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SYNTHESIS OF HIGHLY STABILISED YLIDES FROM N-[2-(1,3-BENZAZOLYLMETHYL)]PYRIDINIUM SALTS

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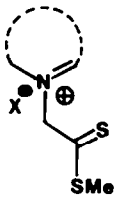
Abstract.- A series of new stable ylides has been synthesized by the reaction of N-[2-(1,3-benzazolylmethyl)]-pyridinium salts with electrophiles such as carbon disulphide, isothiocyanate derivatives, phenylisocyanate and benzoyl chloride in a two-phase system. Preparation of pyridinium ketene dithioacetal derivatives and attempts to transform them into N-(diheteroarylmethyl)pyridinium ylides are also described.

In one of the earlier parts of this series[1] we described a general route to N-[(methylthio)thiocarbonylmethyl]azinium salts 1 based on the reaction of phenacylazinium derivatives with carbon disulphide/methyl iodide followed by acid treatment of the ylides thus formed. We also reported an application of these salts to the synthesis of a series of N-(heteroarylmethyl)azinium salts[1-4] 2 which showed interesting activity as antibacterials.[5]



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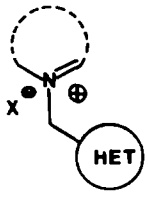

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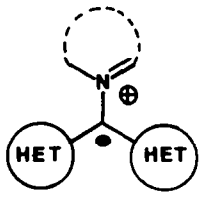

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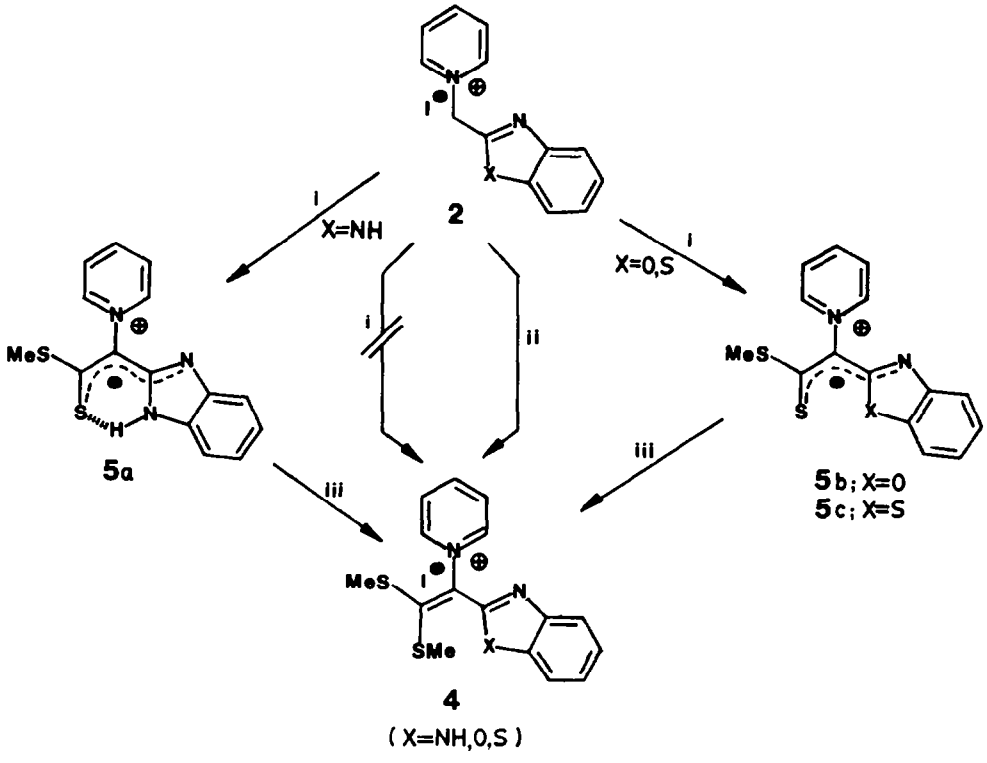
Scheme 1. HET=Heteroaromatic; 1:X=I; 2:X=I or BF_4

In the course of preparing N-(diheteroarylmethyl)azinium salts 3, our initial intention was to prepare the pyridinium ketene dithioacetals 4 in the expectation that these derivatives might be converted into the desired systems 3 by reaction with the appropriate dinucleophiles.

