# SYNTHESIS OF PHENANTHRIDINIUM YLIDES

M. Teresa Gandásegui,[a] Julio Alvarez-Builla,[a*] and Feliciana Florencio[b]

[a] Depto. de Química Orgánica. Universidad de Alcalá de Henares. E-28871 Alcalá de Henares. Madrid. Spain

[b] Instituto de Química "Rocasolano" C. S. I. C., E-28006 Madrid. Spain

**Abstract-** Reaction of phenanthridinium methylides with several dipolarophiles, yielding disubstituted ylides in most of the examples, is described

Cycloiminium ylides are highly interesting compounds due to their reactivity, biological properties and applications.[1] Although azinium derivatives have been extensively studied in the field of 1,3-dipolar cycloadditions,[2] in recent years we have been interested in their reactivity under two phase conditions,[3-7] in which reactions with well-known dipolarophiles tend to generate disubstituted ylides instead of cycloadducts. Phenanthridinium derivatives[8] offer interesting prospects as a test of the method, because their tendency to generate cycloadducts should be higher due to their low aromaticity.

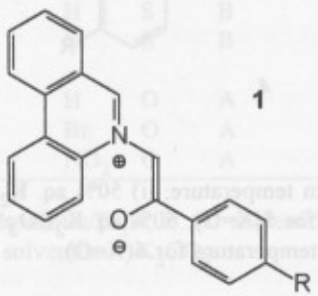


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Figure 1

Surprisingly enough, while 1,3-dipolar cycloaddition has been extensively reported for 5-imino[9-13] and 5-oxide derivatives,[14-18] there was nothing related to the use of phenanthridinium ylides, and only some works on other isomeric azaphenanthrenes have been previously published.[19-22]

In the initial experiments, several 5-phenacylphenanthridinium salts (**2**) were made to react with well-known dipolarophiles, such as dimethyl acetylenedicarboxylate (DMAD), phenyl isocyanate and isothiocyanate and benzoyl isocyanate, using two phase methods in all experiments, and potassium carbonate as base. When 5-phenacylphenanthridinium salts (**2**) were treated with a base, such as triethylamine, in the absence of a dipolarophile, dimers (**3**) were obtained in high yields.

