

HETEROARYL STABILISED AZINIUM YLIDES. 1,3,4-THIADI-
AZOLE AS STABILISING GROUP

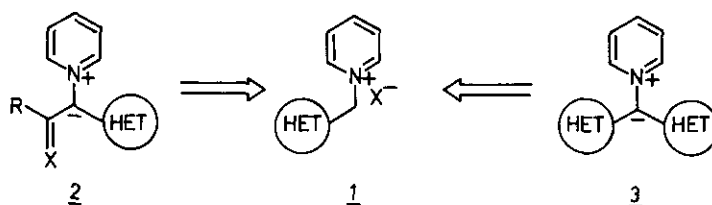
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Abstract— Reaction of 1-[(1,3,5-thiadiazol-2-yl)]-
methylpyridinium derivatives with diverse electrophiles
produced disubstituted heteroarylmethylpyridinium
ylides. Only with phenyl isothiocyanate 1,3-dipolar
cycloaddition was observed.

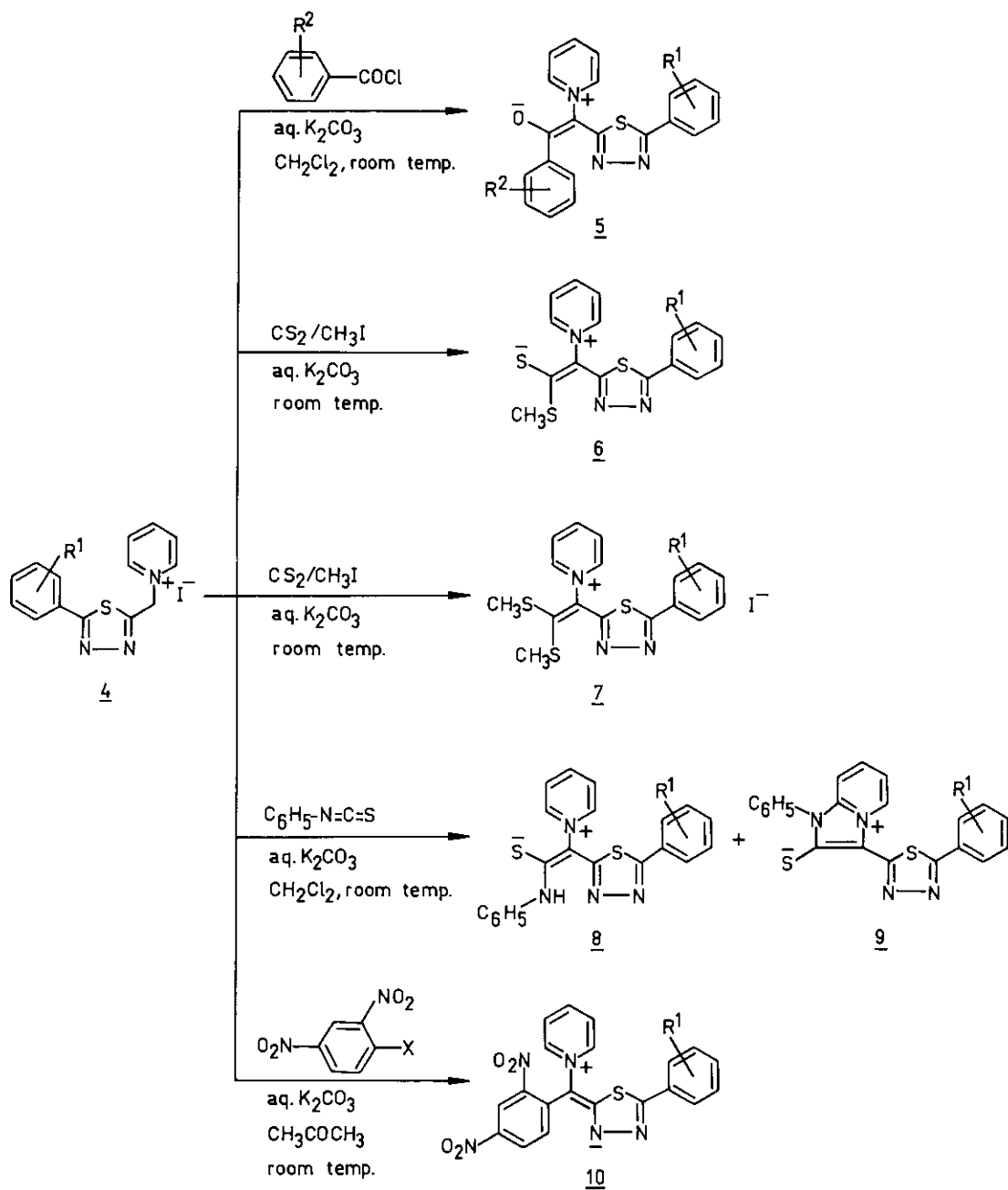
Azinium ylides are highly interesting compounds for their reactivities,
biological properties and applications^{1,2,3}. Usually, simple electron-
attracting groups, as carbonyl, ester, cyano etc., have been used to delocalize
the anion moiety, but the possibility of using heteroaryl groups as stabilisers
has been much less exploited. In recent years, we have been interested in the
preparation of systems such as **2** and **3**, by using 1-heteroarylmethylpyridinium
salts **1** as starting materials^{4,5} (Scheme 1) :



