Bridged 2,2'-Biazole Derivatives by 1,3-Dipolar Cycloaddition

Maria S. de Pablo, Teresa Gandásegui, Juan J. Vaquero, José L. García Navío and Julio Alvarez-Builla*

Departamento de Química Orgánica. Universidad de Alcalá. Alcalá de Henares. Madrid.Spain.

Abstract: Azomethine ylides derived from 3,4-dihydropyrrolo[1,2-a]pyrazinium salts undergo 1,3-dipolar cycloaddition reactions to yield 5,6-dihydrodipyrrolo[1,2-a:2',1'-c]-pyrazine and 5,6-dihydroimidazo[1,2-a]-pyrrolo[2,1-c]pyrazin-4-inium-2-olate and 2-thiolate derivatives. S-Methylation followed by nucleophilic displacement of methylthio group converted the 2-thiolate derivatives into new conjugated betaines.

The properties of bridged azabiaryl systems in which a polymethylene bridge may be used to control the conformation (**1**, Scheme 1) are strongly influenced by both electronic and steric factors. Moreover, the interaction of covalently bound π-systems is favoured by a planar conformation which provides the optimum environment for resonance delocalization. Such interaction has been found to influence both the physical and chemical properties with important implications on the coordination chemistry of the biheteroaryl molecules.[1,2] When the introduction of an N,N'-bridge can lead to quaternary salts,[3-5] the systems are capable of behaving as viologens,[6] a special class of N-substituted salts with reversible electron acceptor properties, applied as redox catalysts and electron relays in photocatalysed water cleavage[7,8] and as effective herbicides.[9]

1

HET=Heteroaromatic

2

X = CH, N

Scheme 1

Our previous experience in this field has been the preparation of pyrido[1,2-a]- and pyridazino[2,3-a] pyrrolo[2,1-c]pyrazin-7-ium derivatives as an example of quaternary systems (**2**, Scheme 1), in which spectroscopic data showed transfer of electron density[10] between the heteroaryl moieties.

The interest of such compounds prompted us to investigate the development of related derivatives. Initially we directed our attention to bridged bipyrroles and we found that previously reported, dipyrrolo-[1,2-a:2',1'-c]pyrazines and their 5,6-dihydroderivatives have been prepared either by Chichibabin reaction on a pyrrolo[1,2-a]pyrazinium salt[11] or by intramolecular oxidative coupling of 1,2-N,N'-dipyrrolethane.[12]

Our interest in representative series of these and analogous biazole derivatives led us to explore the use of 1,3-dipolar cycloaddition reaction on azomethine ylides[13] as a convenient method to prepare this class of compounds. Herein we report preliminary results of our studies.
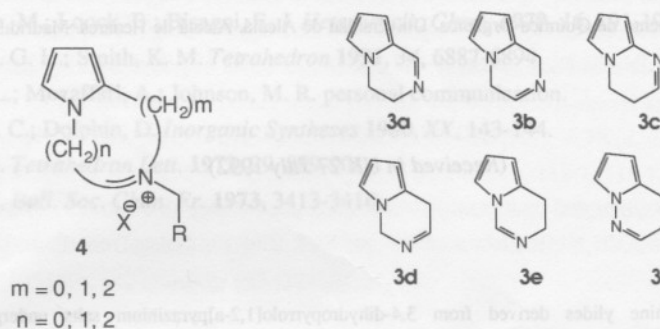
Scheme 2

At the outset it was envisaged that diverse bridged bipyrrole derivatives could be formed by dipolar cycloaddition of azomethine ylides generated from dihydropyrrolo[1,2-a]pyrazinium, -pyridazinium and -pyrimidinium salts **4** with appropriate dipolarophiles. To our surprise, we found that only one of the six possible isomeric structures **3** required, the 3,4-dihydropyrrolo[1,2-a]pyrazine **3a** has been reported, and we focused our attention on it as our initial target.