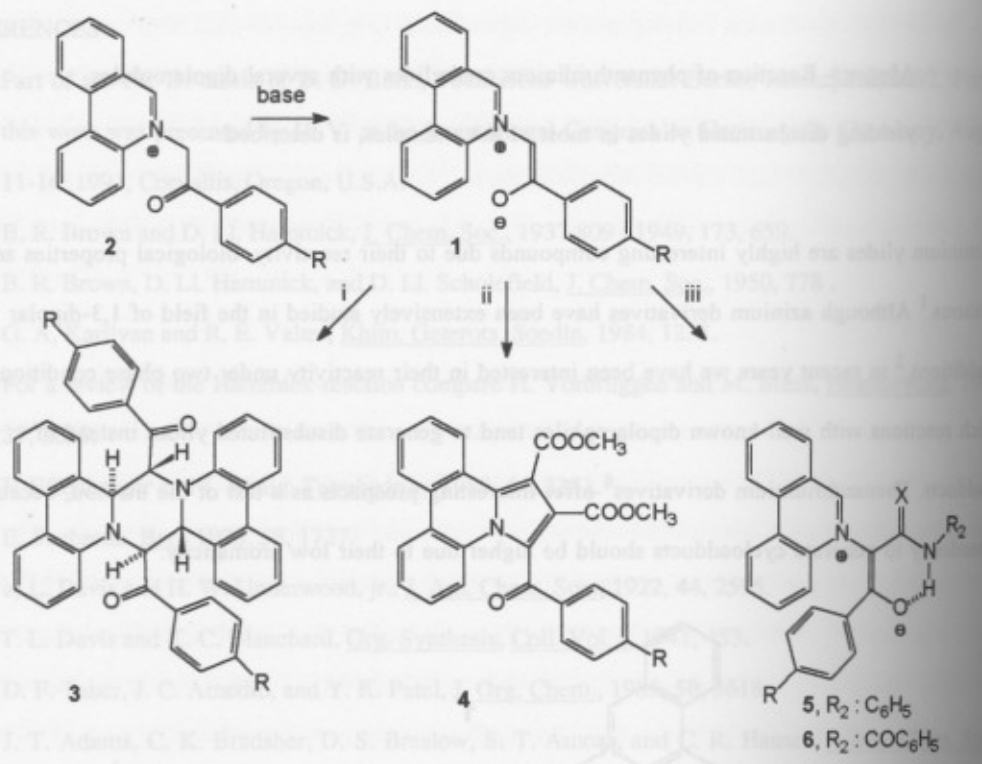


Figure 2. Reagents: i) $Et_3N$/acetonitrile, room temperature; ii) 50% aq. $K_2CO_3$/DMAD, room temperature; iii) $K_2CO_3/C_6H_5N{=}C{=}O$, room temperature for **5**(X=O); 50% aq. $K_2CO_3/C_6H_5N{=}C{=}S$, room temperature for **5**(X=S); $K_2CO_3/C_6H_5CON{=}C{=}O$, room temperature for **6**(X=O).

The tendency for head-to-tail dimerization was so high in this case, that in order to obtain either the

cycloadduct or the disubstituted ylide, a two phase system had to be used in which the organic phase was neat electrophile, so that the probability of ylide trapping was increased to a maximum. A similar technique has been used to prepare dithioester stabilized isoquinolinium ylides.[6]

The reaction with DMAD was performed using 50% aqueous $K_2CO_3$ as the polar phase, and DMAD (2 mol) as the organic phase, with the pyrrolo[1,2-*f*]phenanthridine derivatives (**4**) being produced. The reaction with phenyl isocyanate was performed using anhydrous $K_2CO_3$, and employing an excess of the electrophile (15 mol) to allow suitable stirring of the process, while the reactions with phenyl isothiocyanate were performed using the same liquid-liquid technique as with DMAD. With both

Table 1. Phenanthridiniun derivatives (**2-6**)

| Comp. No. | R | X | Method | Yield (%) |
|---|---|---|---|---|
| **2a** | H | Br | - | 70 |
| **2b** | Cl | Br | - | 35 |
| **2c** | Br | Br | - | 43 |
| **2d** | $NO_2$ | Br | - | 44 |
| **3a** | H | - | A | 24 |
| **3b** | Cl | - | A | 48 |
| **3c** | Br | - | A | 75 |
| **3d** | $NO_2$ | - | A | 47 |
| **4a** | H | - | B | 69 |
| **4b** | $NO_2$ | - | B | 71 |
| **5a** | H | O | C | 15 |
| **5b** | Cl | O | C | 11 |
| **5c** | H | S | B | 36 |
| **5d** | Cl | S | B | 45 |
| **6a** | H | O | A | 32 |
| **6b** | Br | O | A | 80 |
| **6c** | $NO_2$ | O | A | 80 |

Methods: A: acetonitrile/$Et_3N$; B: no solvent/50% aq. $K_2CO_3$;
C: no solvent/anh. $K_2CO_3$.

reagents the disubstituted ylides (**5**) were produced. The reaction with benzoyl isocyanate was performed, as

with the other isocyanate, using the solid-liquid technique and employing an acetonitrile solution of the electrophile as the organic phase, thus giving the disubstituted ylides (**6**).

In the processes **2**→**4** and **2**→**5**, when the dipolarophile was dissolved in dichloromethane, as with DMAD and phenyl isothiocyanate, or acetonitrile, as in the case of phenyl isocyanate, only the dimers (**3**) were isolated in yields of between 30-65%, with only traces of either ylides or cycloadducts being detected. However, with benzoyl isocyanate, the most reactive electrophile, there was no need to exclude the use of solvent, and the corresponding ylides were isolated in comparatively high yields, while only traces of the dimers were detected in the crude material.

As soon as a general process was developed, it was attempted to react other less known dipolarophiles such as carbodiimides, sulfonimines and sulfinimines[23] with **2**. The last two specially[24,25] attracted our attention due to the useful transformations developed from their (4+2) cycloadducts,[26-28] while no (3+2) cycloadditions have been described. No identifyable materials were detected with the first two