Various attempts of preparing the derivative 4a by the reaction of 1-(2'-benzimidazolylmethyl)pyridinium iodide and carbon disulphide/methyl iodide were all unsuccessful, giving a dark red crystalline compound identified as the ylide 5a[1]



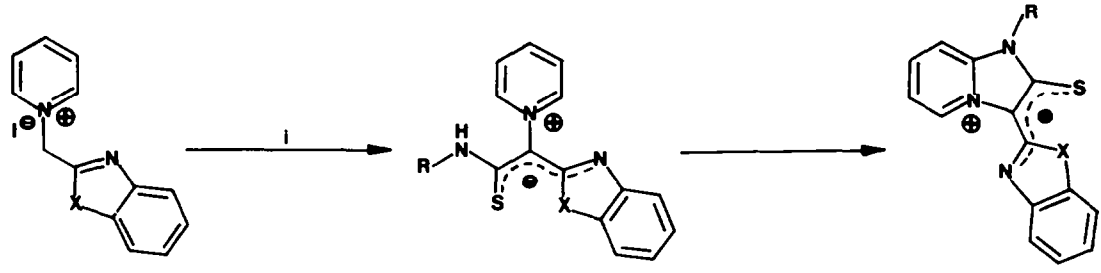
Scheme 2. Reagents: i, CS_2/MeI (2 eq.)/K_2CO_3 (aq., 50%), r.t.;
ii, CS_2/MeI (20 eq.)/K_2CO_3 (aq., 50%), r.t.;
iii, MeI (2 eq.)/MeOH, r.t.

The easy formation and high stability of this ylide towards S-methylation was attributed not only to delocalization of the negative charge but also to the intramolecular hydrogen bonding present in the ylide. It was therefore

expected that if Het were a heteroaromatic moiety other than benzimidazolyl-, for example, benzoxazolyl- or benzothiazolyl- (both unable to form intramolecular hydrogen bonding) the corresponding ylide might be easier S-methylated. However, the reaction of both N-[2-(1,3-benzazolylmethyl)]pyridinium salts 2a and 2b with carbon disulphide/methyl iodide gave the corresponding ylides 5b and 5c as the only products.

Clearly, the use of an excess of the alkyl halide would enhance the formation of the ketene dithioacetal and we found that direct preparation of 4 requires in fact, a large excess of methyl iodide (1:20). However, two equivalents of the alkyl halide in methanol transformed the ylides 5a-c into the corresponding ketene dithioacetals 4, which can be used as a two-step alternative[6,7]

In view of the high stability of all these ylides, attempts to extend the versatility of the use of N-[2-(1,3-benzazolylmethyl)]azinium salts 2 in the preparation of related ylides were undertaken. In the event, the reaction of salts 2 with phenylisothiocyanate was not straightforward, and the corresponding ylides were not obtained or were obtained in varying yields. Thus the reaction of the salt 2a with the isothiocyanate derivative in acetonitrile/K_2CO_3 gave the betaine 9a in 23% yield as the only identifiable product.



Scheme 3. Reagents: i, R-N=C=S/CH_2Cl_2/K_2CO_3 (aq., 50%), r.t.;

When the same reaction was carried out in CH_2Cl_2/K_2CO_3 (aq., 50%), t.l.c. and ^1H n.m.r. analysis indicated the formation of two products. Attempted chromatographic separation was unsuccessful since the minor product is completely transformed into the major product, this latter being identified as the betaine 9a which was isolated in much improved yield (54%).

Table 1. Physical and Analytical Data of Compounds 4-6.

Compd. No.	X	R	Yield (%)	Mp (°C)	Cryst. form	Microanalyses Calc (%) / Found (%) C	H	N
4a	NH	--	91[a], 84[b]	147-148 (EtOH)	Yellow needles	34.5 34.75	3.7 3.85	3.65 3.7
4b	O	--	67[a], 83[b]	178-179 (MeCN)	Yellow powder	[c]41.7 41.5	3.7 3.6	6.1 6.4
4c	S	--	68[a], 80[b]	207-208 (EtOH)	Yellow prisms	41.9 41.6	3.3 3.4	6.1 5.8
5a	NH	--	44	218-219[d] (EtOH)				
5b	O	--	51	188-189 (Acetone)	Red prisms	60.0 59.7	4.0 4.0	9.3 9.7
5c	S	--	70	203-204 (Acetone)	Red prisms	56.9 56.7	3.8 3.7	8.8 8.8
6a	NH	C_6H_5	--					
6b	O	C_6H_5	72	156-157 (MeCN)	Purple needles	69.5 69.3	4.4 4.0	12.2 11.9
6c	S	C_6H_5	72	137-138 (MeCN)	Brown prisms	66.45 66.7	4.2 4.0	11.6 11.4
6d	O	4-H_3C-C_6H_4	95	146-147 (MeOH)	Brown powder	70.2 69.9	4.8 4.5	11.7 11.9
6e	S	4-H_3C-C_6H_4	82	153-154 (EtOH)	Brown powder	67.7 66.9	4.6 4.35	11.2 11.4
6f	O	4-Cl-C_6H_4	80	152-153 (EtOH)	Deep red needles	63.2 63.0	3.7 3.4	11.0 11.4
6g	S	4-Cl-C_6H_4	80	153-154 (EtOH)	Brown prisms	60.7 60.35	3.6 3.4	10.6 10.8
6h	S	CH_3	79	162-163 (EtOH)	Deep red prisms	60.2 59.9	4.4 4.0	14.0 13.9