The starting 3,4-dihydropyrrolo[1,2-a]pyrazine system was prepared either by the method of Flament and col[14] or by an improved alternative developed by us.[15] In our method this compound was prepared from pyrrole according to the scheme 3 in a 42% overall yield (29% in Flament's method, ref. 15).
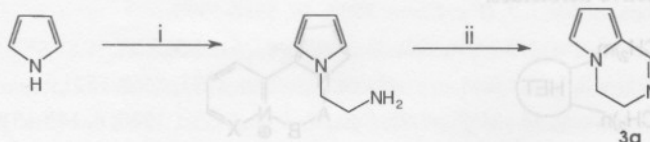
Scheme 3. i) ClCH$_2$CH$_2$NH$_2$·HCl / NaOH / CH$_3$CN / TBAS, r e f l u x;
ii) HCO$_2$H, r e f l u x

The salts **4a** and **4b** were prepared by N-alkylation of the 3,4-dihydrodipyrrolo[1,2-a]pyrazine **3a** with trimethylsilylmethyl trifluoromethanesulfonate[16] and phenacyl bromide[17] respectively. Both salts were hygroscopic compounds especially **4a** and this was used without purification after [1]H-nmr analysis.

Attempts to trap the non-stabilized azomethine ylide generated from **4a** by treatment with caesium fluoride in dimethoxyethane[16] with suitable dipolarophiles failed, with no evidence of formation of the desired cycloadducts. Use of a large excess of dipolarophile, more forcing conditions and different solvents (acetonitrile) and fluoride sources (tetrabutylammonium fluoride and silver fluoride)[18] also resulted in failure of the cycloaddition reaction, and further work with this salt was abandoned.
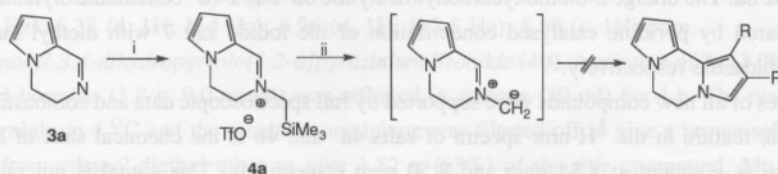
Scheme 4. i) TfOCH$_2$SiMe$_3$, CH$_2$Cl$_2$, r. t.; ii) F$^\ominus$/ R–C≡C–R

A number of different conditions were examined for the cycloaddition reaction of the benzoyl stabilized ylide generated from **4b** with acetylenes, and the best results were obtained by using two-phase media.[19-21] Thus, when the process was performed in dichloromethane/50% aqueous K$_2$CO$_3$, the best yields of **5a** (48%) and **5b** (49%) were obtained due to the lack of ylide decomposition.
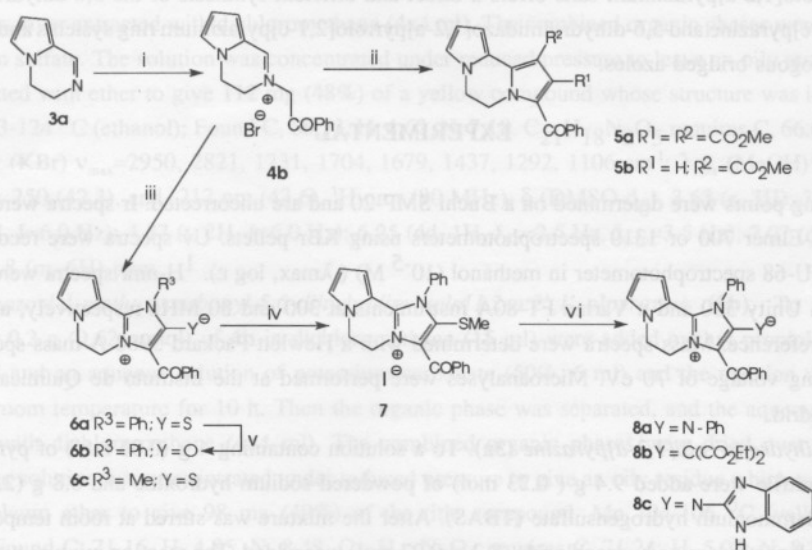
Scheme 5. i) BrCH$_2$COPh /acetone, r.t.; ii) R^1–C=C–R^2 / CH$_2$Cl$_2$/K$_2$CO$_3$
(aq., 50%), r. t.; iii) R–N=C=Y, MeCN/K$_2$CO$_3$, r.t.; iv) MeI, EtOAc, r.t.;
v) MeOH / NaOH (50%), r. t. ; vi) Nucleophile, pyridine, reflux

The cycloaddition reaction of salt **4b** with heterocumulenes under similar conditions was also examined, since it was a potentially a straightforward route to heterobetaines. In this case the best conditions for converting **4b** to **6** among several examined were K$_2$CO$_3$/CH$_3$CN. In this two-phase medium the mesomeric conjugated betaines **6a-c**[22] were obtained in good yield.

