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2-Alkoxycarbonylcycloimmonium Ylides, Efficient 1,4-Dipole Equivalents in the Synthesis of New Conjugated Betaines.

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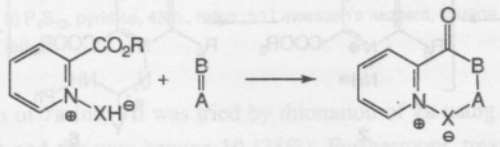
Abstract: Several heterocyclic mesomeric betaines containing the bicyclic systems pyrido[1,2-a]pyrazine and pyrido [2,1-f][1,2,4]triazine have been prepared by reaction of 2-alkoxycarbonyl pyridinium N-ylides with phenyl isocyanate and isothiocyanate.

2-Alkoxycarbonylpyridinium ylides **2** (Scheme 1) are interesting species as they should eventually behave as 1,4-dipoles able to produce, by reaction with the corresponding dipolarophiles, derivatives **3**. Such a strategy has not been described in the literature, apart from a reaction of 2-carbonyl-N-iminopyridinium ylides with amides or nitriles, producing pyrido[2,1-f]-*as*-triazinium-1 and 3-olates.[1-3] Related heterobetaines have been obtained either from pyridinium precursors[4,5] or from 2-functionalized pyrilium salts.[6-9]



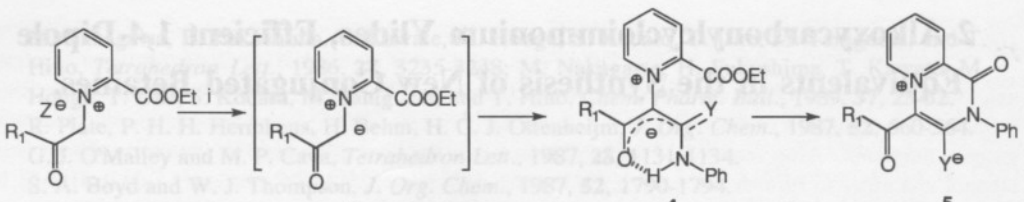
2 **3**

X = CCOR1, N
R1 = OEt, Ph

Scheme 1

In this paper we wish to report the synthetic utility of 2-alkoxycarbonyl pyridinium N-ylides **2** as intermediates for the synthesis of mesomeric betaines **5** and **7** (Scheme 2 and 3) both classified as conjugated and isoconjugate with even alternant hydrocarbon dianions according to Ollis.[10]

N-ylides **2a** and **2b** are readily generated from 2-ethoxycarbonyl pyridinium salts (**1a**,**1b**), and reacted with phenyl isocyanate affording the corresponding pyrido[1,2-a]pyrazinium-3-olates **5** (Y=O) in good yield (see table 1), together with detectable amounts of compounds **4** (Y=O). Similarly, N-imino compounds **1c-f** gave the corresponding pyrido[2,1-f][1,2,4]triazinium-3-olates and their benzologues **7** (Y=O) in excellent yield (see table 2).



1a, R_1 = OEt, Z = Br

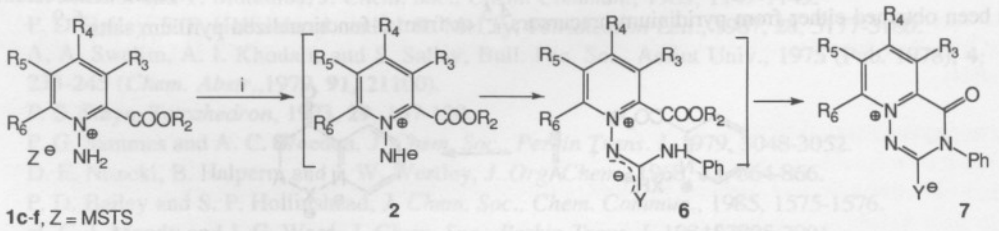
1b, R_1 = Ph, Z = Br

Scheme 2. Reagents and conditions: i) CH_2Cl_2 or CH_3CN, K_2CO_3, PhN=C=Y, 20 h., r. t.

Table 1. Betaines **4** and **5** prepared.