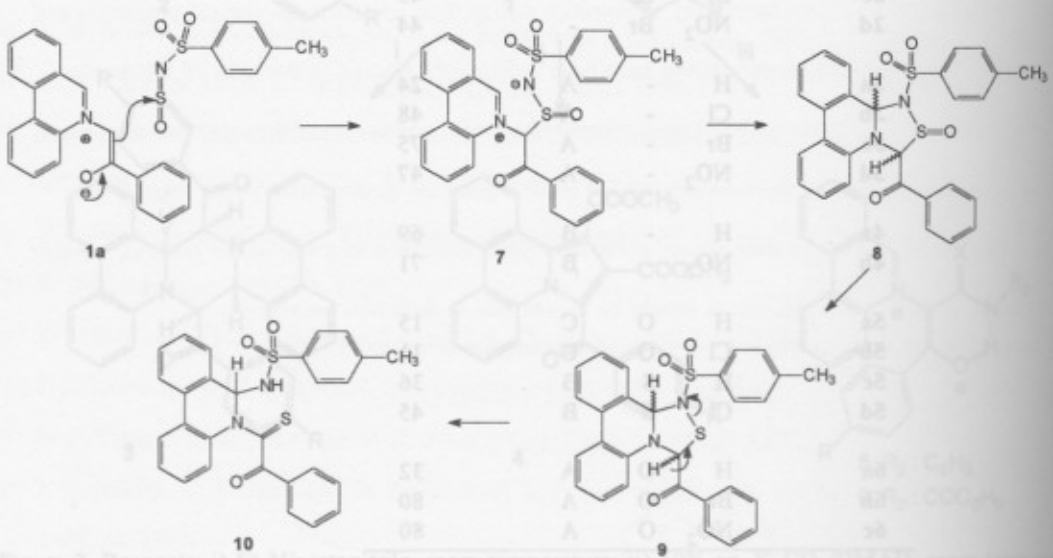


Figure 3

electrophiles, and when sulfinimines were tested, neither the phenyl nor the benzoyl derivatives produced any reaction with the ylides. However, when tosylsulfinimine (2 mol) was allowed to react with 5-phenacyl-

henanthridinium bromide, a 5,6-dihydrophenanthridine adduct (**10**) was isolated in 45% yield, with *p*-toluenesulfonamide also being obtained during the work-up procedure, corresponding to the 50% of the sulfinimine initially added. The process did not work in two phase systems, and was carried out in dry acetonitrile/triethylamine.

Although the mechanism should be further investigated, the formation of **10** could be explained by the formation of the cycloadduct (**8**), whose sulphoxide group can subsequently be reduced under the reaction conditions, generating the 1,3,4-thiadiazolidine derivative (**9**), which then opens under basic catalysis producing **10**. We cannot interpret the "in situ" sulfoxide reduction, but the process could possibly be explained by the excess of sulfinimine present, which would act as an oxygen acceptor, thus being converted to sulphonimine, which would be quickly hydrolysed to the parent *p*-toluenesulfonamide. The structure of **10** was determined by single-crystal X-ray diffraction.

The structures of all new compounds are supported by spectroscopic data and by combustion analysis. The stability of the ylides (**5, 6**) is associated not only with the delocalization of the negative charge but also with the intramolecular hydrogen bond, evident by the low field signals corresponding to the NH proton in the $^1$H-nmr of compounds (**5-6**). Another distinctive signal is the low field singlet, appearing *ca.* $\delta = 10$ ppm, which corresponds to the 6-CH of the azinium moiety, in $\alpha$ position with respect to the quaternary nitrogen. Analytical data of all compounds appear in Tables 2 and 3.

In conclusion, the two phase methods seem to be an easy way of generating disubstituted ylides from azinium derivatives. In those compound with a high tendency to dimerize, as is the case with phenanthridinium ylides, the use of methods without solvent facilitates the isolation of high yields of the disubstituted ylides. As it has been shown before, both the solid-liquid and liquid-liquid methods can be alternatively applied, depending on the stability of the corresponding electrophile.

## EXPERIMENTAL

Melting points were determined on a Büchi SMP-20 and are uncorrected. Ir spectra were recorded on Perkin Elmer 700 or 1310 spectrophotometers. $^1$H-Nmr spectra were obtained on a Varian FT-80 (80 MHz)