HET=Heteroaryl ring
X=S,O

Scheme 1

Both derivatives **2** and **3** would behave as stable dipoles with negatively charged
heterocyclic moieties, from which there is no precedent, except for tetrazolyl
derivatives described by Katritzky and coworkers⁶.



Scheme 2

In a recent paper⁶, we reported the preparation of pyridinium salts of 1 and 2 types bearing a benzimidazole moiety, which are being tested as antibacterials⁷. Initial results stimulated us to develop new series of ylides and we wish to report here the preparation of some pyridinium ylides stabilised by 1,3,4-thiadiazole rings. All results are shown in Scheme 2.

The starting (thiadiazolyl)methylpyridinium iodides 4 were prepared by a previously published method⁵, using 1-methylthiothiocarbonylmethylpyridinium iodide and the corresponding arylhydrazides.

When the corresponding monosubstituted ylide, generated in situ from the pyridinium iodide 4 in 50% aqueous K_2CO_3 , reacted at room temp. with aryl halides, disubstituted ylides 5 were formed, all of them showing strong in absorption around 1620 cm^{-1} characteristic of a carbonyl-stabilised ylide⁸. On treatment of 4 with 50% aqueous K_2CO_3 and CS_2/CH_3I as organic phase, using 2 equivalents of methyl iodide⁸, ylides 6 were isolated in almost quantitative yield, after vigorous stirring at room temperature, for 20 h. 1H -Nmr spectra of crude 6 showed no sign of the corresponding cycloadduct⁹. When the process was conducted by increasing the amount of methyl iodide to a 25-fold excess, ketene dithioacetal iodides 7 were isolated after 9 days.

When the 1H -nmr spectra of 7 were compared with those of ylides 6 it could be observed a low field shift for all the pyridinium resonances (approx. 0.2 ppm) showing the disappearance of anionic moiety influence.

In the reaction of 4 with phenyl isothiocyanate in a two-phase medium¹⁰, the formation of two products was observed. After separation by column chromatography, they were identified as the ylides 8 and the pyrido[1,2-a]-imidazolium-2-thiolate derivatives 9 produced by oxidation of the initial cycloadduct. Using biphasic techniques, the reaction of pyridinium ylides with heterocumulenes usually gives disubstituted ylides^{6,8,10}, 1,3-dipolar cycloaddition being observed only with very reactive azinium systems like phenantridinium derivatives⁹.

The 1H -nmr spectra for compounds 9 showed a clear disappearance of the pyridinium proton signals, due to the dipolar character of the products. The structure was confirmed by X-ray crystallography of 9c, represented in the scheme 3. All data are given in Tables 3-7.

Several experiments were carried out to prepare pyridinium ylides with two heteroaromatic substituents, like 3 (scheme 1), by nucleophilic displacement with an aryl halide¹¹. Initially, 2- and 4-chloropyridines were used, but 4 was recovered untransformed in more than 80-85% yields. The same was observed with 2- and 4-nitrochlorobenzene, and only 2,4-dinitrohalobenzenes produced ylides 10, the fluorine derivative giving the higher yield. Alternative

a Yields in isolated pure products. Compounds 8 and 9 were produced as mixtures in the same process.