Comp.	Starting Material	Y	R_1	Yield % 4	5
4,5a	**1a**	O	OEt	3	70
4,5b	**1a**	S	OEt	30	63
4,5c	**1b**	O	Ph	traces	68
4,5d	**1b**	S	Ph	31	66

Compounds **7** (Y=S) were directly obtained when phenyl isothiocyanate was added to a suspension of the salts **1c-f** in dichloromethane and potassium carbonate. However, following the above procedure, the salts **1a** and **1b** afforded compounds **4** (Y=S) which underwent easy cyclization to **5** (Y=S) in the presence of triethylamine.



1c-f, Z = MSTS

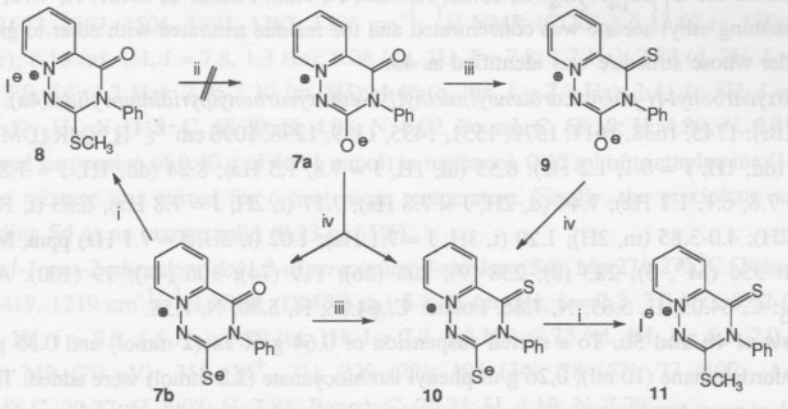
Scheme 3. Reagents and conditions: i) CH_2Cl_2 or CH_3CN, K_2CO_3, PhN=C=Y, 20 h., r. t.; MSTS = mesytilenesulphonate.

All new compounds gave satisfactory spectroscopic (IR, MS, $^1H/^{13}C$-NMR) and analytical data. IR spectra of compounds **7** were highly characteristic. As an example, **7a** shows a strong C=O stretching band at 1700 cm^{-1} in addition to the band at 1635 cm^{-1} attributable to the 3-olate group. Alternatively, **7b** only shows a strong band at 1701 cm^{-1}.

Several transformations were tested, as indicated in Scheme 4, allowing the preparation of new derivatives. Conversion of **7b** into **7a** was attempted via **8**, obtained by S-methylation of **7b**, but **8**, when submitted to basic hydrolysis gave decomposition products.

Table 2. Betaines **7** prepared.

Comp.	Starting Material	Y	R_2	R_3	R_4	R_5	R_6	Yield %
7a	**1c**	O	Et	H	H	H	H	74
7b	**1c**	S	Et	H	H	H	H	70
7c	**1d**	O	Et	H	H	$(CH=CH)_2$		66
7d	**1d**	S	Et	H	H	$(CH=CH)_2$		53
7e	**1e**	O	Et	$(CH=CH)_2$		H	H	80
7f	**1e**	S	Et	$(CH=CH)_2$		H	H	61
7g	**1f**	O	Me	H	$(CH=CH)_2$		H	60
7h	**1f**	S	Me	H	$(CH=CH)_2$		H	45



Scheme 4. Reagents and conditions: i) CH_3I, AcOEt, r. t.; ii) NaOH (aq., 50%), r. t.; iii) P_4S_{10}, pyridine, 48 h., reflux; iv) Lawesson's reagent, toluene, 72 h. reflux.

Alternative conversion of **7a** into **7b** was tried by thionation of **7a** using Lawesson's reagent in boiling toluene, affording **7b** (20%) and the new betaine **10** (38%). Furthermore, treatment of **7a** with phosphorus pentasulfide in dry pyridine afforded the mesomeric betaine **9** (50%); however, reaction of **7b** under similar conditions gave a complex mixture, the betaine **10** (7%) being the only isolated product. On the other hand, treatment of **9** with Lawesson's reagent gave **10** (63%).

In summary, a simple and useful preparation of new betaines **5** and **7** have been achieved and alternative methods have surfaced for the synthesis of betaines **10**. Further experiments are in progress to extend this methodology to other heterocyclic systems.