Table 2. Physical and Spectroscopic Data of Compounds (2 - 6)

| Compd no. | mp (°C) Solv. | Molecular Formula | ir (KBr) ν ($cm^{-1}$) | $^1$H nmr δ (ppm) |
|---|---|---|---|---|
| **2a**[a] | 208-210 EtOH | $C_{21}H_{16}NOBr$ | 1700, 1610, 1440 | 7.25(s, 2H); 7.75(d, J=6 Hz, 3H);7.90-8.60(m, 9H); 9.15(d, 2H); 10.60(s, 1H). |
| **2b**[a] | 240-242 MeCN | $C_{21}H_{15}NOBrCl$ | 1690, 1620, 1440 | 7.10(s, 2H); 7.69-8.60(m, 10H); 9.17 (d, J=7 Hz, 2H); 10,41(s, 1H). |
| **2c**[a] | 244-245 MeCN | $C_{21}H_{15}NOBr_2$ | 1690, 1630, 1590 | 7.07(s, 2H); 7.82-8.60(m, 10H); 9.17 (d, J=7 Hz, 2H); 10.39(s, 1H). |
| **2d**[a] | 250-252 EtOH-$H_2O$ | $C_{21}H_{15}N_2O_3Br$ | 1710, 1630, 1530 | 7.11(s, 2H); 8.02-8.63(m, 10H); 9.20 (d, J=8 Hz, 2H). |
| **3a**[b] | 198-200 MeOH-$CH_2Cl_2$ | $C_{42}H_{30}N_2O_2$ | 1680, 1600, 1490, 1450, 1260 | 5.19(d, J=8.5 Hz, 2H); 5.63(d, J=8.5 Hz, 2H); 7.05-7.81(m, 26H) |
| **3b**[b] | 188-190 MeOH-$CH_2Cl_2$ | $C_{42}H_{28}N_2O_2Cl_2$ | 1680, 1600, 1580 1490, 1440 | 5.00(d, J=5.6 Hz, 2H);5.52(d, J=5.5 Hz 2H); 7.03-7.80(m, 24H). |
| **3c**[b] | 224-226 MeCN | $C_{42}H_{28}N_2O_2Br$ | 1670, 1600, 1580 1490, 1440 | 5.66(d, J=4 Hz, 2H); 5.96(d, J=4 Hz; 2H); 7.04-7.51(m, 24H). |
| **3d**[b] | 212-215 MeOH-$CH_2Cl_2$ | $C_{42}H_{28}N_4O_6$ | 1680, 1600, 1520 1490, 1440, 1350 | 5.57(d, J=8.5 Hz, 2H); 6.01(d, J=8.2 Hz 2H); 6.87-7.59(m, 24H). |
| **4a**[c] | 264-266 MeCN | $C_{27}H_{19}NO_5$ | 1724, 1715, 1672 1224 | 3.47(s, 3H); 3.98(s, 3H); 7.19-7.58 (m, 9H); 7.90-8.30(m, 4H). |
| **4b**[c] | 211-212 MeCN | $C_{27}H_{18}N_2O_7$ | 1730, 1721, 1663 1219 | 3.61(s, 3H); 4.06(s, 3H); 8.24(q, J=8.8 Hz, 4H); 7.26-7.62(m, 6H); 8.13-8.40(m, 6H). |
| **5a**[a] | 222-224 EtOH | $C_{28}H_{20}N_2O_2$ | 1631, 1590, 1541 1495 | 6.81-9.02(m, 18H);10.25(s, 1H); 12.72 (s, 1H). |
| **5b**[a] | 228-229 MeOH-$CH_2Cl_2$ | $C_{28}H_{19}N_2O_2Cl$ | 1624, 1590, 1540 1503 | 6.92-8.52(m, 15H); 9.01-9.10(m, 2H); 10.35(s, 1H); 12.71(s, 1H). |
| **5c**[a] | 175-178 MeOH | $C_{28}H_{20}N_2OS$ | 1621, 1483, 1185 | 6.90-7.02(m, 3H); 7.06-7.40(m, 5H); 7.70-8.36(m, 8H); 8.64-8.61(m, 2H), 9.94(s, 1H); 14.48(s, 1H). |

[a]DMSO-$d_6$, 80 MHz. [b]$CDCl_3$, 80 MHz. [c]$CDCl_3$, 300 MHz.