An interest in derivatives containing the imidazo[1,2-a]pyrrolo[2,1-c]pyrazinium system lead us to try to synthesise more representatives of this series of betaines. Thus, the derivative **6** with the thiolate group (scheme 5, **6a**, Y=S) was easily transformed into new conjugated betaines by S-methylation to **7** and displacement of the methylthio group by nucleophiles. Thus, basic hydrolysis of **6a** produced **6b**, and attack with aniline in pyridine yielded 3-benzoyl-1-phenyl-5,6-dihydroimidazo[1,2-a]pyrrolo[2,1-c]pyrazin-4-ium-2-anilide **8a**. The orange 2-diethoxycarbonylmethylide **8b** and 2-(2'-benzimidazolylamide) **8c** were similarly prepared by pyridine catalysed condensation of the iodide salt **7** with diethyl malonate and 2-aminobenzimidazole respectively.[23]

Structures of all new compounds were supported by full spectroscopic data and combustion analysis. A characteristic feature in the [1]H-nmr spectra of salts **4a** and **4b** is the chemical shift of H-1 protons which resonate as a singlet at 8.84 ppm and 8.50 ppm respectively. This signal is not present in the cycloadducts and the extent of the cycloaddition reaction may be monitored conveniently by [1]H-nmr analysis on the basis of this signal. The analytical and [1]H-nmr data of the cycloadducts are also consistent with the structures of the 2-thiolate and 2-olate assigned to compounds **6**. The conversion of **6a** into **6b** via the salt **7** is a simple and useful confirmation of the structural feature of these betaines.

In summary, although the attempted 1,3-dipolar cycloaddition reaction to 3,4-dihydropyrrolo[1,2-a]-pyrazine azomethine ylides failed with non-stabilized ylides, the cycloaddition of 2-phenacyl-3,4-dihydropyrrolo[1,2-a]pyrazinium salts offers a direct and efficient synthesis of the 5,6-dihydrodipyrrolo-[1,2-a:2',1'-c]pyrazine and 5,6-dihydroimidazo[1,2-a]pyrrolo[2,1-c]pyrazinium ring systems and opens the way to analogous bridged azoles.

EXPERIMENTAL

Melting points were determined on a Buchi SMP-20 and are uncorrected. Ir spectra were recorded on a Perkin-Elmer 700 or 1310 spectrophotometers using KBr pellets. Uv spectra were recorded on a Beckman DU-68 spectrophotometer in methanol (10^{-5} M) (λmax, log ε). [1]H-nmr spectra were obtained on a Varian Unity 300 and a Varian FT-80A instruments at 300 and 80 MHz respectively, using TMS as internal reference. Mass spectra were determined with a Hewlett-Packard 5988 A mass spectrometer at an ionizing voltage of 70 eV. Microanalyses were performed at the Instituto de Química Organica (CSIC), Madrid.

3,4-Dihydropyrrolo[1,2-a]pyrazine (**3a**). To a solution containing 4 g (0.06 mol) of pyrrole in 33 ml of acetonitrile were added 9.4 g (0.23 mol) of powdered sodium hydroxide and 0.8 g (2.36 mmol) of tetrabutylammonium hydrogensulfate (TBAS). After the mixture was stirred at room temperature for 30 min, 2-chloroethylamine hydrochloride (8.2 g, 0.07 mol) was added. The reaction mixture was refluxed for 24 h. Then, the inorganic solid was filtered off and the solvent was removed under reduced pressure to give crude 1-(2-aminoethyl)pyrrole (6.15 g).

The above product was refluxed in formic acid (98%) (45 ml) for 15 h and then concentrated under reduced pressure to give a brown residue which was dissolved in 100 ml of sodium hydroxide solution (40%). This solution was extracted in continuous with dichloromethane for 12 h. The organic layer was washed with water until neutral (4x10 ml), dried over magnesium sulfate and evaporated under reduced pressure to give a brown oil which crystallised under vacuum. Mp 27-29 °C (lit. 26-28 °C, ref. 14).