| Compd. | R ¹ | R ² | X | Reaction Time (h) ^a | Yield (%) ^a |
|--------|----------------|-------------------|----|--------------------------------|------------------------|
| 4a | H | - | - | 6 | 76 ^b |
| 4b | 2-Cl | - | - | 6 | 99 |
| 4c | 4-Cl | - | - | 6 | 99 |
| 5a | H | H | - | 1 | 64 |
| 5b | H | 4-NO ₂ | - | 1 | 62 |
| 5c | H | 4-Cl | - | 1 | 68 |
| 6a | H | - | - | 24 | 99 |
| 6b | 2-Cl | - | - | 24 | 93 |
| 7a | H | - | - | 216 | 62 |
| 7b | 2-Cl | - | - | 216 | 30 |
| 8a | H | - | - | 1.5 | 36 |
| 8b | 2-Cl | - | - | 1.5 | 21 |
| 8c | 4-Cl | - | - | 1.5 | 41 |
| 9a | H | - | - | 1.5 | 14 |
| 9b | 2-Cl | - | - | 1.5 | 31 |
| 9c | 4-Cl | - | - | 1.5 | 41 |
| 10a | H | - | F | 14 | 85 |
| 10a | H | - | Cl | 14 | 73 |

Table 1. New Pyridinium Derivatives Prepared

Table 2. Physical and Spectroscopic Data of Compounds 4 to 10

| Compd. No | mp (°C) | Molecular Formula ^a | ¹ H-Nmr ^b (ppm) |
|-----------|---------|---|--|
| 4a | 191-193 | C ₁₄ H ₁₂ N ₃ Si ^c | |
| 4b | 175-176 | C ₁₄ H ₁₁ N ₃ SClI | 9.24 (d, J=5.5 Hz, 2H); 8.69 (t, J=7.8 Hz, 1H); 8.30-8.01 (m, 3H); 7.64-7.39 (m, 3H); 6.48 (s, 1H) |
| 4c | 214-215 | C ₁₄ H ₁₁ N ₃ SClII | 9.21 (d, J=5.5 Hz, 2H); 8.68 (t, J=7.8 Hz, 1H); 8.29-7.44 (m, 6H); 6.43 (s, 2H) |
| 5a | 228-230 | C ₂₁ H ₁₅ N ₃ OS | 9.02 (d, J=5.4 Hz, 2H); 8.46 (t, J=7.2 Hz, 1H); 8.05-7.82 (m, 4H); 7.50-7.42 (m, 3H); 7.17 (br s, 5H) |
| 5b | 237-239 | C ₂₁ H ₁₄ N ₄ O ₃ S ₂ ·2/3H ₂ O | 9.03 (d, J=5.6 Hz, 2H); 8.46 (t, J=7.3 Hz, 1H); 8.05-7.78 (m, 6H); 7.44-7.33 (m, 5H) |
| 5c | 267-268 | C ₂₁ H ₁₄ N ₃ OSC1·H ₂ O | 9.01 (d, J=5.5 Hz, 2H); 8.46 (t, J=7.4 Hz, 1H); 8.05-7.98 (m, 4H); 7.47-7.38 (m, 2H); 7.18 (br s, 5H) |
| 6a | 226-227 | C ₁₆ H ₁₃ N ₃ S ₃ | 9.10 (d, J=5.4 Hz, 2H); 8.76 (t, J=7.0 Hz, 1H); 8.24 (t, J=7.0 Hz, 2H); 7.91-7.79 (m, 2H); 7.47-7.39 (m, 3H); 2.45 (s, 3H) |
| 6b | 212-214 | C ₁₆ H ₁₂ N ₃ S ₃ Cl | 9.11 (d, J=6.1 Hz, 2H); 8.76 (t, J=7.4 Hz, 1H); 8.23 (t, J=7.2 Hz, 2H); 8.04-7.87 (m, 1H); 7.62-7.35 (m, 3H); 2.46 (s, 3H) |

^a Satisfactory microanalyses were obtained for all new compounds described, within 0.4% error.

^b In DMSO-d₆

^c Described in ref.⁵.