Table 2 (Cont). Physical and Spectroscopic Data of Compounds (**2 - 6**)

| Compd no. | mp (°C) Solv. | Molecular Formula | ir (KBr) ν ($cm^{-1}$) | $^1$H nmr δ (ppm) |
|---|---|---|---|---|
| **5d** | 188-189 MeCN | $C_{28}H_{19}N_2OClS$ | 1580, 1545, 1179 | 7.02-8.85(m, 17H); 9.88(s, 1H); 14.46 (s, 1H). |
| **6a** | 223-225 MeOH | $C_{29}H_{20}N_2O_3$ | 1700, 1640, 1620 1470, 1410 | 6.91-8.76(m, 18H); 9.67(s, 1H). |
| **6b** | 208-210 MeOH-$CH_2Cl_2$ | $C_{29}H_{19}N_2O_3Br$ | 1690, 1630, 1610 1510, 1460, 1410 | 7.09-8.51(m, 15H); 9.03(d, J=7.6 Hz, 2H); 10.38(s, 1H); 14.23(s, 1H). |
| **6c** | 230-232 MeOH-$CH_2Cl_2$ | $C_{29}H_{19}N_3O_5$ | 1690, 1620, 1530 1470, 1410 | 9.00(d, J=8.3 Hz, 2H); 7.52-8.59(m, 11H); 9.00(d, J=8.3 Hz, 2H); 10.46(s, 1H) 14.13(s, 1H). |

[a]DMSO-$d_6$, 80 MHz. [b]$CDCl_3$, 80 MHz. [c]$CDCl_3$, 300 MHz.

instrument using TMS as internal reference. *N*-Sulfinyl-*p*-toluenesulfonamide was obtained according Kresze and Wucherpfenning.[25]

**Synthesis of 5-Phenanthridinium Salts (2)**. To a solution of 30 mmol of the corresponding 2-bromoacetophenone in ethyl acetate (30 ml), phenanthridine (5.43 g, 30 mmol) was added in portions. The mixture was refluxed with stirring for 1 h. Then, the salt was recovered as a precipitate, which was recrystallised from the solvent indicated in Table 2.

**Dimerization of 5-Phenanthridinium Salts (2). Compounds (3)**. 0.19 g (0.5 mmol) of the corresponding 5-phenacylphenanthridinium bromide were suspended in a solution of 0.15 g (1.5 mmol) of triethylamine in dry acetonitrile (5 ml). The mixture was stirred at room temperature for 3 h, yielding a yellow product which was recrystallized from the solvent indicated in Table 2.

**Reaction of Phenanthridinium Salts (2) with DMAD. Compounds (4)**. The corresponding 5-phenacylphenanthridinium halide (**2**) (1 mmol) and 0.28 g of dimethyl acetylenedicarboxylate (DMAD) (0.25ml, 2 mmol) were suspended in 50% aqueous potassium carbonate (5 ml). The mixture was stirred at room temperature for 24 h. Then, the reaction mass was extracted with methylene chloride (3x5 ml).

Table 3. Structure of compound (**10**). Atomic Parameters for Nonhydrogen Atoms. Coordinates and Thermal Parameters as:

$$U_{eq} = (1/3).\ (U_{ij}a_i^{*}a_j^{*}a_ia_j\cos(a_i,a_j)).10^3$$

| Atom | x | y | z | $U_{eq}$ |
|---|---|---|---|---|
| S1 | 0.13282 (04) | -0.10725 (09) | 0.72098 (09) | 785 (03) |
| N2 | 0.39666 (11) | -0.03582 (19) | 0.62647 (21) | 419 (07) |
| C3 | 0.32799 (13) | -0.11783 (22) | 0.68254 (23) | 385 (08) |
| C4 | 0.36549 (13) | -0.20924 (23) | 0.75299 (23) | 394 (08) |
| C5 | 0.39350 (15) | -0.14422 (29) | 0.91832 (26) | 505 (10) |
| C6 | 0.42695 (17) | -0.23006 (36) | 0.98181 (33) | 637 (13) |
| C7 | 0.43216 (17) | -0.37969 (34) | 0.88107 (34) | 635 (13) |
| C8 | 0.40579 (16) | -0.44467 (28) | 0.71657 (32) | 552 (11) |
| C9 | 0.37192 (13) | -0.36039 (23) | 0.64876 (24) | 414 (08) |
| C10 | 0.34408 (13) | -0.42134 (23) | 0.47364 (24) | 428 (08) |
| C11 | 0.37304 (16) | -0.54359 (28) | 0.35362 (31) | 591 (11) |
| C12 | 0.34862 (18) | -0.58962 (33) | 0.19130 (32) | 696 (12) |
| C13 | 0.29544 (17) | -0.51566 (35) | 0.14386 (30) | 677 (12) |
| C14 | 0.26421 (15) | -0.39482 (31) | 0.26059 (26) | 547 (10) |
| C15 | 0.28752 (13) | -0.35225 (23) | 0.42301 (23) | 416 (08) |
| N16 | 0.25746 (10) | -0.22812 (19) | 0.54894 (19) | 399 (07) |
| C17 | 0.17137 (13) | -0.23285 (25) | 0.56685 (26) | 454 (09) |
| S18 | 0.39577 (03) | 0.13423 (05) | 0.64152 (06) | 419 (02) |
| O19 | 0.47814 (10) | 0.18161 (17) | 0.59003 (21) | 562 (07) |
| O20 | 0.37786 (10) | 0.22768 (17) | 0.80135 (17) | 550 (07) |
| C21 | 0.30885 (14) | 0.11852 (23) | 0.50428 (24) | 423 (08) |
| C22 | 0.30964 (18) | 0.03566 (33) | 0.33862 (28) | 622 (12) |
| C23 | 0.24594 (20) | 0.03722 (36) | 0.23297 (32) | 685 (13) |
| C24 | 0.18263 (16) | 0.12309 (28) | 0.28793 (28) | 539 (10) |
| C25 | 0.19969 (29) | 0.19969 (29) | 0.45255 (29) | 548 (11) |
| C26 | 0.24337 (15) | 0.19804 (27) | 0.56139 (27) | 497 (10) |
| C27 | 0.11789 (24) | 0.13496 (50) | 0.17087 (43) | 780 (18) |
| C28 | 0.10355 (13) | -0.37573 (25) | 0.44478 (26) | 457 (09) |
| 029 | 0.10237 (11) | -0.49809 (19) | 0.44875 (21) | 598 (08) |
| C30 | 0.03969 (14) | -0.35924 (27) | 0.33540 (28) | 504 (10) |
| C31 | -0.02867 (17) | -0.48648 (34) | 0.23926 (30) | 632 (12) |
| C32 | -0.08861 (21) | -0.47303 (48) | 0.13470 (39) | 854 (17) |
| C33 | -0.08004 (23) | -0.33605 (51) | 0.12423 (47) | 960 (22) |
| C34 | -0.01263 (23) | -0.21239 (51) | 0.21745 (53) | 966 (23) |
| C35 | 0.04755 (18) | -0.22133 (35) | 0.32360 (41) | 717 (15) |

Table 4. Structure of compound (**10**). Atomic Paramenters for Hydrogen Atoms. Coordinates and Thermal Parameters as:

$$Exp(-8\ \pi^2\ U\ (\sin\theta/\lambda)^2.10^3)$$

| Atom | x | y | z | U |
|---|---|---|---|---|
| H2 | 0.429 (2) | -0.086 (3) | 0.555 (3) | 21 (06) |
| H3 | 0.301(1) | -0.045(2) | 0.762(2) | 10 (04) |
| H5 | 0.389(2) | -0.038(3) | 0.982(3) | 31 (16) |
| H6 | 0.447(2) | -0.182(3) | 1.091(4) | 53 (08) |
| H7 | 0.455(2) | -0.439(4) | 0.923(4) | 55 (09) |
| H8 | 0.409(2) | -0.554(3) | 0.639(3) | 44 (08) |
| H11 | 0.414(2) | -0.595(3) | 0.385(4) | 46 (08) |
| H12 | 0.374(2) | -0.674(4) | 0.111(4) | 59 (09) |
| H13 | 0.279(2) | -0.542(4) | 0.030(4) | 52 (08) |
| H14 | 0.226(2) | -0.341(3) | 0.233(3) | 33 (06) |
| H22 | 0.354(2) | -0.016(3) | 0.300(3) | 43 (08) |
| H23 | 0.248(2) | -0.013(4) | 0.131(4) | 69 (10) |
| H25 | 0.138(2) | 0.254(3) | 0.491(3) | 39 (07) |
| H26 | 0.240(2) | 0.250(3) | 0.672(4) | 35 (08) |
| H271 | 0.101(3) | 0.030(5) | 0.079(6) | 93 (14) |
| H272 | 0.153(3) | 0.187(5) | 0.119(6) | 110 (16) |
| H273 | 0.068(3) | 0.164(5) | 0.218(5) | 88 (15) |
| H31 | -0.033(2) | -0.581(3) | 0.250(3) | 46 (08) |
| H32 | -0.131(3) | -0.557(5) | 0.081(5) | 84 (13) |
| H33 | -0.125(3) | -0.336(4) | 0.047(5) | 89 (12) |
| H34 | -0.005(3) | -0.126(5) | 0.213(5) | 92 (15) |
| H35 | 0.094(2) | -0.134(4) | 0.387(4) | 51 (09) |

All the organic extracts were combined, washed with water to eliminate base traces, dried over $MgSO_4$, concentrated and the residue was recrystallized as indicated in Table 2.