EXPERIMENTAL

Melting points were determined on an Electrothermal IA6304 and are uncorrected. IR spectra were recorded on Perkin-Elmer 700 or 1310 spectrophotometers using KBr pellets. ^{1}H- y ^{13}C-NMR spectra were recorded on a Varian Unity 300 instrument at 300 and 75.429 MHz respectively. Mass spectra were

determined on a Hewlett-Packard 5988A (70 eV) spectrometer. Satisfactory microanalyses were obtained for all new compounds described, within 0.4% error.

The starting heterocyclic precursors were obtained using previously described methods.[4,11,12]

Synthesis of 4a and 5a. To a stirred suspension of 0.63 g of the pyridinium salt **1a** (2 mmol) and 1.10 g of K_2CO_3 (8 mmol) in dry acetonitrile (10 ml), 0.24 ml of phenyl isocyanate (2.2 mmol) were added, and the reaction mixture was stirred at room temperature for 20 h. Then, the inorganic residue was filtered off and the liquid was concentrated to dryness. The resulting residue was triturated with 10 ml of ethyl acetate, yielding **5a** as a yellow crystalline solid (0.43 g, 70%)

4-Ethoxycarbonyl-1-oxo-2-phenylpyrido[1,2-a]pyraziniun-3-olate (**5a**). Mp 249-250°C (EtOH). IR (KBr): 1688, 1641, 1453, 1323, 1206 cm^{-1}; ^1H NMR (DMSO-d_6) δ 9.70 (d, 1H, J = 6.9 Hz); 8.40 (dd, 1H, J=7.8, 2.0 Hz); 7.90 (td, 1H, J = 6.9, 2.0 Hz); 7.80 (td, 1H, J = 7.8, 1.2 Hz); 7.51-7.20 (m, 5H); 4.19 (q, 2H, J = 7.1 Hz); 1.21 (t, 3H, J = 7.1 Hz) ppm; MS (70 eV) m/e (rel intensity): 310 (M^+,24); 238 (70); 106 (23); 78 (100). Anal. calcd. for $C_{17}H_{14}N_2O_4$: C, 65.80; H, 4.55; N, 9.03. Found: C, 65.81; H, 4.75; N, 9.20.

The remaining ethyl acetate was concentrated and the residue triturated with ether to give 20 mg (3%) of a red powder whose structure was identified as **4a**.

1-[(Ethoxycarbonyl-N-phenylcarbamoyl)methyl]-2-ethoxycarbonylpyridinium ylide (**4a**). Mp 110-111°C (Et_2O). IR (KBr): 1745, 1638, 1611, 1579, 1531, 1435, 1339, 1298, 1096 cm^{-1}; ^1H NMR (DMSO-d_6) δ 10.57 (s, 1H); 8.91 (dd, 1H, J = 6.1, 1.2 Hz); 8.55 (td, 1H, J = 7.8, 1,5 Hz); 8.24 (dd, 1H, J = 7.8, 1.7 Hz); 8.09 (ddd, 1H, J = 7.8, 6.1, 1.7 Hz); 7.44 (d, 2H, J = 7.8 Hz); 7.17 (t, 2H, J = 7.8 Hz); 6.85 (t, 1H, J = 7.2 Hz); 4.35-.15 (m, 2H); 4.0-3.85 (m, 2H); 1.20 (t, 3H, J = 7.1 Hz); 1.02 (t, 3H, J = 7.1 Hz) ppm; MS (70 eV) m/e (rel intensity): 356 (M^+, 3); 283 (8); 238 (9); 208 (26); 119 (74); 106 (44); 79 (100). Anal. calcd. for $C_{19}H_{20}N_2O_5$: C, 64.05; H, 5.65; N, 7.86. Found: C, 64.06; H, 5.80; N, 7.58.

Synthesis of 4b and 5b. To a stirred suspension of 0.64 g of **1a** (2 mmol) and 0.55 g of K_2CO_3 (4 mmol) in dichloromethane (10 ml), 0,26 g of phenyl isothiocyanate (2.2 mmol) were added. The mixture was stirred for 20 h at room temperature. Then, the inorganic solid was separated by filtration and the liquids were concentrated to dryness. The residue was purified by column chromatography (silica gel 60 A, 230-400 mesh; ethyl acetate) yielding **4b** as a red solid (0.21 g, 30%).