Table 2 (Cont.). Physical and Spectroscopic Data of Compounds 4 to 10

| Compd. No | mp (°C) | Molecular Formula ^a | ¹ H-Nmr ^b (ppm) |
|-----------|---------|---|---|
| 7a | 217-218 | C ₁₇ H ₁₆ N ₃ S ₃ I | 9.35 (d, J=5.5 Hz, 2H); 8.92 (t, J=7.6 Hz, 1H); 8.43 (t, J=7.4 Hz, 2H); 8.06-7.95 (m, 2H); 7.66-7.53 (m, 3H); 2.71 (s, 3H); 2.54 (s, 3H) |
| 7b | 210-212 | C ₁₇ H ₁₅ N ₃ S ₃ ClI | 9.36 (d, J=5.6 Hz, 2H); 8.93 (t, J=7.3 Hz, 1H); 8.44 (t, J=7.0 Hz, 2H); 8.16-8.05 (m, 1H); 7.70-7.48 (m, 3H); 2.71 (s, 3H); 2.54 (s, 3H). |
| 8a | 200-203 | C ₂₁ H ₁₄ N ₄ S ₂ .H ₂ O | 9.05 (d, J=5.5 Hz, 2H); 8.63 (t, J=7.1 Hz, 1H); 8.15 (t, J=6.8 Hz, 2H); 7.85-7.74 (m, 2H); 7.63-7.15 (m, 9H) |
| 8b | 134-135 | C ₂₁ H ₁₅ N ₄ S ₂ Cl.H ₂ O | 8.98 (d, J=5.7 Hz, 2H); 8.54 (t, J=7.4 Hz, 1H); 8.15-7.84 (m, 3H); 7.64-6.87 (m, 9H) |
| 8c | 116-117 | C ₂₁ H ₁₅ N ₄ S ₂ Cl.H ₂ O | 9.03 (d, J=5.7 Hz, 2H); 8.21 (t, J=7.5 Hz, 1H); 8.13-6.93 (m, 12H) |
| 9a | 304-306 | C ₂₁ H ₁₄ N ₄ S ₂ | 10.20 (d, J=6.2 Hz, 1H); 8.07-7.60 (m, 2H); 7.69-7.21 (m, 11H) |
| 9b | 273-275 | C ₂₁ H ₁₃ N ₄ S ₂ Cl | 10.05 (d, J=6.2 Hz, 1H); 8.04-7.06 (m, 14H) |
| 9c | 310-312 | C ₂₁ H ₁₃ N ₄ S ₂ Cl.2/3Cl ₂ CH ₂ | 10.15 (d, J=6.1 Hz, 1H); 8.05-7.15 (m, 14H) |
| 10a | 180-182 | C ₂₀ H ₁₃ N ₄ O ₅ | 9.10 (d, J=5.5 Hz, 2H); 8.64-8.55 (m, 2H); 8.19 (t, J=6.8 Hz, 2H); 7.92-7.72 (m, 3H); 7.57-6.71 (m, 4H) |

^a Satisfactory microanalyses were obtained for all new compounds described, within 0.4% error.

^b In DMSO-d₆

Table 3. Structure of Compound 9c. Atomic Parameters for Non-Hydrogen Atoms. Coordinates and Thermal Parameters as