2-Trimethylsilylmethyl-3,4-dihydropyrrolo[1,2-a]pyrazinium trifluoromethanesulfonate (**4a**). A mixture of **3a** (0.5 g, 4.1 mmol) and trimethylsilylmethyl trifluoromethanesulfonate (0.98 g, 4.1 mmol) in dry dichloromethane (25 ml) was stirred at room temperature under argon for 2 h. The solvent was evaporated under reduced pressure to leave an oily residue which consisted mainly of the salt **4a** (95% by ^{1}H-nmr) and was used without further purification. Ir (CHCl$_3$) v_{max} 3112, 1632, 1610, 1450, 1082 cm^{-1}; ^{1}H-nmr (80 MHz), δ (DMSO-d$_6$) 0.20 (s, 9H); 3.87 (s, 2H); 3.4-3.6 (m, 4H); 6.28 (dd, 1H, J$_{6-7}$=4 Hz, J$_{7-8}$=2.5 Hz); 6.33 (d, 1H, J=4 Hz); 6.96 (d, 1H, J=2.5 Hz); 8.50 (s, 1H) ppm.

2-Phenacyl-3,4-dihydropyrrolo[1,2-a]pyrazinium Bromide (**4b**). A mixture of **3a** (1.08 g, 9.0 mmol) and phenacyl bromide (1.8 g, 9.0 mmol) was refluxed in acetone (20 ml) for 4 h. The reaction mixture was left overnight at 4 °C and the resulting precipitate was filtered off to give a brown solid which was crystallised from ethanol-diethyl ether to give 1.82 g (63%) of the title compound. Mp 208-209 °C; Found: C, 56.33; H, 4.78; N, 8.82. C$_{15}$H$_{15}$BrN$_2$O$_2$ requires C,56.44; H,4.74; N,8.78. Ir (KBr) v_{max} 3117, 2903, 1690, 1629, 1190, 1036, 802 cm^{-1}; ^{1}H-nmr (80 MHz), δ (DMSO-d$_6$), 4.20 (t, 2H, J=7.0 Hz); 4.42 (t, 2H, J=7.0 Hz); 5.74 (s, 2H); 6.6 (dd, 1H, J$_{6-7}$=4.0 Hz, J$_{7-8}$=3.0 Hz); 7.4-8.0 (m, 7H); 8.84 (s, 1H) ppm.

3-Benzoyl-1,2-dimethoxycarbonyl-5,6-dihydrodipyrrolo[1,2-a:2',1'-c]pyrazine (**5a**). To a solution containing 0.2 g (0.62 mmol) of **4b** in dichloromethane (15 ml) were added dimethylacetylene dicarboxylate (DMAD) (120 mg, 0.84 mmol) and an aqueous solution of potassium carbonate (50%, 6 ml) and the mixture was stirred at room temperature for 15 h. Then the organic phase was separated, and the aqueous layer extracted with dichloromethane (4x4 ml). The combined organic phases were dried over magnesium sulfate. The solution was concentrated under reduced pressure to leave an oily residue, which was triturated with ether to give 112 mg (48%) of a yellow compound whose structure was identified as **5a**. Mp 123-124 °C (ethanol); Found C, 66,52, H, 4,62, N, 7,18. C$_{21}$H$_{18}$N$_2$O$_5$ requires C, 66.66; H, 4.80; N, 7.40. Ir (KBr) v_{max}=2950, 2821, 1731, 1704, 1679, 1437, 1292, 1106 cm^{-1}; λ_{max} (MeOH) 372 (39.5), 314 (40.4), 250 (42.3), and 212 nm (43.6). ^{1}H-nmr (80 MHz), δ (DMSO-d$_6$), 3.63 (s, 3H); 3.82 (s, 3H); 4.41 (t, 2H, J=6.0 Hz); 4.87 (t, 2H, J=6.0 Hz); 6.25 (dd, 1H, J$_{8-9}$=2.5 Hz, J$_{9-10}$=3.5 Hz); 7.07 (d, 1H, J=2.5 Hz); 7.2-7.8 (m, 6H) ppm.