[a]Method A; [b]Method B; [c]Molecular formula $C_{16}H_{15}IN_2OS_2.H_2O$;

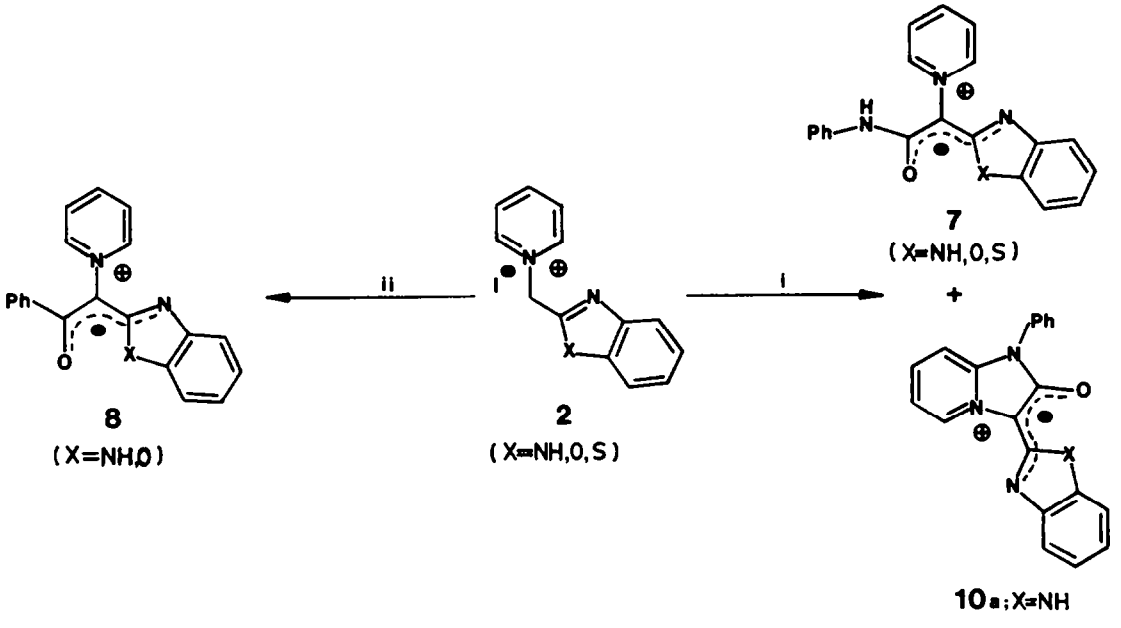
[d]Described in ref 2.

Table 2. Spectroscopic Data of Compounds 4-6.

Compound No.	Ir (KBr) ν (cm^{-1})	^{1}H-Nmr[a] δ (ppm)
4a	870,1175,1235,1320, 1435,1480,1630,3210	2.45 (s, 3H) ; 2.63 (s, 3H) ; 7.0-7.8 (m, 4H) ; 8.39 (t, 2H) ; 8.90 (t, J=8 Hz, 1H) ; 9.37 (d, J=6 Hz, 2H)
4b	860,1160,1245,1445, 1460,1545,1620,3050	2.59 (s, 3H) ; 2.84 (s, 3H) ; 7.4-8.0 (m, 6H) ; 8.53 (t, 2H) ; 9.04 (t, J=8 Hz, 1H) ; 9.54 (d, J=6 Hz, 2H)
4c	880,1150,1320,1420, 1460,1620,3040	2.62 (s, 3H) ; 2.81 (s, 3H) ; 7.4-8.3 (m, 4H) ; 8.51 (t, 2H) ; 9.00 (t, J=8 Hz, 1H) ; 9.44 (d, J=6 Hz, 2H)
5b	870,939,1163,1242, 1404,1453,1465,1508, 1623	2.57 (s, 3H) ; 7.0-7.5 (m, 4H) ; 8.15 (t, 2H) ; 8.63 (t, J=8 Hz, 1H) ; 8.98 (d, J=5 Hz, 2H)
5c	852,935,1148,1259, 1434,1446,1452,1462, 1474,1615,3054,3075	2.43 (s, 3H) ; 7.0-7.9 (m, 4H) ;8.22 (t,2H) ; 8.74 (t, J=8 Hz, 1H) ; 9.07 (d, J=5 Hz, 2H)
6b	935,1220,1250,1285 1305,1340,1395,1460, 1500,1530,1600	6.8-7.9 (m, 9H) ; 8.00 (t, 2H) ; 8.50 (t, J=8, Hz, 1H) ; 9.00 (d, J=6 Hz, 2H) ; 12.03 (s, 1H)
6c	881,1113,1293,1340, 1461,1494,1562,1593, 1619	6.9-7.4 (m, 5H) ; 7.5-7.9 (m, 4H) ;8.19 (t,2H) ; 8.60 (t, J=8 Hz, 1H) ; 9.04 (d, J=6 Hz, 2H) ; 12.70 (s, 1H)
6d	919,1208,1238,1296, 1317,1381,1456,1467, 1621	2.29 (s, 3H) ; 6.8-7.4 (m, 6H) ; 7.65 (d, 2H) ; 8.12 (t, 2H) ; 8.62 (t, J=8 Hz, 1H) ; 9.06 (d, J=6 Hz, 2H) ; 11.86 (s, 1H)
6e	882,1110,1297,1350, 1440,1471,1510,1556 1612	2.27 (s, 3H) ; 6.9-7.8 (m, 8H) ; 8.17 (t, 2H) ; 8.67 (t, J=8 Hz, 1H) ; 9.02 (d, J=6 Hz 2H) ; 12.56 (s, 1H)
6f	924,1212,1246,1324, 1380,1410,1455,1464 1489,1529,1620	6.9-7.5 (m, 6H) ; 7.88 (d, 2H) ; 8.14 (t, 2H) ; 8.64 (t, J=8 Hz, 1H) ; 9.06 (d, J=6 Hz, 2H) ; 12.01 (s, 1H)
6g	883,1116,1261,1298, 1354,1439,1465,1487 1554,1619	6.9-7.4 (m, 4H) ; 7.65 (d, 2H) ; 7.90 (d, 2H) ; 8.19 (t, 2H) ; 8.69 (t, J=8 Hz, 1H) ; 9.04 (d, J=6 Hz,2H) ; 12.81 (s, 1H)
6h	860,1044,1067,1100, 1296,1350,1443,1469 1547,1618	3.14 (d, 3H) ; 6.7-7.6 (m, 4H) ; 8.13 (t, 2H) ; 8.64 (t, J=8 Hz, 1H) ; 8.93 (d, J=6 Hz, 2H) ; 10.33 (s, 1H)