1-[(Ethoxycarbonyl-N-phenylthiocarbamoyl)methyl]-2-ethoxycarbonylpyridinium ylide (**4b**). Mp 100-101°C (Et_2O). IR (KBr): 1741, 1587, 1400, 1373, 1346 cm^{-1}; ^1H NMR ($CDCl_3$) δ 11.84 (s, 1H); 8.68 (dd, 1H, J = 6.1 Hz); 8.32 (td, 1H, J = 7.8, 1.5 Hz); 8.13 (dd, 1H, J = 7.8, 1.7 Hz); 7.84 (ddd, 1H, J = 7.8, 6.1, 1.7 Hz); 7.73 (d, 2H, J = 8.5 Hz); 7.29 (t, 2H, J = 7.6 Hz); 7.06 (t, 1H, J = 7.3 Hz); 4.5-4.3 (m, 2H); 4.15-3.95 (m, 2H); 1.35 (t, 3H, J = 7.1 Hz); 1.09 (t, 3H, J = 7.1 Hz) ppm. Anal. calcd. for $C_{19}H_{20}N_2O_4S$: C, 61.27; H, 5.41; N, 7.52. Found: C, 60.98; H, 5.19; N, 7.28.

To a stirred solution of 0.38 g of **4b** (1 mmol) in methanol (10 ml), 0.15 ml of triethylamine (1.1 mmol) were added. The mixture was stirred for 6 h at room temperature. Then, the precipitate was isolated by filtration, yielding **5b** as a red crystalline solid (0.20 g, 62%)

4-Ethoxycarbonyl-1-oxo-2-phenylpyrido[1,2-a]pyrazinium-3-thiolate (**5b**). Mp 204-205°C (EtOH). IR (KBr) 1709, 1675, 1451, 1413, 1371, 1216 cm^{-1}; ^1H NMR (DMSO-d_6) δ 8.33 (dd, 1H, J = 8.0 Hz); 8.16 (d, 1H, J = 6.6 Hz); 7.86 (td, J = 7.3, 6.6, 1.7 Hz); 7.78 (t, 1H, J = 8.0, 7.3 Hz); 7.50-7.15 (m, 5H); 4.34 (q, 2H, J = 7.2 Hz); 1.29 (t, 3H, J = 7.2 Hz) ppm; MS (70 eV) m/e (rel intensity) 326 (M^+, 28); 297 (25); 253 (52); 106 (20); 78 (100). Anal. calcd. for $C_{21}H_{14}N_2O_3S$: C, 62.56; H, 4.32; N, 8.58. Found: C. 62.28; H, 4.14; N, 8.24.

4-Benzoyl-1-oxo-2-phenylpyrido[1,2-a]pyrazinium-3-olate (**5c**). To a suspension of 0.70 g of the

pyridinium salt **1b** (2 mmol) and 1.10 g of K_2CO_3 (8 mmol) in dry acetonitrile, 0.24 ml of phenyl isocyanate (2.2 mmol) were added. The mixture was stirred for 20 h at room temperature. Then, the precipitate was isolated by filtration and washed with distilled water until neutral, yielding the betaine **5c** which crystallised from ethanol affording yellow crystals (0.47 g, 70%). Mp 264-265°C (EtOH); IR (KBr) 1683, 1632, 1449, 1334, 1197 cm^{-1}; ^1H NMR (DMSO-d_6) δ 10.18 (m, 1H, J = 6.0, 1.8 Hz); 8.51 (m, 1H, J = 7.2, 2.9 Hz); 8.02-7.92 (m, 2H); 7.60-7.19 (m, 10H) ppm; MS (70 eV) m/e (rel intensity): 342 (M^+, 80); 265 (16); 195 (71); 105 (100). Anal. calcd. for $C_{21}H_{14}N_2O_3$: C, 73.67; H, 4.12; N, 8.18. Found: C, 74.01; H, 4.41; N, 8.04.

Synthesis of 4d and 5d. To a stirred suspension of 0.70 g of **1b** (2 mmol) and 0.55 g of K_2CO_3 (4 mmol) in dichloromethane (10 ml), 0.26 ml of phenyl isothiocyanate (2.2 mmol) were added. The mixture was stirred for 20 h at room temperature. Then, the inorganic residue was separated by filtration and the liquids were concentrated to dryness. The residue was purified by column chromatography (silica gel 60 A, 230-400 mesh; ethyl acetate) yielding the betaine **4d** as a red solid (0.25 g, 31%) .