3-Benzoyl-1-methoxycarbonyl-5,6-dihydrodipyrrolo[1,2-a:2',1'-c]pyrazine (**5b**). To a solution containing 0.2 g (0.62 mmol) of **4b** in dichloromethane (15 ml) were added methyl propiolate (60 mg, 0.8 mmol) and an aqueous solution of potassium carbonate (50%, 6 ml) and the reaction mixture was stirred at room temperature for 10 h. Then the organic phase was separated, and the aqueous layer was extracted with dichloromethane (4x4 ml). The combined organic phases were dried over magnesium sulfate. The solution was concentrated under reduced pressure to give an oily residue which was triturated with petroleum ether to give 98 mg (49%) of the title compound. Mp 104-106 °C (yellow powder, ethanol); Found C, 71.16, H, 4.85, N, 8.48. C$_{19}$H$_{16}$N$_2$O$_3$ requires C, 71.24; H, 5.03; N, 8.75. Ir (KBr) v_{max}=2947, 1706, 1617, 1472, 988 cm^{-1}; ^{1}H-nmr (300 MHz), δ (DMSO-d$_6$), 3.82 (s, 3H); 4.41 (t, 2H, J=6.3 Hz); 4.86 (t, 2H, J=6.3 Hz); 6.35 (dd, 1H, J$_{8-9}$=2.3 Hz, J$_{9-10}$=3.4 Hz); 7.07 (d, 1H, J=2.3 Hz); 7.2-7.8 (m, 7H) ppm.

3-Benzoyl-1-phenyl-5,6-dihydroimidazo[1,2-a]pyrrolo[2,1-c]pyrazin-4-ium-2-thiolate (**6a**). To a stirred two-phase mixture comprising a solution of the salt **4b** (200 mg, 0.62 mmol) in dry acetonitrile (12 ml) and potassium carbonate (0.23 g, 1.66 mmol), phenylisothiocyanate (100 mg, 0.74 mmol) was added, and stirring was continued at room temperature for 24 h; then the precipitate was filtered and washed with dichloromethane (3x5 ml). The combined organic phases were dried over magnesium sulfate

and evaporated to leave a pale yellow solid. Silica gel chromatography of this material using a 7:3 hexane-ethyl acetate mixture gave 170 mg (74%) of the betaine **6a**. Mp 177-179 $^{\circ}$C (acetone); Found: C, 71.25; H, 4,58; N, 11.43. $C_{22}H_{17}N_3OS$ requires C, 71.13; H, 4,61; N, 11.31. Ir (KBr) v_{max}=3057, 2928, 1592, 1529, 1391, 1281, 1206, 1172, 1074 cm^{-1}; λ_{max} (MeOH) 396 (36), 332 (38.5), and 206 nm (42.1). ^{1}H-nmr (300 MHz), δ (DMSO-d$_6$), 4.46 (t, 2H, J=5.8 Hz); 4.72 (t, 2H, J=6.0 Hz); 5.97 (t, 1H, J=3.5 Hz); 6.36 (t, 1H, J=3.9 Hz); 7.10 (d, 1H, J= 2.4 Hz); 7.3-7.5 (m, 6H); 7.6-7.8 (m, 2H); 8.2-8.3 (m, 2H) ppm.

3-Benzoyl-1-phenyl-5,6-dihydroimidazo[1,2-a]pyrrolo[2,1-c]pyrazin-4-ium-2-olate (**6b**). To a stirred two-phase mixture comprising a solution of the salt **4b** (160 mg, 0.50 mmol) in dry acetonitrile (7 ml) and potassium carbonate (0.19 g, 1.37 mmol), phenylisocyanate (80 mg, 0.67 mmol) was added, and stirring was continued at room temperature for 10 h; then the precipitate was filtered and washed with dichloromethane (3x4 ml). The combined organic phases were dried over magnesium sulfate and evaporated to leave a yellowish oil. Silica gel chromatography of this oil using a 7:3 hexane-ethyl acetate mixture gave 150 mg (84%) of the title compound. Mp 144-145 $^{\circ}$C (ethanol); Found: C, 74.49; H, 4.57; N, 11.53. $C_{22}H_{17}N_3O_2$ requires C, 74.35; H, 4.82; N, 11.82. Ir (KBr) v_{max}=3053, 1666, 1600, 1538, 1424, 1127, 1078 cm^{-1}; ^{1}H-nmr (300 MHz), δ (DMSO-d$_6$), 4.2-4.5 (m, 4H); 5.93 (d, 1H, J=3.5 Hz); 6.36 (t, 1H, J=3.8 Hz); 7.2-7.3 (m, 3H); 7.5-7.6 (m, 6H); 8.0-8.1 (m, 2H) ppm.