$$U_{EQ} = (1/3) (U_{ij} a_i^2 a_j^2 a_i a_j \cos(a_i, a_j)).10^3$$

| Atom | x | y | z | U_{EQ} |
|------|------------|-------------|------------|----------|
| N1 | 0.7362(7) | -0.0830(7) | 0.3173(8) | 42(3) |
| C2 | 0.7061(8) | -0.0242(7) | 0.2582(9) | 39(3) |
| S3 | 0.8192(3) | -0.0490(2) | 0.0893(3) | 53(1) |
| C4 | 0.8373(8) | 0.0597(7) | 0.3671(9) | 37(3) |
| C5 | 0.8958(9) | 0.1539(7) | 0.3549(9) | 39(3) |
| S6 | 0.9329(2) | 0.1727(2) | 0.2023(2) | 42(1) |
| C7 | 0.9876(8) | 0.2937(7) | 0.2952(9) | 40(3) |
| N8 | 0.9766(8) | 0.3111(7) | 0.4272(8) | 51(4) |
| N9 | 0.9244(9) | 0.2318(7) | 0.4628(9) | 55(4) |
| C10 | 1.0493(8) | 0.3649(8) | 0.2418(9) | 40(4) |
| C11 | 1.0958(9) | 0.3258(8) | 0.1238(10) | 44(4) |
| C12 | 1.1584(9) | 0.3925(9) | 0.0809(11) | 55(4) |
| C13 | 1.1718(10) | 0.5003(9) | 0.1516(12) | 51(4) |
| C14 | 1.1255(10) | 0.5412(9) | 0.2675(12) | 58(5) |
| C15 | 1.0682(10) | 0.4711(8) | 0.3127(10) | 47(4) |
| C116 | 1.2496(3) | 0.5857(3) | 0.0959(4) | 76(2) |
| N17 | 0.8037(7) | 0.0460(6) | 0.4872(7) | 37(3) |
| C18 | 0.8278(9) | 0.1030(8) | 0.6260(10) | 45(4) |
| C19 | 0.7818(11) | 0.0715(9) | 0.7231(11) | 58(5) |
| C20 | 0.7139(11) | -0.0153(10) | 0.6922(11) | 58(5) |
| C21 | 0.6935(10) | -0.0747(9) | 0.5520(11) | 53(4) |
| C22 | 0.7404(9) | -0.0403(8) | 0.4565(10) | 47(4) |
| C23 | 0.6750(10) | -0.1784(9) | 0.2491(11) | 51(4) |
| C24 | 0.7411(11) | -0.2948(9) | 0.2833(14) | 64(5) |
| C25 | 0.6773(14) | -0.3825(11) | 0.2161(17) | 79(8) |
| C26 | 0.5582(13) | -0.3524(14) | 0.1243(16) | 87(7) |
| C27 | 0.4892(11) | -0.2340(12) | 0.0874(15) | 73(6) |
| C28 | 0.5492(10) | -0.1456(10) | 0.1470(13) | 63(5) |
| C129 | 0.4904(0) | 0.2077(0) | 0.2756(0) | 144(0) |
| C130 | 0.4894(0) | 0.3370(0) | 0.5214(0) | 193(0) |
| C31 | 0.5300(0) | 0.3402(0) | 0.3683(0) | 177(0) |

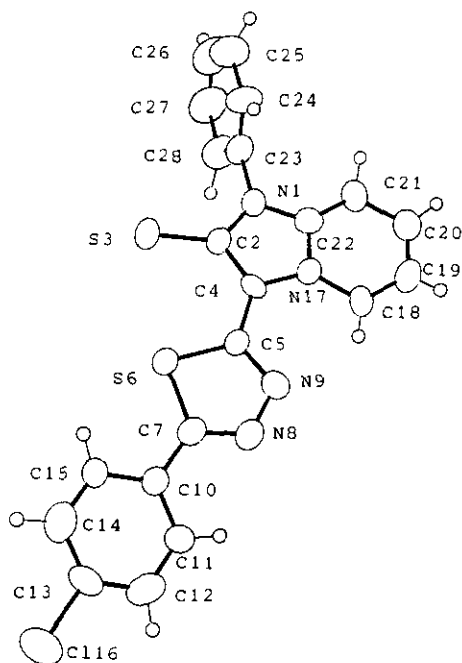
Table 4. Structure of Compound 9c. Atomic Parameters for Hydrogen Atoms. Coordinates and Thermal Parameters as

$$\exp(-8\pi^2 U(\sin \theta/\lambda)^2).10^3$$

| Atom | x/a | y/b | z/c | U |
|------|-------|--------|--------|-----|
| H11 | 1.083 | 0.256 | 0.088 | 44 |
| H12 | 1.185 | 0.627 | -0.004 | 51 |
| H14 | 1.109 | 0.627 | 0.278 | 50 |
| H15 | 1.051 | 0.475 | 0.398 | 45 |
| H18 | 0.866 | 0.162 | 0.636 | 45 |
| H19 | 0.822 | 0.091 | 0.817 | 61 |
| H20 | 0.666 | -0.042 | 0.749 | 56 |
| H21 | 0.650 | -0.143 | 0.544 | 53 |
| H24 | 0.840 | -0.318 | 0.356 | 62 |
| H25 | 0.677 | -0.449 | 0.264 | 91 |
| H26 | 0.505 | -0.379 | 0.074 | 82 |
| H27 | 0.396 | -0.216 | 0.017 | 81 |
| H28 | 0.512 | -0.050 | 0.111 | 69 |
| H311 | 0.483 | 0.417 | 0.306 | 170 |
| H312 | 0.623 | 0.340 | 0.392 | 170 |