**Reaction of Phenanthridinium Salts (1) with Phenyl and Benzoyl Isocyanate. Ylides (5a, b and 6).** To a mixture of the corresponding 5-phenacylphenanthridinium halide (**1**) (1 mmol), and either pure phenyl isocyanate (15 mmol, compounds **5**) or benzoyl isocyanate (1.2 mmol) in acetonitrile (8 ml, compounds **6**), finely ground anhydrous potassium carbonate (0.55 g, 4 mmol) was added. The mixture was vigorously stirred at room temperature for 8 h. The inorganic solid was filtered off, and washed with methylene chloride until no color remained.The organic extracts were combined, washed with water until neutral, dried over $MgSO_4$ and concentrated. The residue was recrystallized

Table 5. Structure of **10**. Bond Distances (Å).

| | | | |
|---|---|---|---|
| S1-C17 | 1.645(2) | N2-C3 | 1.450(3) |
| N2-S18 | 1.615(2) | C3-C4 | 1.504(4) |
| C3-N16 | 1.475(2) | C4-C5 | 1.388(3) |
| C4-C9 | 1.396(3) | C5-C6 | 1.383(5) |
| C6-C7 | 1.372(4) | C7-C8 | 1.283(4) |
| C8-C9 | 1.400(4) | C9-C10 | 1.473(3) |
| C10-C11 | 1.395(3) | C10-C15 | 1.393(4) |
| C11-C12 | 1.379(4) | C12-C13 | 1.377(5) |
| C13-C14 | 1.393(4) | C14-C15 | 1.384(3) |
| C15-N16 | 1.438(3) | N16-C17 | 1.344(3) |
| C17-C28 | 1.519(3) | S18-O19 | 1.437(2) |
| S18-020 | 1.426(2) | S18-C21 | 1.761(2) |
| C21-C22 | 1.384(3) | C21-C26 | 1.380(3) |
| C22-C23 | 1.377(5) | C23-C24 | 1.384(4) |
| C24-C25 | 1.373(3) | C24-C27 | 1.513(5) |
| C25-C26 | 1.382(4) | C28-029 | 1.214(3) |
| C28-C30 | 1.477(4) | C30-C31 | 1.387(3) |
| C30-C35 | 1.386(5) | C31-C32 | 1.388(5) |
| C32-C33 | 1.370(7) | C33-C34 | 1.365(5) |
| C34-C35 | 1.378(6) | | |

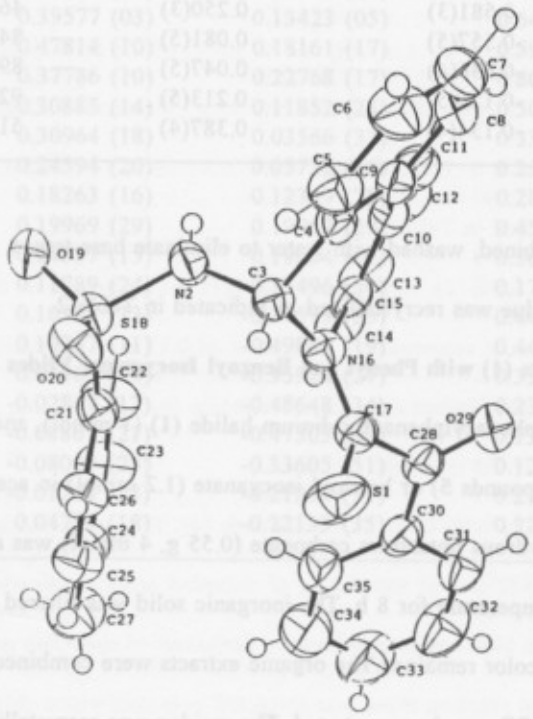


Figure 4

**10**

Table 6. Structure of **10.** Bond Angles (°).

