.8 (m, 3H, phenyl H), 7.35 (s, 1H, 3-H).

$C_{15}H_{11}ClN_4O_4$ (346.7) Calcd. N 16.16 Found N 16.11

3-(Benzoylmethyl)-2-(4-bromophenylhydrazono)-2H-pyrido[1,2-b]-as-triazine (**12a**): Using the same procedure as for the synthesis of **9**, treatment of **5** (0.70 g, 2 mmol) with *p*-bromophenylhydrazine (0.37 g; 2 mmol) resulted in 0.85 g (98%) of crude product, which was recrystallized from toluene to give 0.70 g (80%) of red crystals; mp 218 – 219°C. – IR (KBr): $\tilde{\nu}$ = 3300, 3050, 1660, 1620, 1580, 1480, 1230, 1120, 740 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.4 (s, 1H, NH), 8.05 (d, 2H, 2′,6′-H), 7.62 (t, 1H, 4′-H), 7.51 (d, 2H, 3′,5′-H), 7.44 (d, 1H, 6-H, J_o = 6.5 Hz), 7.19 (t, 1H, 8-H, J_o = 8.5 and 7.0), 7.11, 6.64 (d, d, 4H, *p*-Br-C_6H_4), 6.7 (d, 1H, 9-H, J_o = 8.5), 6.24 (t, 1H, 7-H, J_o, = 7.0 and 6.5), 4.2 (s, 2H, CH_2). The product proved to be unsuitable for elementary analysis.

$C_{21}H_{16}BrN_5O$ (434.3) Mol. mass 434 (MS)

3-(Benzoylmethyl)-2-hydrazono-2H-pyrido[1,2-b]-as-triazine (**12b**): To a suspension of **5** (0.7 g, 2 mmol) in acetonitrile (6 ml), hydrazine hydrate (1 ml) was added, whereupon red crystals immediately separated. The mixture was diluted with water (10 ml), and the precipitate was filtered off to give 0.5 g (90%) of product; mp 178 – 180°C. – IR (KBr): $\tilde{\nu}$ = 3400, 3000, 1670, 1630, 1590, 1500, 1440, 1400, 1310, 1200, 750, 680 cm^{-1}. – ^1H NMR ($CDCl_3$, 100 MHz): δ = 8.0 (m, 2H, phenyl H), 7.65 – 7.45 (m, 3H, phenyl H), 7.38 (d, 1H, 6-H, J_o = 6 Hz), 7.14 (t, 1H, 8-H, J_o = 8.5 and 7.0), 6.68 (d, 1H, 9-H, J_o = 8.5 Hz), 6.16 (t, 1H, 7-H, J_o = 6.7 Hz), 4.15 (s, 2H, CH_2), 4.6 (broad s, NH). – ^{13}C NMR ($CDCl_3$): δ = 195.21 (C-2′), 154.27, 149.94 (C-2, C-9a), 139.21 (C-3), 136.83 (C-6), 136.67 (C-3′), 133.47 (C-9), 133.35 (C-6′), 128.64, 128.50 (C-4′,5′), 122.58 (C-8), 108.22 (C-7), 40.66 (C-1′). The product proved to be unsuitable for elementary analysis.

$C_{15}H_{13}N_5O$ (279.3) Mol. mass 279 (MS)

2-(4-Bromophenyl)-1,2-dihydro-3-phenylpyrido[1,2-b]pyridazino[3,4-e]-as-triazinium Trifluoroacetate (**13a**, A = CF_3COO): Hydrazone **12a** (0.86 g, 2.0 mmol) was dissolved in trifluoroacetic acid (5 ml), and the solution was allowed to stand at room temperature for 1 h. The mixture was then evaporated in vacuo, the residue suspended in a mixture of ethyl acetate and ether, and the solid filtered off and recrystallized from methanol to give 0.6 g (57%) of deep red crystals; mp > 320°C. For analytical purposes, a sample of the trifluoroacetate salt was converted into the perchlorate salt by adding perchloric acid to the acetonitrile suspension of this product; mp 304 – 307°C. – Data of the perchlorate salt (**13a**; A = ClO_4): IR (KBr): $\tilde{\nu}$ = 3400 – 2700, 1650, 1620, 1550, 1480, 1400, 1190, 1100, 760, 600 cm^{-1}.