Table 5. Structure of Compound 9c. Bond Distances (Å)

| | | | |
|------------|-----------|-----------|-----------|
| N1 - C2 | 1.369(13) | N1 - C22 | 1.368(11) |
| N1 - C23 | 1.451(12) | C2 - S3 | 1.677(9) |
| C2 - C4 | 1.401(10) | C4 - C5 | 1.459(13) |
| C4 - N17 | 1.387(12) | C5 - S6 | 1.715(10) |
| C5 - N9 | 1.320(10) | S6 - C7 | 1.729(8) |
| C7 - N8 | 1.308(12) | C7 - C10 | 1.461(14) |
| N8 - N9 | 1.342(13) | C10 - C11 | 1.408(13) |
| C10 - C15 | 1.376(11) | C11 - C12 | 1.360(16) |
| C12 - C13 | 1.383(13) | C13 - C14 | 1.383(16) |
| C13 - C116 | 1.733(12) | C14 - C15 | 1.367(17) |
| N17 - C18 | 1.397(10) | N17 - C22 | 1.341(12) |
| C18 - C19 | 1.350(16) | C19 - C20 | 1.374(16) |
| C20 - C21 | 1.436(13) | C21 - C22 | 1.361(16) |
| C23 - C24 | 1.335(12) | C23 - C28 | 1.377(11) |
| C24 - C25 | 1.376(16) | C25 - C26 | 1.313(16) |
| C26 - C27 | 1.364(17) | C27 - C28 | 1.371(17) |
| C129- C31 | 1.783 | C130- C31 | 1.703 |



Scheme 3

Table 6. Structure of Compound 9c. Bond Angles

| | | | |
|-----------------|-----------|-------------------|-----------|
| C22 - N1 - C23 | 121.6(7) | C2 - N1 - C23 | 127.5(7) |
| C2 - N1 - C22 | 110.9(7) | N1 - C2 - C4 | 105.0(7) |
| N1 - C2 - S3 | 125.7(6) | S3 - C2 - C4 | 129.2(7) |
| C2 - C4 - N17 | 107.8(7) | C2 - C4 - C5 | 127.8(7) |
| C5 - C4 - N17 | 124.2(7) | C4 - C5 - N9 | 122.2(7) |
| C4 - C5 - S6 | 123.7(6) | S6 - C5 - N9 | 114.1(7) |
| C5 - S6 - C7 | 87.0(4) | S6 - C7 - C10 | 125.0(6) |
| S6 - C7 - N8 | 112.8(6) | N8 - C7 - C10 | 122.1(7) |
| C7 - N8 - N9 | 114.3(7) | C5 - N9 - N8 | 111.8(7) |
| C7 - C10 - C15 | 119.1(8) | C7 - C10 - C11 | 121.9(7) |
| C11 - C10 - C15 | 119.0(8) | C10 - C11 - C12 | 119.9(8) |
| C11 - C12 - C13 | 119.7(9) | C12 - C13 - C116 | 119.4(7) |
| C12 - C13 - C14 | 121.3(9) | C14 - C13 - C116 | 119.3(7) |
| C13 - C14 - C15 | 118.4(8) | C10 - C15 - C14 | 121.6(8) |
| C4 - C17 - C22 | 109.1(6) | C4 - C17 - C18 | 130.7(7) |
| C18 - N17 - C22 | 120.2(7) | N17 - C18 - C19 | 117.9(8) |
| H18 - C18 - C19 | 127.1(9) | C18 - C19 - C20 | 122.6(8) |
| C19 - C20 - C21 | 119.0(9) | C20 - C21 - C22 | 116.2(9) |
| N17 - C22 - C21 | 123.9(8) | N1 - C22 - C21 | 129.0(8) |
| N1 - C22 - N17 | 107.2(7) | N1 - C23 - C28 | 117.7(8) |
| N1 - C23 - C24 | 120.5(9) | C24 - C23 - C28 | 121.8(9) |
| C23 - C24 - C25 | 118.0(10) | C24 - C25 - C26 | 121.5(11) |
| C25 - C26 - C27 | 121.3(13) | C26 - C27 - C28 | 118.8(11) |
| C23 - C28 - C27 | 118.6(10) | C129 - C31 - C130 | 100.1 |