Alternatively, a solution of **6a** (100 mg, 0.27 mmol) in methanol (5 ml) was added dropwise to a solution of sodium hydroxide (0.3 ml, 50%) and the reaction mixture was stirred at room temperature for 12 h. The solvent was removed under reduced pressure, water (5 ml) was added to the residue and the solution was extracted with dichloromethane. The organic phase was dried over magnesium sulfate, evaporated and the residue chromatographed on silica gel. Elution with hexane-ethyl acetate afforded 63 mg (66%) of **6b**.

3-Benzoyl-1-methyl-5,6-dihydroimidazo[1,2-a]pyrrolo[2,1-c]pyrazin-4-ium-2-thiolate (**6c**). To a stirred two-phase mixture comprising a solution of the salt **4b** (560 mg, 1.7 mmol) in dry acetonitrile (25 ml) and potassium carbonate (0.66 g, 4.78 mmol), methylisothiocyanate (154 mg, 2.1 mmol) was added, and stirring was continued at room temperature for 14 h; then the precipitate was filtered and washed with dichloromethane (2x5 ml). The combined organic phases were dried over magnesium sulfate and evaporated to give a brown solid residue. Silica gel chromatography of this material using a 7:3 hexane-ethyl acetate mixture gave 320 mg (59%) of the betaine **6c**, which crystallised from hexane-ethyl acetate afforded orange crystals. Mp 151-152 $^{\circ}$C; Found: C, 66.08; H, 4,53; N, 13.62. $C_{17}H_{15}N_3OS$ requires C, 65.99; H, 4,88; N, 13.58. Ir (KBr) v_{max}=3065, 2925, 1697, 1605, 1365, 1076, 1037 cm^{-1}; ^{1}H-nmr (300 MHz), δ (DMSO-d$_6$), 3.94 (s, 3H); 4.42 (t, 2H, J=6.1 Hz); 4.81 (t, 2H, J=5.9 Hz); 6.46 (t, 1H, J=3.8 Hz); 6.92 (d, 1H, J=3.9 Hz); 7.05 (d, 1H, J=2.5 Hz); 7.3-7.4 (m, 2H); 7.5-7.9 (m, 3H) ppm.

3-Benzoyl-1-phenyl-2-methylthio-5,6-dihydroimidazo[1,2-a]pyrrolo[2,1-c]pyrazin-4-ium iodide (**7**). To a stirred suspension of the betaine **6a** (150 mg, 0.4 mmol) in dry ethyl acetate (12 ml), methyl iodide (220 mg, 1.55 mmol) was added, and stirring was continued at room temperature for 48 h. The resultant precipitate was filtered off and recrystallised from ethyl acetate to give the salt **7** as pale yellow crystals (180 mg, 88%). Mp>260 $^{\circ}$C. Found: C,53.98; H,3,85; N,8.24. $C_{23}H_{20}IN_3OS$ requires C, 53.80; H, 3,92; N, 8.18. Ir (KBr) v_{max}=3078, 1642, 1608, 1375, 1227, 1010 cm^{-1}; λ_{max} (MeOH) 318 (37.7), and 208 nm (41.8); ^{1}H-nmr (300 MHz), δ (DMSO-d$_6$), 2.07 (s, 3H); 4.73 (t, 2H, J=5.9 Hz); 4.76 (t, 2H, J=6.2 Hz);

5.61 (d, 1H, J=4.1 Hz); 6.01 (t, 1H, J=4.2 Hz); 7.02 (d, 1H, J=2.4 Hz); 7.5-7.7 (m, 6H); 8.0-8.1 (m, 2H); 8.4-8.5 (m, 2H) ppm.