| | | | |
|---|---|---|---|
| C3I-N2-S18 | 121.6(2) | N2-C3-N16 | 111.5(2) |
| N2-C3-C4 | 111.0(2) | C4-C3-N16 | 107.7(2) |
| C3-C4-C9 | 118.8(2) | C3-C4-C5 | 120.6(2) |
| C5-C4-C9 | 120.6(2) | C4-C5-C6 | 120.0(2) |
| C5-C6-C7 | 119.9(3) | C6-C7-C8 | 120.7(3) |
| C7-C8-C9 | 120.7(3) | C4-C9-C8 | 118.1(2) |
| C8-C9-C10 | 123.7(2) | C4-C9-C10 | 118.3(2) |
| C9-C10-C15 | 119.0(2) | C9-C10-C11 | 123.4(2) |
| C11-C10-C15 | 117.5(2) | C10-C11-C12 | 120.7(2) |
| C11-C12-C13 | 120.8(3) | C12-C13-C14 | 119.9(3) |
| C13-C14-C15 | 118.6(3) | C10-C15-C14 | 122.3(2) |
| C14-C15-N16 | 121.1(2) | C10-C15-N16 | 116.5(2) |
| C3-N16-C15 | 123.6(2) | C15-N16-C17 | 123.2(2) |
| C3-N16-C17 | 121.1(2) | S1-C17-N16 | 125.8(2) |
| N16-C17-C28 | 117.5(2) | S1-C17-C28 | 116.3(2) |
| N2-S18-C21 | 110.0(1) | N2-S18-020 | 107.8(1) |
| N2-S18-019 | 104.5(1) | 020-S18-C2 | 107.3(1) |
| 019-S18-C2 | 107.9(1) | 019-S18-C20 | 119.3(1) |
| S18-C21-C26 | 120.0(2) | S18-C21-C22 | 120.0(2) |
| C22-C21-C26 | 119.9(2) | C21-C22-C23 | 119.2(3) |
| C22-C23-C24 | 121.8(3) | C23-C24-C27 | 121.3(3) |
| C23-C24-C25 | 118.0(3) | C25-C24-C27 | 120.7(3) |
| C24-C25-C26 | 121.4(3) | C21-C26-C25 | 119.7(2) |
| C17-C28-C30 | 119.7(2) | C17-C28-029 | 116.9(2) |
| 029-C28-C30 | 123.2(2) | C28-C30-C35 | 121.8(3) |
| C28-C30-C31 | 119.0(3) | C31-C30-C35 | 119.3(3) |
| C30-C31-C32 | 119.5(3) | C31-C32-C33 | 120.6(3) |
| C32-C33-C34 | 119.7(4) | C33-C34-C35 | 121.3(5) |
| C30-C25-C34 | 119.7(3) | | |

as described in Table 2.

**Reaction of Phenanthridinium Salts (1) with Phenyl Isothiocyanate. Ylides (5c, d).** To a suspension of the corresponding 5-phenacylphenanthridinium halide **(1)** (1 mmol) in phenyl isothiocyanate (0,54 g, 4 mmol), 50% aqueous potassium carbonate (5 ml) was added. The reaction mixture was vigorously stirred at room temperature for 8 h. The mixture was then extracted with methylene chloride (4x10 ml). All the organic extracts were combined, washed with water until alkalinity disappeared, dried over $MgSO_4$, concentrated and recrystallized as indicated in Table 2.

**Reaction of Phenanthridinium Salts (1) with *N*-Sulfinyl-*p*-toluenesulfonamide. Compound (10).** To a stirred

suspension of 5-phenacylphenanthridinium bromide (**1a**) (0.756 g, 2 mmol) in dry acetonitrile (25 ml), was added *N*-sulfinyl-*p*-toluenesulfonamide (0.868 g, 4 mmol) followed by dry triethylamine (1.5 ml, 20 mmol). The mixture was heated in a water bath at 40-50° C for 6 h. The reaction mixture was then concentrated and the residue was triturated with acetone (3x5 ml) to precipitate the triethylamine hydrobromide, which was separated by filtration. The filtrate was concentrated and the residual oil was flashed through neutral alumina, with dichloromethane as eluant. The extract collected (ca. 20 ml) was concentrated, giving an oil which on trituration with drops of ethanol, yielded 0.46 g (47%) of yellow prisms, mp 214-216° C, (MeCN); ir (KBr) υ: 3250, 1590, 1495, 1425, 1400 $cm^{-1}$; $^1H$ nmr($CDCl_3$) δ:2.52 (s, 3H); 5.10 (d, J=8.5 Hz, 1H); 7.00-7.85 (m, 17H) ; 8.05 (d, J=8.5 Hz,1H) ppm.

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