Table 7. Structure of Compound 9c. Torsion Angles

| | | | |
|----------------------|-----------|------------------------|------------|
| C2 - N1 - C22 - N17 | -0.6(10) | C2 - N1 - C22 - C21 | -179.9(9) |
| C22 - N1 - C2 - C4 | -0.5(9) | C22 - N1 - C2 - S3 | -179.3(7) |
| N1 - C2 - C4 - N17 | 1.4(9) | C2 - C4 - N17 - C22 | -1.8(9) |
| S6 - C5 - N9 - N8 | 0.7(10) | N9 - C5 - S6 - C7 | -0.8(7) |
| C5 - S6 - C7 - N8 | 0.7(7) | S6 - C7 - N8 - N9 | -0.5(10) |
| C7 - N8 - N9 - C5 | -0.2(11) | C11 - C12 - C13 - C116 | -179.2(8) |
| C4 - N17 - C22 - N1 | 1.5(9) | C4 - N17 - C18 - C19 | 179.9(9) |
| C20 - C21 - C22 - N1 | 178.8(9) | | |

Table 8. Microanalyses

| Compound | C | H | Calcd (%) | | S |
|----------|-------|------|-----------|-------|--|
| | | | Found | (%) | |
| 4b | 40.43 | 2.65 | 10.11 | | |
| | 40.40 | 2.50 | 10.02 | | |
| 4c | 40.43 | 2.65 | 10.11 | | |
| | 40.20 | 2.98 | 10.43 | | |
| 5a | 70.56 | 4.23 | 11.76 | | |
| | 70.48 | 4.33 | 11.65 | | |
| 5b | 60.87 | 3.70 | 13.50 | | (2/3 H ₂ O) |
| | 60.68 | 3.89 | 13.50 | | |
| 5c | 61.54 | 3.91 | 10.26 | | (H ₂ O) |
| | 61.29 | 3.97 | 10.23 | | |
| 6a | 55.98 | 3.79 | 12.24 | | |
| | 56.10 | 4.10 | 11.96 | | |
| 6b | 50.86 | 3.18 | 11.13 | | |
| | 50.57 | 3.34 | 10.89 | | |
| 7a | 42.06 | 3.30 | 8.66 | | |
| | 42.21 | 3.49 | 8.88 | | |
| 7b | 39.27 | 2.89 | 8.08 | | |
| | 39.57 | 3.09 | 8.18 | | |
| 8a | 62.07 | 4.43 | 13.79 | | (H ₂ O) |
| | 62.42 | 4.29 | 13.58 | | |
| 8b | 57.21 | 3.86 | 12.71 | | (H ₂ O) |
| | 57.50 | 3.87 | 12.42 | | |
| 8c | 57.21 | 3.86 | 12.71 | | (H ₂ O) |
| | 57.64 | 3.79 | 12.54 | | |
| 9a | 65.28 | 3.62 | 14.51 | | |
| | 65.12 | 3.84 | 14.55 | | |
| 9b | 59.93 | 3.09 | 13.32 | 15.22 | |
| | 59.55 | 3.55 | 13.49 | 14.89 | |
| 9c | 54.49 | 3.00 | 11.74 | 13.42 | (2/3 CH ₂ Cl ₂) |
| | 54.25 | 3.27 | 11.97 | 13.69 | |
| 10a | 57.28 | 3.10 | 16.71 | | |
| | 57.14 | 3.06 | 16.59 | | |

recovered untransformed in more than 80-85% yields. The same was observed with 2- and 4-nitrochlorobenzene, and only 2,4-dinitrohalobenzenes produced ylides 10, the fluorine derivative giving the higher yield. Alternative approaches to 3 are being developed.

EXPERIMENTAL

Melting points were determined on a Buchi SMP-20 and are uncorrected. Infrared spectra were recorded on Perkin Elmer 883 or 1310 spectrophotometers. $^1\text{H-Nmr}$ spectra were obtained on Bruker WP 60 Wc and Varian FT-80A instruments using TMS as internal reference. All 1-(2-(5-phenyl)thiadiazolylmethyl)pyridinium iodides 4 were prepared as in ref. 5, from 1-(methylthiothiocarbonylmethyl)pyridinium iodide and the corresponding phenylhydrazide.