[a] In DMSO-d_6.

This suggests that under the above mentioned reaction conditions the corresponding ylide **6a** is probably formed but it cyclizes to the bicyclic system **9a** under chromatographic and reaction conditions. On the other hand, the reaction of azinium salts **2b** and **2c** with isothiocyanate derivatives under similar conditions gave mixtures containing only traces of the corresponding betaines, being the ylides **6b–h** the major products. These ylides seem to be less susceptible to intramolecular nucleophilic attack and can be readily purified by chromatography on silica gel. Phenylisocyanate reacted with the salt **2a** in acetonitrile/K_2CO_3 to give a mixture of the ylide **7a** and the betaine **10a**. Again the chromatographic conditions favoured betaine formation though to a smaller but still significant extent, although in this case the ylide is the major product. The reaction of phenylisocyanate with salts **2b,c**



Scheme 4. Reagents: i, Ph–N=C=O/MeCN/K_2CO_3, r.t.
ii, Ph–COCl/CH_2Cl_2/K_2CO_3 (aq., 50%), r.t.

afforded the ylides **7b,c** and no detectable amounts of the corresponding betaines were observed. The analogous reaction of the salts with benzoyl chloride gave the ylides **8a,b** but this reaction failed to give the expected ylide when the salt **2c** was used. The complete absence of the ylide **8c** is striking since the ylides **8a,b** were obtained in good yield in spite of their lower stability.

Table 3. Physical and Analytical Data of Ylides 7 and 8

Compd. No.	X	Yield (%)	Mp (°C)	Cryst. form	Microanalyses Calc (%) Found (%) C	H	N
7a	NH	34	291-292 (Acetone)	Yellow powder	[a]69.8 70.15	4.6 4.3	16.3 16.0
7b	O	65	179-180 (MeCN)	Brown prisms	72.9 72.7	4.6 4.4	12.75 12.6
7c	S	90	105-106 (MeCN)	Purple prisms	69.5 69.4	4.4 4.2	12.2 11.9
8a	NH	73	222-223[b]	Orange powder	76.4 76.8	5.1 4.9	13.15 12.8
8b	O	66	133-134[c] (Toluene)	Orange powder	72.3 72.7	4.8 4.9	8.4 8.5
8c	S	--					

[a]Molecular formula $C_{20}H_{16}N_4O.H_2O$. [b]This ylide extensively decomposes upon recrystallization from acetonitrile and ethanol or in chromatographic conditions (silica gel, 60 Merck, 230-400 mesh). No decomposition was observed when the product was recrystallized in a mixture of ethyl acetate-ethanol. [c]Hygroscopic. [d]Molecular formula $C_{20}H_{14}N_2O_2.1/2H_2O$.