3-Benzoyl-1-phenyl-5,6-dihydroimidazo[1,2-a]pyrrolo[2,1-c]pyrazin-4-ium-2-anilide (**8a**). To a solution of **7** (210 mg, 0.4 mmol) in dry pyridine (4 ml), aniline (110 mg, 1.18 mmol) was added and the mixture was stirred at reflux temperature for 16 h. The reaction mixture was then allowed to reach room temperature and evaporated under reduced pressure. The residue was chromatographed on silica gel using a mixture of hexane-ethyl acetate to give 100 mg (58%) of a orange solid. Recrystallisation from hexane-ethyl acetate afforded pure derivative **8a**. Mp 224-225 $^{\circ}$C; Found: C,78.21; H,4.95; N,12.85. $C_{28}H_{22}N_4O$ requires C,78.11; H,5.15; N,13.01. Ir (KBr) v_{max}=2923, 1729, 1649, 1479, 1314, 1070 cm^{-1}; ^{1}H-nmr (300 MHz), δ (CDCl$_3$), 4.47 (t, 2H, J=6.3 Hz); 4.70 (t, 2H, J=6.2 Hz); 5.20 (d, 1H, J=3.0 Hz); 6.09 (t, 1H, J=2.5 Hz); 7.1-7.2 (m, 1H); 7.4-7.6 (m, 13H); 7.8-7.9 (m, 2H) ppm.

3-Benzoyl-1-phenyl-5,6-dihydroimidazo[1,2-a]pyrrolo[2,1-c]pyrazin-4-ium-2-diethoxycarbonylmethylide (**8b**). To a solution of **7** (160 mg, 0.31 mmol) in dry pyridine (4 ml), diethyl malonate (150 mg, 0.93 mmol) was added and the mixture was stirred at reflux temperature for 4 h. The reaction mixture was then allowed to reach room temperature. Evaporation of the solvent under reduced pressure and chromatography of the residue on silica gel using acetone as eluent gave 90 mg (58%) of the betaine **8b**. Recrystallisation from acetone afforded orange crystals. Mp 256-257 $^{\circ}$C; Found: C, 69.75; H, 5.54; N, 8.24. $C_{29}H_{27}N_3O_5$ requires C, 70.01; H, 5.47; N, 8.45. Ir (KBr) v_{max}=2924, 1722, 1643, 1605, 1423, 1266, 1013 cm^{-1}; ^{1}H-nmr (300 MHz), δ (CDCl$_3$), 1.27 (t, 6H, J=5.6 Hz); 4.21 (q, 4H, J=4.7 Hz); 4.73 (t, 2H, J=6.2 Hz); 4.76 (t, 2H, J=5.7 Hz); 5.62 (d,1H, J=4.1 Hz); 6.14 (t, 1H, J=4.1 Hz); 6.99 (d, 1H, J=3.5 Hz); 7.3-7.4 (m, 2H); 7.5-7.7 (m, 4H); 8.0-8.4 (m, 4H) ppm.

3-Benzoyl-1-phenyl-5,6-dihydroimidazo[1,2-a]pyrrolo[2,1-c]pyrazin-4-ium-2-(2'-benzimidazoylamide) (**8c**). To a solution of **7** (100 mg, 0.19 mmol) in dry pyridine (3 ml) was added 2-aminobenzimidazole (80 mg, 0.60 mmol) and the mixture was stirred at reflux temperature for 16 h. The reaction mixture was then allowed to reach room temperature and evaporated under reduced pressure. The residue was chromatographed on silica gel (hexane-ethyl acetate 7:3) to give 50 mg (56%) of a product identified as the title compound. Recrystallisation from hexane-ethyl acetate afforded orange crystals. Mp >260 $^{\circ}$C; Found: C, 74.23; H, 4.77; N, 17.78. $C_{29}H_{22}N_6O$ requires C, 74.02; H, 4.71; N, 17.86. Ir (KBr) v_{max}=3150, 1588, 11538, 1171 cm^{-1}; ^{1}H-nmr (300 MHz), δ (DMSO-d$_6$), 4.45 (t, 2H, J=5.9 Hz); 4.72 (t, 2H, J=5.6 Hz); 5.19 (d, 1H, J=4.1 Hz); 6.08 (t, 1H, J=3.9 Hz); 7.1-7.2 (m, 1H); 7.4-7.7 (m, 13H); 7.8-7.9 (m, 2H) ppm.