1-[(Benzoyl-N-phenylthiocarbamoyl)methyl]-2-ethoxycarbonylpyridinium ylide (**4d**). Mp 134-135°C. IR (KBr): 1734, 1627, 1567, 1501, 1393, 1307, 1195 cm^{-1}; ^1H NMR ($CDCl_3$) δ 13.62 (s, 1H); 8.42 (dd, 1H, J = 6.1, 1.3 Hz); 8.16 (td, 1H, J = 7.8, 1.3 Hz); 8.08 (dd, 1H, J = 7.8, 1.7 Hz); 7.83 (d, 2H, J = 7.4 Hz); 7.56 (ddd, 1H, J = 7.8, 6.1, 1.7 Hz); 7.36-7.10 (m, 8H); 4.46 (q, 2H, J = 7.1 Hz); 1.41 (t, 3H, J = 7.1 Hz) ppm. Anal. calc. for $C_{23}H_{20}N_2O_3S$: C, 68.30; H, 4.98; N, 6.92. Found: C, 68.10; H, 4.80; N, 6.71.

To a stirred suspension of 0.40 g of **4d** (1 mmol) in methanol, 0.15 ml of triethylamine (1.1 mmol) were added, and the mixture was stirred for 6 h at room temperature. Finally, the precipitate was isolated by filtration, yielding **5d** as an orange solid (0.23 g, 65%).

4-Benzoyl-1-oxo-2-phenylpyrido[1,2-a]pyrazinium-3-thiolate (**5d**). Mp 271-272°C (Toluene). IR (KBr): 1666, 1450, 1419, 1219 cm^{-1}; ^1H NMR (DMSO-d_6) δ 8.43 (m, 1H, J = 7.2, 2.0 Hz); 8.12 (d, 2H, J = 7.1 Hz); 7.96 (dd, 1H, J = 5.5, 1.5 Hz); 7.79 (td, 1H, J = 7.2, 1.5 Hz); 7.75 (td, 1H, J = 5.5, 2.0 Hz); 7.32-7.22 (m, 8H) ppm; MS (70 eV): 358 (M^+, 21); 329 (22); 105 (34); 78 (57); 77 (100). Anal. calcd. for $C_{21}H_{14}N_2O_2S$: C, 70.37; H, 3.93; N, 7.81. Found: C, 70.25; H, 4.10; N, 7.79.

Synthesis of betaines 7a, c, e, g. General procedure. To a suspension of the corresponding azinium salt (2 mmol) and 1.10 g (8 mmol) of K_2CO_3 in dry acetonitrile (10 ml), 0.24 ml of phenyl isocyanate (2.2 mmol) were added. The mixture was stirred for 20 h at room temperature. Then, the solid obtained was filtered off and purified by column chromatography (silica gel 60 A, 230-400 mesh; acetone for **7a** or ethyl acetate for **7c**, **e**).

1-Oxo-2-phenylpyrido[2,1-f][1,2,4]triazinium-3-olate (**7a**). 0.35 g (70%) of a white crystalline solid. *Mp 308-309°C (CH_3CN); IR (KBr): 1700, 1634, 1444, 1180 cm-1; ^1H NMR (DMSO-d_6) δ 8.71-8.67 (m,1H); 8.33-8.29* (m, 1H); 7.98-7.93 (m, 2H); 7.50-7.24 *(m, 5H)* ppm; *^{13}C NMR (DMSO-d_6) δ 157.1; 153.2; 135.8; 135.4; 133.8; 132.9; 129.6; 128.7; 128.4; 128.0; 125.7* ppm; MS (70 eV) m/e (rel intensity): 239 (M^+, 12); 197 (29); 120 (11); 78 (100). *Anal. calcd. for $C_{13}H_9N_3O_2$: C, 65.27; H, 3.79; N, 17.56. Found: C, 65.05; H, 3.87; N, 17.37.*

4-Oxo-3-phenyltriazino[1,6-a]quinolinium-2-olate (**7c**). 0.38 g (66%) as a yellow solid. Mp 334-335°C (CH_2Cl_2/EtOH); IR (KBr) 1701, 1630, 1412, 1193, 1138 cm^{-1}; ^1H NMR (DMSO-d_6) δ 9.05 (d, 1H, J = 8.8 Hz); 8.46 (d, 1H, J = 8.8 Hz); 8.28 (dd, 1H, J = 7.8, 1.2 Hz); 8.25 (d, 1H, J = 8.8 Hz); 8.09 (ddd, 1H, J = 8.8, 7.2, 1.5 Hz); 8.02-7.95 (m, 1H); 7.55-7.30 (m, 5H) ppm; MS (70 eV) m/e (rel intensity): 289 (M^+, 36); 247 (61); 128 (100); 114 (65). Anal. calcd. for $C_{17}H_{11}N_3O_2$: C, 70.58; H, 3.83; N, 14.52. Found: C, 70.19; H, 4.15; N, 14.19.