$C_{21}H_{15}BrClN_5O_4$ (516.8) Calcd. C 48.81 H 2.92 N 13.55
Found C 49.04 H 2.91 N 13.57

1,2-Dihydro-3-phenylpyrido[1,2-b]pyridazino[3,4-e]-as-triazinium Trifluoroacetate (**13b**, A = CF_3COO): Hydrazone **12b** was dissolved in trifluoroacetic acid (3 ml), and the solution was allowed to stand at room temperature for 1 h. Evaporation of the solution and treatment of the residue with ethyl acetate gave red crystals which were recrystallized from methanol/ether to give 0.45 g (60%) of product; mp 292 – 293°C. – IR (KBr): $\tilde{\nu}$ = 3400 – 2700, 1650, 1600, 1520, 1460, 1400, 1230, 1190, 1160, 1110, 780, 750, 700, 600 cm^{-1}. – MS (70 eV): m/z = 261 [M^+ – CF_3COOH], 114 [CF_3COOH^+].

$C_{17}H_{12}F_3N_5O_2$ (375.3) Calcd. C 54.40 H 3.22 N 18.66
Found C 54.62 H 3.36 N 18.69

2-(4-Bromophenyl)-3-phenyl-2H-pyrido[1,2-b]pyridazino[3,4-e]-as-triazine (**14a**): To a mixture of trifluoroacetate salt **13a** (0.27 g, 0.5 mmol) and chloroform (5 ml), a few drops of triethylamine were added. The immediately formed deep blue solution was evaporated, then the residue was triturated with acetonitrile. Recrystallization from acetonitrile afforded 0.18 g (86%) of product; mp 228 – 229°C. – IR (KBr): $\tilde{\nu}$ = 3050, 1620, 1550, 1530, 1470, 1430, 1320, 1280, 1130, 1120, 1060, 1000, 960, 810, 740, 710, 690 cm^{-1}. – ^1H NMR ($CDCl_3$, 100 MHz): δ = 7.3 – 7.0 (m, 5H, phenyl H), 7.20 (d, 2H, 3″-H), 6.85 (d, 2H, 2″-H), 6.75 (d, 1H, 7-H, J_o = 7), 6.8 (t, 1H, 9-H), 6.17 (d, 1H, 10-H, J_o = 9 Hz), 5.91 (t, 1H, 8-H, J_o = 7.7 Hz), 4.80 (s, 1H, 4-H). – ^{13}C NMR ($CDCl_3$): δ = 156.43, 154.69, 153.71, 151.20 (C-3a,4a,10a,11a), 141.91 (C-1″), 137.76, 135.99 (C-7,10), 134.17 (C-1′), 131.12 (C-3″), 129.45 (C-4′), 128.53, 127.58 (C-2′,3′), 126.65 (C-2″), 121.09 (C-9), 119.46 (C-4″), 109.70 (C-8), 101.36 (C-4).

$C_{21}H_{14}BrN_5$ (416.3) Cacld. C 60.59 H 3.39 N 16.82
Found C 60.43 H 3.34 N 16.77

3-Phenyl-2H-pyrido[1,2-b]pyridazino[3,4-e]-as-triazine (**14b**): To a suspension of trifluoroacetate salt **13b** (0.37 g; 1 mmol) in chloroform (5 ml) a few drops of triethylamine were added. The resulting deep green solution was evaporated, and the residue was chromatographed on silica gel using chloroform/methanol (9:1) as eluent. The green fraction was collected and recrystallized from dimethylformamide to give 0.10 g (38%) of product; mp 278 – 284°C. – IR (KBr): $\tilde{\nu}$ = 3000, 1600, 1490, 1460, 1430, 950, 900, 740, 690 cm^{-1}. – ^1H NMR ([D_6]DMSO/$CDCl_3$, 400 MHz): δ = 8.2 (NH), 7.46 – 7.30 (m, 5H, phenyl H), 6.94 (d, 1H, 7-H), 6.87 (t, 1H, 9-H), 6.10 (d, 1H, 10-H), 5.93 (t, 1H, 8-H), 4.75 (s, 1H, 4-H). The product proved to be unsuitable for elementary analysis.

$C_{15}H_{11}N_5$ (261.3) Mol. mass 261 (MS)

CAS Registry Numbers

1: 121232-59-5 / **2**: 17571-17-4 / **3**: 121232-60-8 / **4**: 121232-61-9 / **5**: 121232-63-1 / **7a**: 121232-64-2 / **7b**: 121232-65-3 / **8a**: 121232-67-5 / **8b**: 121232-75-5 / **9**: 121232-68-6 / **10**: 121232-69-7 / **11**: 121232-70-0 / **12a**: 121232-71-1 / **12b**: 121232-76-6 / **13a**: 121232-73-3 / **13b**: 121232-78-8 / **14a**: 121232-72-2 / **14b**: 121232-77-7 / *p*-bromophenylhydrazine: 589-21-9

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