REFERENCES

1. (a) Thummel, R.P; Lefoulon, F.; Mahadevan, R. *J. Org. Chem.*, **1985**, *50*, 3824. (b) Thumel R.P.; Jahng, Y.; *J.Org. Chem.*, **1985**, *50*, 2407. (c) Thummel, R.P.; Lefoulon, F.; Cantu, D.; Mahadevan R.; *J. Org. Chem.*, **1984**, *49*, 2208. (d) Thummel, R.P.; Hegde, V. *J. Org. Chem.*, **1989**, *54*, 1720.

2.   (a) Thummel, R.P.; Lefoulon, F.; Korp, J.D. *Inorg. Chem.*, **1987**, *26*, 2370. (b) Thummel, R.P.; Lefoulon, F. *Inorg. Chem.*, **1987**, *26*, 675. (c) Thummel, R.P.; Decloitre, Y. *Inorg. Chim. Acta*, **1987**, *128*, 245.

3.   Thummel, R.P.; Lefoulon, F.; Chirayil, S.; Guolle, V. *J. Org. Chem.*, **1988**, *53*, 4745.

4.   Thummel, R.P.; Guolle, V.; Chen, B. *J. Org. Chem.*, **1989**, *54*, 3057.

5.   Goulle, V.; Chirayil, s.; Thummel, R.P. *Tetrahedron Lett.*, **1990**, *31*, 1539.

6.   Sliwa, W.; Bachowska, B.; Zelichowicz, N. *Heterocycles*, **1991**, *32*, 2241.

7.   Coche, L.; Moutet, J.C. *J. Electroanal. Chem.*, **1987**, *224*, 111.

8.   Willner, I.; Steinberger-Willner, B. *Int. J. Hydrogen Energy*, **1988**, *13*, 593.

9.   Kitazawa, K.; Kobayashi, T.; Shibamoto, T.; Hirai, K. *Am. Rev. Respir. Dis.*, **1988**, *137*, 173. (*Chem. Abstr.*, **1988**, *108*, 10779s).

10. Matia, M.P.; Ezquerra, J.; Sanchez-Ferrando, F., Garcia-Navio, J.L., Vaquero, J.J.; Alvarez-Builla, J. *Tetrahedron*, **1990**, *47*, 7329.

11. Buchman, R.; Fraser, M.; Kong Thoo Lin, P.V.S. *Heterocycles*, **1989**, *28*, 857.

12. Berger, V.; Dreier, F.; *Tetrahedron*, **1983**, *39*, 2065.

13. Lown, J.W. in *1,3-Dipolar Cycloaddition Chemistry*, Padwa, A., Ed. Wiley-Interscience, New **1984**, vol. 2, pp. 653-732.

14. Flament, I.; Sonney, P.; Ohloff, G.; *Helv. Chim. Acta*, **1977**, *60*, 1872.

15. Cuadro, A.M.; Matía, M.P.; García, J.L.; Vaquero, J.J.; Alvarez-Builla, J. *Synthetic Comm.*, **1991**, *21*, 535.

16. Tsuge, O.; Kanemasa, S.; Kuraoka, S.; Takenaka, S; *Chem. Lett.*, **1984**, 279.

17. Katritzky, A.R; Grzeskowiak, N.E.; Alvarez-Builla, J. *J. Chem. Soc., Perkin Trans. I*, **1981**, 1180.

18. Padwa, A.; Fryxel, G.E.; Gasdaska, J.R.; Venkatramanan, M.K.; Wong, G.S.K. *J. Org. Chem.*, **1989**, *54*, 644 and references.

19. Alvarez-Builla, J.; Quintanilla, G.; Abril, C.; Gandásegui, M.T.; *J. Chem. Research (S)*, **1984**, 202.

20. Gandásegui, M.T.; Alvarez-Builla, J. *J. Chem. Research (S)*, **1986**, 74.

21. Molina, A.; Cuadro, A.M.; Novella, J.L.; Vaquero, J.J.; García, J.L.; Alvarez-Builla, J. *Tetrahedron*, **1990**, *46*, 6033.

22. Ollis, W.D.; Stanforth, S.P.; Ramsden, C.A.; *Tetrahedron*, **1985**, *41*, 2239.

23. Newton, C.G.; Ollis, W.D.; Wright, D.; *J. Chem. Soc., Perkin Trans. I*, **1984**, 69.