1-Oxo-2-phenyltriazino[6,1-a]isoquinolinium-3-olate (**7e**). 0.43 g (74%) as yellow needles. Mp 330-

331°C (CH_2Cl_2/EtOH); IR (KBr): 1689, 1631, 1457, 1336, 1138 cm^{-1}; ^1H NMR (DMSO-d_6) δ 9.67-9.63 (m, 1H); 8.53 (d, 1H, J = 7.3 Hz); 8.38 (d, 1H, J = 7.3 Hz); 8.19-8.14 (m, 1H); 7.92-7.86 (m, 2H); 7.53-7.29 (m, 5H); MS (70 eV) m/e (rel. intensity): 289 (M^+, 7); 247 (38); 142 (14); 128 (100); 114 (48). Anal. calcd. for $C_{17}H_{11}N_3O_2$: C, 70.58; H, 3.83; N, 14.52. Found: C, 70.29, H, 3.91; N, 14.81.

1-Oxo-2-phenyltriazino[1,6-b]isoquinolinium-3-olate (**7g**). The final precipitate was washed with distilled water until neutral, and dried, yielding **7g** (0.34 g, 60%) as a yellow solid. Mp >350°C (DMF/EtOH); IR (KBr): 1692, 1629, 1485, 1269, 1210 cm^{-1}; ^1H NMR (CF_3COOD) δ 9.36 (s, 1H); 8.98 (s, 1H); 8.08 (dd, 1H, J = 8.2, 1.2 Hz); 8.04 (d, 1H, J = 7.8 Hz); 7.94-7.76 (m, 2H); 7.16-6.88 (m, 5H); MS (70 eV) m/e (rel intensity): 289 (M^+, 11); 247 (16); 142 (38); 128 (100). Anal.calcd. for $C_{17}H_{11}N_3O_2$: C, 70.58; H, 3.83; N, 14.52. Found: C, 70.31; H, 4.04; N, 14.70.

Synthesis of betaines 7b, f, h, d. General procedure. To a stirred suspension of the corresponding azinium salt (2 mmol) and 0.55 g (4 mmol) of K_2CO_3 in dichloromethane, 0.26 ml (2,2 mmol) of phenyl isothiocyanate were added. The mixture was stirred for 20 h at room temperature. Then, the precipitate was isolated by filtration, washed with distilled water until neutral, and petroleum ether and finally recrystallized.

1-Oxo-2-phenylpyrido[2,1-f][1,2,4]triazinium-3-thiolate (**7b**). Recrystallization from CH_2Cl_2/EtOH yield 0.36 g of **7b** as a pale orange crystalline solid (70%). Mp 212-213°C. IR (KBr) 1701, 1498, 1417, 1212 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ 8.87 (dd, 1H, J = 6.1, 1.2 Hz), 8.35 (dd, 1H, J = 7.9, 1.9 Hz), 8.14 (td, 1H, J = 7.8, 1.2 Hz), 8.07 (ddd, 1H, J = 7.8, 6.1, 1.9 Hz), 7.49-7.18 (m, 5H) ppm; ^{13}C NMR (75.429 MHz,DMSO-d_6) δ 176.8, 154.8, 138.9, 136.4, 136.3, 136.0, 130.2, 130.0, 128.9, 128.8, 125.7 ppm; MS (70 eV) m/e (rel intensity) 255 (M^+, 11), 223 (17), 106 (93), 78 (100). Anal. calcd. for $C_{13}H_9N_3OS$: C, 61.16; H, 3.55; N, 16.46. Found: C, 60.98; H 3.66; N, 16.71.