Table 4. Spectroscopic Data of Ylides 7 and 8

Compound No.	Ir (KBr) ν (cm^{-1})	^{1}H-Nmr[a] δ (ppm)
7a	1211,1263,1425,1452, 1470,1491,1566,1634, 1693,3126	7.0-7.4 (m, 9H); 7.9-8.1 (m, 3H); 8.42 (t, J=8 Hz); 9.17 (d, J=6 Hz, 2H); 12.47 (bs, 1H)
7b	1190,1240,1285,1350, 1428,1450,1485,1520, 1570,1592	6.7-7.8 (m, 9H); 8.05 (t, 2H); 8.46 (t, J=8 Hz, 1H); 9.05 (d, J=6 Hz, 2H); 11.06 (s, 1H)
7c	1167,1247,1293,1317, 1443,1479,1541,1578, 1629	6.8-7.7 (m, 9H); 8.21 (t, 2H); 8.61 (t, J=8 Hz, 1H); 9.02 (d, J=6 Hz, 1H); 11.00 (s, 1H)
8a	707,1242,1268,1307, 1363,1501,1530,1618, 3056,3306,3501	6.9-7.6 (m, 9H); 7.95 (t, 2H); 8.44 (t, J=8 Hz, 1H); 8.98 (d, J=6 Hz, 2H); 12.49 (bs, 1H)
8b	998,1250,1355,1380, 1465,1505,1610,3040,	6.8-7.5 (m, 9H); 8.05 (t, 2H); 8.50 (t, J=8 Hz, 1H); 9.05 (d, J=6 Hz, 2H)

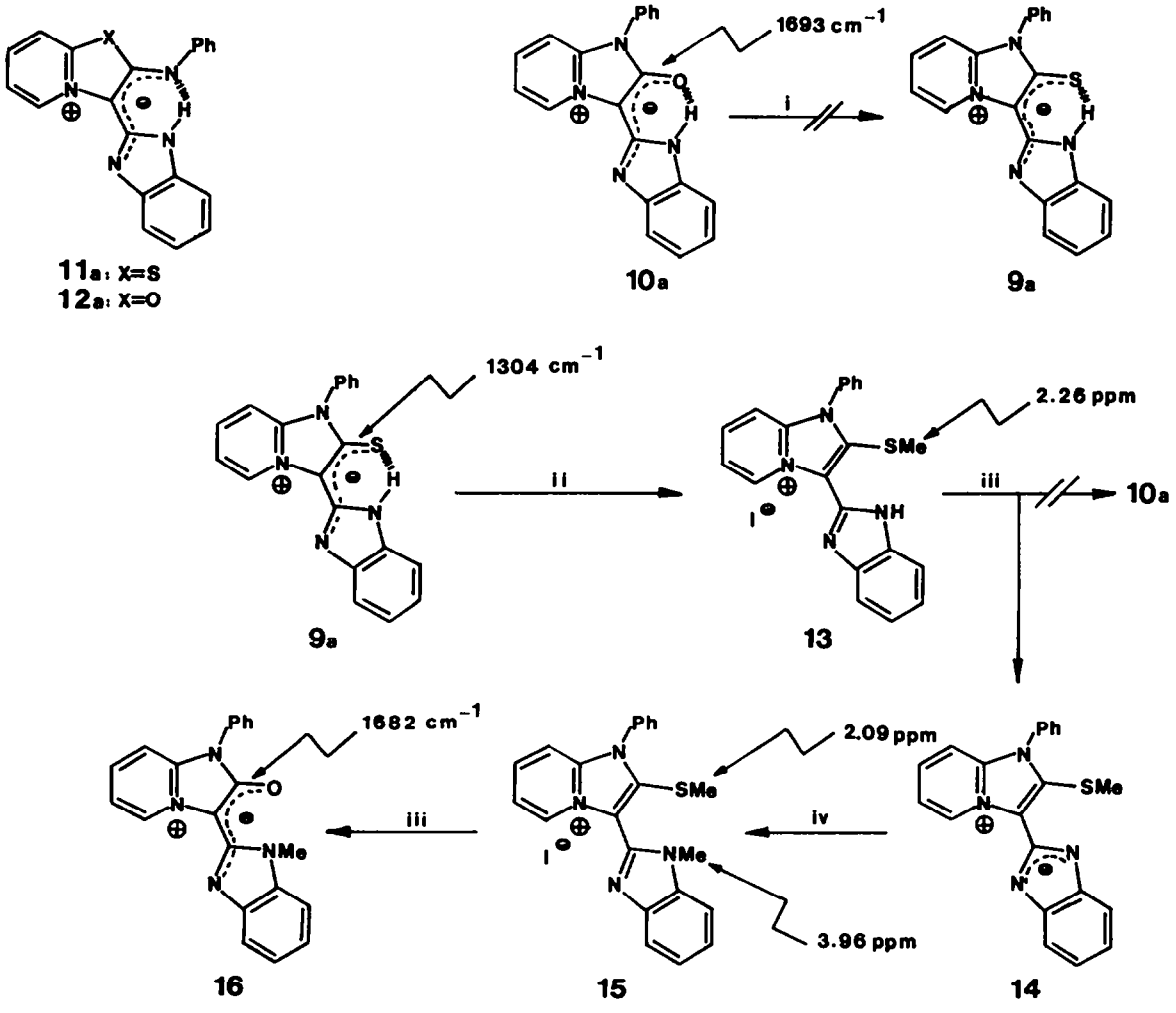
[a]In DMSO-d_6.