Preparation of Ylides 5 and 8. General procedure: To a well stirred suspension of the corresponding pyridinium salt 4 (1 mmol) in 50% aqueous potassium carbonate (10 ml) and dichloromethane (10 ml), the corresponding electrophile (1.2 mmol) was added. After vigorous stirring at room temperature for the time given in Table 1, the reaction mixture was extracted with dichloromethane, and the organic solution was dried over MgSO_4 , concentrated and chromatographed (silica gel 60 Merck, 230-400 mesh) with dichloromethane-acetone (1:1) as eluent.

In the reaction of 4 with phenyl isothiocyanate two main products were detected, and the residue from dichloromethane extract was chromatographed (silica gel 60 Merck, 230-400 mesh) with hexane-ethyl acetate (7:3) to give 9, and then with dichloromethane-acetone (1:1) to give 8. All compounds 9 were recrystallised from ethanol. However, recrystallization of 8 in the same way always caused partial conversion into 9. Finally, they were purified by two runs through a chromatographic column as described, using dichloromethane-acetone (1:1) as eluent.

Preparation of Ylides 6. To a well stirred suspension of the corresponding pyridinium salt 4 (1 mmol) in 50% aqueous potassium carbonate (10 ml), a solution of methyl iodide (2 mmol) in carbon disulphide (10 ml) was added. After stirring at room temperature for 24 h, ylides 6 were collected as a precipitate which was recrystallised from ethanol.

Preparation of Ketene Dithioacetals 7. The process was the same for compounds 6, but using a larger excess of methyl iodide (25 mmol). After stirring at room temperature for 9 days, the reaction mixture was extracted with

dichloromethane, and the extract was dried over MgSO_4 , concentrated, and the residue was recrystallised from methanol, yielding the corresponding **7** as described in Table 1.

Preparation of Ylide 10. To a stirred mixture of potassium carbonate (6 mmol) in water (2 ml) and acetone (10 ml), **4a** (3 mmol) was added. After 10 min, the 2, 4-dinitrohalobenzene (3 mmol) was added dropwise (the fluoride) or in small portions (the chloride) to the deep yellow solution. The reaction mixture was stirred overnight at room temperature. The crude ylide was extracted with dichloromethane, the extract was dried over MgSO_4 , concentrated and chromatographed (silica gel 60 Merck, 230-400 mesh) with dichloromethane-acetone (1:1) as eluent.

Crystal data. Compound **9c**. $\text{C}_{21}\text{H}_{13}\text{N}_4\text{S}_2\text{Cl}$. $2/3 \text{CH}_2\text{Cl}_2$. $a = 11.460(4)$, $b = 11.514(5)$, $c = 9.596(3)$ Å, $\alpha = 95.31(3)$, $\beta = 111.62(2)$, $\gamma = 73.10(3)^\circ$, $V = 1126.1(8)\text{Å}^3$, $M = 505.866$, $Z = 2$, $D_c = 1.492 \text{ g/cm}^3$, $F(000) = 516$, $\mu = 6.036 \text{ cm}^{-1}$, space group P-1.

Crystallographic Measurements. Symmetry independent reflections of a prismatic crystal (0.20x0.10x0.40 mm) were collected on an Enraf-Nonius CAD4 four-circle diffractometer with graphite-monochromated $\text{Mo K}\alpha = 0.7170$ Å radiation. 6530 reflections were measured but only 2393 were considered as observed applying the conditions $I > 2\sigma(I)$ and included in the refinement. Intensity data up to $\theta = 30^\circ$, $(-16 < h < 16, -16 < k < 16, 0 < l < 12)$, $\omega/2\theta$ scan mode.

X-Ray Structure Analysis. The MULTAN 80 ¹² computer program was initially used and revealed a part of the molecule, which was used as input of the DIRDIF program ¹³. This showed the complete molecule and other three peaks belonging to a solvating CH_2Cl_2 , having a high thermal agitation. Isotropic cycles and one anisotropic cycle of least squares refinement were applied to all atoms and progressive refinements were made with the fixed CH_2Cl_2 molecule. Positions of H atoms were found from ΔF and geometrical considerations and were non refined. The final agreement parameter R was 0.085 (Δ/σ max = 0.09). The maximum height in final F synthesis was 0.20 out the around of the CH_2Cl_2 atoms, due to their disordered character. Scattering and anomalous dispersion factors have been taken from International Tables for X-Rays Crystallography ¹⁴. Calculations have been performed with the X-Ray 76 System ¹⁵. Scheme 3 shows a view of the molecule with the atomic numbering used in the crystallographic study.

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