1-Oxo-2-phenyltriazino-[6,1-a]isoquinolinium-3-thiolate (**7f**). Work up of the mixture gave 0.37 g of **7f** as an orange solid (61%). Mp 258-259 (DMF). IR (KBr) 1679, 1465, 1370, 1232 $^{-1}$; ^1H NMR (300 MHz,CF_3COOD) δ 9.98 (d, 1H, J = 8.8 Hz), 8.84 (d, 1H, J = 7.1 Hz), 8.70 (d, 1H, J = 7.1 Hz), 8.40-8.21 (m, 3H), 7.81-7.49 (m, 5H); MS (70 eV) m/e (rel intensity) 305 (M^+, 6), 273 (17), 156 (12), 128 (100). Anal. calcd. for $C_{17}H_{11}N_3OS$: C, 66.87; H, 3.63; N, 13.76. Found: C,66.40; H, 3.96; N, 13.81.

1-Oxo-2-phenyltriazino[1,6-b]isoquinolinium-3-thiolate (**7h**). 0.26 g (45%) as a yellow solid. Mp 240-241°C (DMF). IR (KR) 1681, 1487, 1450, 1217 cm^{-1}; ^1H NMR (300 MHz,CF_3COOD) δ 9.85 (s, 1H), 9.50 (s, 1H), 8.65 (d, 1H, J = 8.5 Hz), 8.56 (d, 1H, J = 8.3 Hz), 8.44 (td, 1H, J = 8.3, 7.1, 1.2 Hz), 8.35 (ddd, 1H, J = 8.5, 7.1, 1.2 Hz), 7.82-7.50 (m, 5H) ppm; MS (70 eV) m/e (rel intensity) 305 (M^+, 5), 273(8), 156(34), 128 (100). Anal. calcd. for $C_{17}H_{11}N_3OS$: C, 66.87; H, 3.63; N, 13.76. Found: C, 66.80; H, 3.82; N, 13.83.

4-Oxo-3-phenyltriazino[1,6-a]quinolinium-2-thiolate (**7d**). After stirring at room temperature for 20 h, by addition of distilled water (20 ml) and extraction with dichloromethane (3x20 ml), the residue was treated with petroleum ether and the resulting precipitate was filtered off, giving 0.32 g of **7d** as a red crystalline solid (53%). Mp 213-214°C (CH_3CN). IR (KBr) 1678, 1468, 1411, 1205, 1121 cm^{-1}; ^1H NMR (300 MHz,DMSO-d_6) δ 9.06 (d, 1H, J = 8.8 Hz), 8.67 (d, 1H, J = 8.5 Hz), 8.35 (dd, 1H, J = 8.2, 1.5 Hz), 8.29 (d, 1H, J = 8.5 Hz), 8.17 (ddd, 1H, J = 8.8, 7.2, 1.5 Hz), 8.06-8.00 (m, 1H), 7.53-7.37 (m, 5H) ppm; MS (70 eV) m/e (rel intensity) 305 (M^+, 22), 273 (13), 156 (11), 128 (100). Anal. calcd. for $C_{17}H_{11}N_3OS$: C, 66.87; H, 3.63; N, 13.76. Found: C, 66.74; H, 3.80; N, 14.01.

2-Phenyl-1-thiopyrido[2,1-f][1,2,4]triazinium-3-olate (**9**). To a suspension of **7a** (0.48 g, 2 mmol) in dry pyridine (10 ml), phosphorus pentasulfide 0.67 g (1.5 mmol) was added. After refluxing for 48 h., distilled water (20 ml) was added and the suspension was extracted with dichloromethane (3x50 ml), the organic phase was separated, dried with magnesium sulphate and concentrated to dryness. The residue was purified by

column chromatography (silica 60 Merck, 230-400 mesh), using dichloromethane/acetone (8:2), giving 0.26 g of **9** as an orange crystalline solid (50%). Mp 308-309°C (Acetone). IR (KBr) 1655, 1436, 1302, 1280, 1204, 1167 cm^{-1}; ^1H NMR (300 MHz,DMSO-d_6) δ 8.83-8.77 (m, 1H), 8.68-8.64 (m, 1H), 8.00-7.93 (m, 2H), 7.53-7.19 (m, 5H) ppm; ^{13}C NMR (75.429 MHz) δ 183.63, 151.49, 140.65, 137.00, 136.43, 133.43, 130.03, 129.43, 129.30, 128.18, 127.74 ppm; MS (70 eV) m/e (rel intensity) 255 (M^+, 62), 213 (100), 181 (8), 78 (17). Anal. calcd. for $C_{13}H_9N_3OS$: C, 61.16; H, 3.55; N, 16.46. Found: C, 60.91; H, 3.80; N, 16.21.