The formation of all these stable ylides 5–8 with the exclusion of other products suggests that the heteroaromatic moiety may be a significant factor for their stability probably due to the highly effective delocalization of the negative charge, as found with other azinium ylides.[8–11]

Structures of all new compounds are supported by full spectroscopic data and combustion analysis. The structures of the betaines **9a** and **10a** were assigned by comparison of their spectroscopic properties with those of the ylides **6–8** and other heteroaromatic betaines and on the basis of some chemical transformations of **9a**. A characteristic feature in the ^{1}H n.m.r. spectra of the ylides **5–8** is the chemical shift and coupling of the pyridinium moiety protons which resonate as typical triplets at δ=8.0–8.2 (3- and 5-H) and δ=8.4–8.6 (4-H) and doublet at δ=8.9–9.2 (2- and 6-H). Comparison of the aromatic region of the ^{1}H n.m.r spectra of ylides **6–8** with that of **9a** (twelve proton multiplet at δ=7.1–7.7 and one proton doublet at δ=10.40) and **10a** (twelve proton multiplet at δ=7.0–7.9 and one proton doublet at δ=9.85) clearly suggests the bicyclic structure for the latter compounds although two possible isomers could be generated by the cyclisation reactions shown in schemes 3 and 4. The analytical and ^{1}H n.m.r. spectral data of the cyclisation products are consistent with the structures assigned for **9a** and **10a** but also with isomeric possibilities **11a** and **12a**. However, the i.r. spectra strongly support the structure of the 2-thiolate and 2-olate for **9a** and **10a** respectively. The i.r. spectrum of **10a** exhibits a strong C=O stretching band at 1693 cm^{-1} close to values described for other imidazo[1,2-a]pyridinium-2-olates (1705–1710 cm^{-1}).[12] Although in the only previously described example of imidazo[1,2-a]pyridinium-2-thiolate of which we are aware, the absortion of the C=S (stretching band) is not reported[12] the i.r. spectrum of **9a** shows a strong band at 1304 cm^{-1} (C=S stretching) which is comparable to the absortion observed in mesoionic derivatives of imidazo[2,3-a]isoquinolinium-2-thiolates;[13] 1,2,4-triazoliumthiolates;[14] 1,2,4[triazolo[1,5-a]pyrimidinium-2-thiolates;[15] and 1,2,4-triazolo[1,5-a]pyrimidinium-2-thiolates[16] (1315–1380 cm^{-1}). Thus, i.r. spectra suggest that the imidazo[1,2-a]pyridium-2-thiolate **9a** and imidazo[1,2-a]pyridinium-2-olate **10a** rather than the possible isomeric betaines **11a** and **12a** are the correct structures.

The structural assignments made for **9a** and **10a** on the basis of their spectral data were also supported by some chemical transformations (Scheme 5). Since conversion of **10a** into **9a** or desulphurisation of **9a** to form **10a** would be a simple and useful confirmation of both structures, several attempts were made to form **9a** from **10a** by reaction with Lawessson's reagent[16,17] under various conditions, but these were unsuccessful giving different decomposition products. Alternative conversion of **9a** into **10a** was attempted via the

derivative 13 obtained by S-methylation of 9a. In the event, the S-methylated derivative 13 when treated with base afforded the unusually stable betaine 14 as the sole product. This betaine was methylated to give the salt 15 which was finally converted into the ylide 16, which exhibits the typical spectroscopic characteristics of the ylide 10a, inter alia, a strong band at 1682 cm^{-1} (C=O stretching). The sequence 9a→16 is considered to provide further support for the structural assignment made for 9a and 10a on the basis of their spectroscopical properties.



Scheme 5. i, Lawesson's reagent, CH_2Cl_2-toluene, reflux. ii, EtOAc/MeI, r.t.; iii, MeOH/NaOH (aq., 50%), r.t.; iv, EtOAc/MeI, r.t.

In order to prepare the diheteroarylmethyl azinium ylides 3 we undertook a study of the reaction of the ketene dithioacetals **4a** and **4b** with 1,2-diaminobenzene. Unfortunately, numerous attempts to prepare the desired compounds failed, and further work with this dinucleophile was abandoned. Other dinucleophiles such as 1,8-diaminonaphthalene were also totally ineffective, the starting material being recovered in all cases.

In summary, although our attempts to prepare the diheteroarylmethyl azinium ylides 3 far thus been thwarted, a useful preparation of a series of ylides stabilized by a heteroaromatic moiety have surfaced. Alternative methods for the synthesis of ylides 3 are currently being investigated.

EXPERIMENTAL

Melting points were determined on a Buchi SMP-20 and are uncorrected. Ir spectra were recorded on Perkin-Elmer 700 or 1310 spectrophotometers. ^{1}H-nmr spectra were obtained on Bruker WP 60 Wc and Varian FT-80A instruments using TMS as internal reference.