2-Phenyl-1-thiopyrido[2,1-f][1,2,4]triazinium-3-thiolate (**10**). **Method A.** A suspension of **7a** (0.48 g, 2 mmol) and 0.81 g (2 mmol) of Lawesson's reagent in dry toluene (20 ml) were refluxed over 72 h. After this time a mixture of two compounds was observed by t.l.c. Chromatography of the mixture (silica gel 60 Merck, 230-400 mesh) with ethyl acetate gave 0.22 g of the betaine **10** (40%) and 0.11 g of **7b** (20%).

Method B. A suspension of 0.51 g (2 mmol) of the betaine **9** and 0.81 g (2 mmol) of Lawesson's reagent in dry toluene (20ml) were refluxed over 48 h. After this time, the reaction mixture was concentrated to dryness and the residue purified by column chromatography (silica gel 60 Merck, 230-400 mesh), using dichloromethane/acetone (9:1) as eluents, giving 0.32 g of **10** as a brown-reddish solid (63%). Mp 215-216°C (Acetone). IR (KBr) 1414, 1267, 1153, 1124 cm^{-1}; ^1H NMR (300 MHz,DMSO-d_6) δ 8.81 (dd, 1H, J = 5.6, 1.3 Hz), 8.74 (dd, 1H, J = 7.9, 2.2 Hz), 8.16-8.04 (m,2H), 7.50-7.11 (m, 5H); MS (70 eV) m/e (rel intensity) 271 (M^+, 13), 213 (32), 181 (37), 78 (100). Anal. calcd. for $C_{13}H_9N_3S_2$: C, 57.54; H, 3.34; N, 15.48. Found: C, 57.84; H, 3.62; N,15.40.

Synthesis of compounds 8 and 11. General procedure. To a suspension of the corresponding betaine **7b/10** (1 mmol) in ethyl acetate (5 ml), 0.44 ml (4 mmol) of methyl iodide were added. After stirring at room temperature for 2 h, the resulting precipitate was filtered off and washed with ethyl acetate. Recrystallization from ethanol gave 0.34 g (85 %) of **8** and 0.33 g (81%) of **11** as yellow and orange crystalline solids respectively.

3-Methylthio-1-oxo-2-phenylpyrido[2,1-f][1,2,4]triazinium iodide (**8**). Mp 213-214°C (EtOH). IR (KBr) 1727, 1635, 1543, 1443, 1271cm^{-1}; ^1H NMR (300 MHz,DMSO-d_6) δ 9.44 (d, 1H, J = 6.3 Hz), 8.78 (dd, 1H, J = 7.8, 1.7 Hz), 8.70 (t, 1H, J = 7.8 Hz), 8.53-8.46 (m, 1H), 7.69-7.44 (m, 5H), 2.61 (s, 3H) ppm; MS (70 eV) m/e (rel intensity) 255 (M^+-15, 6), 223 (17), 142 (58), 106 (67), 78 (100). Anal. calcd. for $C_{14}H_{12}N_3OSI$: C, 42.33; H, 3.05; N, 10.58. Found: C, 41.85; H, 2.98; N, 10.23.

3-Methylthio-1-thio-2-phenylpyrido[2,1-f][1,2,4]triazinium iodide (**11**). Mp 225-226°C (EtOH). IR (KBr) 1533, 1468, 1440, 1310, 1271 cm^{-1}: ^1H NMR (300 MHZ,DMSO-d_6) δ 9.36 (d, 1H, J = 6.3 Hz), 9.07 (dd, 1H, J = 8.1, 1.3 Hz), 8.67 (t, 1H, J = 8.1, 7.8 Hz),8.53-8.47 (m, 1H), 7.72-7.39 (m, 5H), 2.60 (s, 3H) ppm; MS (70 eV) m/e (rel intensity) 254 (M^+-32, 31), 213 (24), 181 (28), 78 (38). Anal. calcd. for $C_{14}H_{12}N_3S_2I$: C, 40.70; H, 2.93; N, 10.17. Found: C, 41.00; H, 3.12; N, 10.22.

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