Reaction of N-[2-(1,3-benzazolylmethyl)]pyridinium salts 2 with carbon disulphide/methyl iodide.

A) Preparation of pyridinium ketene dithioacetals derivatives (4a-c). Method A: A mixture of the corresponding salt of N-[2-(1,3-benzazolylmethyl)]pyridinium iodide (2 mmol), carbon disulphide (20 ml), an aqueous solution of potassium carbonate (20 ml, 50%) and methyl iodide (40 mmol) was stirred at room temperature for 4 days. The reaction mixture was then extracted with methylene chloride (3x30 ml) and the organic phase was washed with water until neutral, dried with magnesium sulphate and evaporated to give a solid residue. Recrystallization from the solvent indicated in Table 1 gave the corresponding pyridinium ketene dithioacetal derivatives **4a-c**.

B) **Preparation of N-[2-(1,3-benzazolyl)(methylthiothiocarbonyl)]pyridinium methylides (5a-c).** A mixture of the corresponding salt of N-[2-(1,3-benzazolylmethyl)]pyridinium iodide (2 mmol), carbon disulphide (20 ml), methyl iodide (4 mmol) and an aqueous solution of potassium carbonate (20 ml, 50%) was stirred at room temperature for 20 h. The precipitate obtained was filtered and washed with water until neutral. Recrystallization from ethanol or acetone gave pure ylides **5a-c**.

Reaction of ylides 5a-c with methyl iodide. Preparation of pyridinium ketene dithioacetals derivatives (4a-c). Method B: A solution of the corresponding ylide (2 mmol) and methyl iodide (4 mmol) in methanol (20 ml) was stirred at reflux temperature for 30 minutes. After removal of the solvent and the excess of methyl iodide, the residue obtained was recrystallized as indicated in Table 1 to give pure compounds **4a-c**.

Reaction of N-[2-(1,3-benzazolylmethyl)]pyridinium salts 2 with isothiocyanate derivatives. Preparation of ylides (6b-h). A mixture of the corresponding salt of N-[2-(1,3-benzazolylmethyl)]pyridinium iodide (1 mmol), the isothiocyanate derivative (1.2 mmol), methylene chloride (10 ml) and an aqueous solution of potassium carbonate (10 ml, 50%) was stirred at room temperature for 2 h. The organic phase was separated, washed with water until neutral, dried with magnesium sulphate and evaporated to give the corresponding ylides **6b-h** which were purified by chromatography on silica gel using acetone as eluent. Analytical samples were obtained by recrystallization from the solvent indicated in Table 1.

From the reaction of **2a** with phenylisothiocyanate a mixture of two compounds was formed. Chromatography of the mixture on silica gel using methylene chloride as eluent, gave as the sole product the betaine **9a** (54%) as yellow crystals; m.p. 276-277 °C (EtOH-CH_2Cl_2). Anal. Calcd. for $C_{20}H_{14}N_4S$: C, 70.15; H, 4.1; N, 16.4. Found: C, 70.4; H, 4.0; N, 16.4. Ir ν_{max} (KBr): 1141, 1262, 1304, 1436, 1505, 1565, 3163 cm1; ^{1}H-Nmr δ ($CDCl_3$): 7.1-7.7(m, 12H); 10.40(d, J=6 Hz, 1H); 13.11(s, 1H) ppm.

Reaction of N-[2-(1,3-benzazolylmethyl)]pyridinium salts 2 with phenylisocyanate. Preparation of ylides (7a-c). A mixture of the corresponding salt of N-[2-(1,3-benzazolylmethyl)]pyridinium iodide (2 mmol), potassium carbonate (5 mmol), phenylisocyanate (2.2 mmol) and dry acetonitrile (30 ml) was stirred at room temperature 16 h. Then the precipitate formed was filtered off and washed with methylene chloride (4x15 ml). The filtrate was evaporated, dissolved in methylene chloride and the organic phase washed with water until neutral. The combined organic phase was dried with magnesium sulphate and evaporated to give a residue that was purified by recrystallization to give pure ylides **7b,c**.

From the reaction of **2a** with phenylisocyanate a mixture of two compounds was formed. Chromatography of the mixture on silica gel gave the ylide **7a** using acetone as eluent and the betaine **10a** with methylene chloride (15%).

Recrystallization from ethyl acetate-acetone gave yellow crystals of **10a**; m.p. 264-266 °C. Anal. Calcd for $C_{20}H_{14}N_4O$: C, 73.6; H, 4.3; N, 17.2. Found: C, 73.3; H, 3.4; N, 17.4. Ir ν_{max} (KBr): 1236, 1275, 1311, 1423, 1480, 1520, 1547, 1615, 1693, 3058, 3418 cm^{-1}. ^{1}H-Nmr δ ($CDCl_3$): 7.0-7.9 (m, 12H); 9.85 (d, J=6 Hz, 1H); 12.49 (s, 1H) ppm.

Reaction of N-[2-(1,3-benzazolylmethyl)]pyridinium salts 2 with benzoyl chloride. Preparation of ylides (8a,b). To a mixture of the corresponding salt of N-[2-(1,3-benzazolylmethyl)]pyridinium iodide (2 mmol), methylene chloride (20 ml) and an aqueous solution of potassium carbonate (20 ml, 50%) was added dropwise benzoyl chloride (2.2 mmol) and the reaction mixture was stirred at room temperature for 3 h. The solid obtained was filtered off and purified (see Table 2) by recrystallization to give ylides **8a,b**.

3-(2'-Benzimidazolyl)-2-methylthio-1-phenylimidazo[1,2-a]pyridinium iodide (13). A mixture of **9a** (0.69 g, 2 mmol) and methyl iodide (0.5 ml, 8 mmol) in methyl acetate (60 ml) was stirred at room temperature for 24 h. The precipitate formed was filtered off and recrystallized from ethyl acetate-methanol to give the title compound as white plates (0.85 g, 88%); m. p. 265-267 °C. Anal. Calcd. for $C_{21}H_{17}IN_4S$: C,52.1; H, 3.5; N, 11.6. Found: C, 52.0; H, 3.7; N, 11.55. Ir ν_{max} (KBr): 1173, 1235, 1320, 1414, 1448, 1508, 1638, 3247 cm^{-1}; ^{1}H-Nmr δ (DMSO-d_6): 2.26 (s, 3H); 7.3-8.2 (m, 12H); 10.13 (d, J=7 Hz, 1H); 12.57 (bs, 1H) ppm.

3-[2'(1'-Methylbenzimidazolyl)]-2-methylthio-1-phenylimidazo[1,2-a]-pyridinium iodide (15). To a suspension of **13** (0.97 g, 2 mmol) in methanol (30 ml) was added dropwise a solution of sodium hydroxide (0.3 ml, 50%) and the reaction mixture was stirred at room temperature for 1 h. The solvent was removed under reduced pressure, water (20 ml) was added to the residue and the solution was extracted with methylene chloride. The organic phase was dried over magnesium sulphate, evaporated and the residue washed with acetone to give the ylide **14** (0.65 g, 91%) sufficiently pure for further use. An analytical sample was prepared by recrystallization from ethyl acetate-methylene chloride (yellow needles); m.p. 212-213 °C. Anal. Calcd. for $C_{21}H_{16}N_4S$: C, 70.8; H, 4.5; N, 15.7. Found: C, 71.0; H, 4.5; N, 15.9. Ir ν_{max} (KBr): 1124, 1228, 1274, 1316, 1354, 1440, 1508, 1590, 1639, 3039 cm^{-1} ^{1}H-Nmr δ (DMSO-d_6): 2.37 (s, 3H); 7.0-7.9 (m, 12H); 10.39 (d, J=7 Hz,1H) ppm.

A mixture of the ylide **14** (0.71 g, 2 mmol) thus obtained and methyl iodide (0.5 ml, 8 mmol) in methyl acetate (60 ml) was stirred at room temperature

for 16 h. The precipitate obtained was filtered off and recrystallized from methyl acetate-methanol to give the title compound 15 (0.87, 87%) as white plates; m.p. 225-226 °C. Anal. Calcd. for $C_{22}H_{19}IN_4S$: C, 53.0; H, 3.8; N, 11.2. Found: C, 53.0; H, 4.0; N, 11.4. Ir ν_{max} (KBr): 1239, 1400, 1448, 1510, 1641, 3017 cm^{-1}. ^{1}H-Nmr δ (DMSO-d_6): 2.09 (s, 3H); 3.96 (s, 3H); 7.3-8.2 (m, 12H); 8.87 (d, J=7 Hz, 1H) ppm.

3-[2'(1'-Methylbenzimidazolyl)-1-phenylimidazo[1,2-a]pyridinium-2-olate (16). To a solution of 15 (1 g, 2 mmol) in methanol (25 ml) was added dropwise a solution of sodium hydroxide (0.3 ml, 50%) and the reaction mixture was stirred at room temperature for 1 h. The solvent was removed under reduced pressure, water (20 ml) was added to the residue and the solution was extracted with methylene chloride. The organic phase was dried over magnesium sulphate, evaporated and the solid residue washed with acetone (3 ml). Recrystallization from acetonitrile give pure yellow crystals of the ylide 16 (0.41 g, 60%); m.p. 226-227 °C. Anal. Calcd. for $C_{21}H_{16}N_4O$: C, 74.1; H, 4.7; N, 16.5; Found: C, 74.0; H, 4.9; N, 16.3. Ir ν_{max} (KBr): 1243, 1458, 1508, 1545, 1618, 1682, 3060 cm^{-1}. ^{1}H-Nmr δ ($CDCl_3$): 4.04 (s, 3H); 7.0-7.3 (m, 12H); 9.62 (d, J=6 Hz, 1H) ppm.

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