Cycloaddition Reactions of *N*-Phenylsulfonyl-1-azabuta-1,3-dienes with Mesoionic 2,4-Diphenyl-1-methyl-1,3-oxazolium 5-oxide

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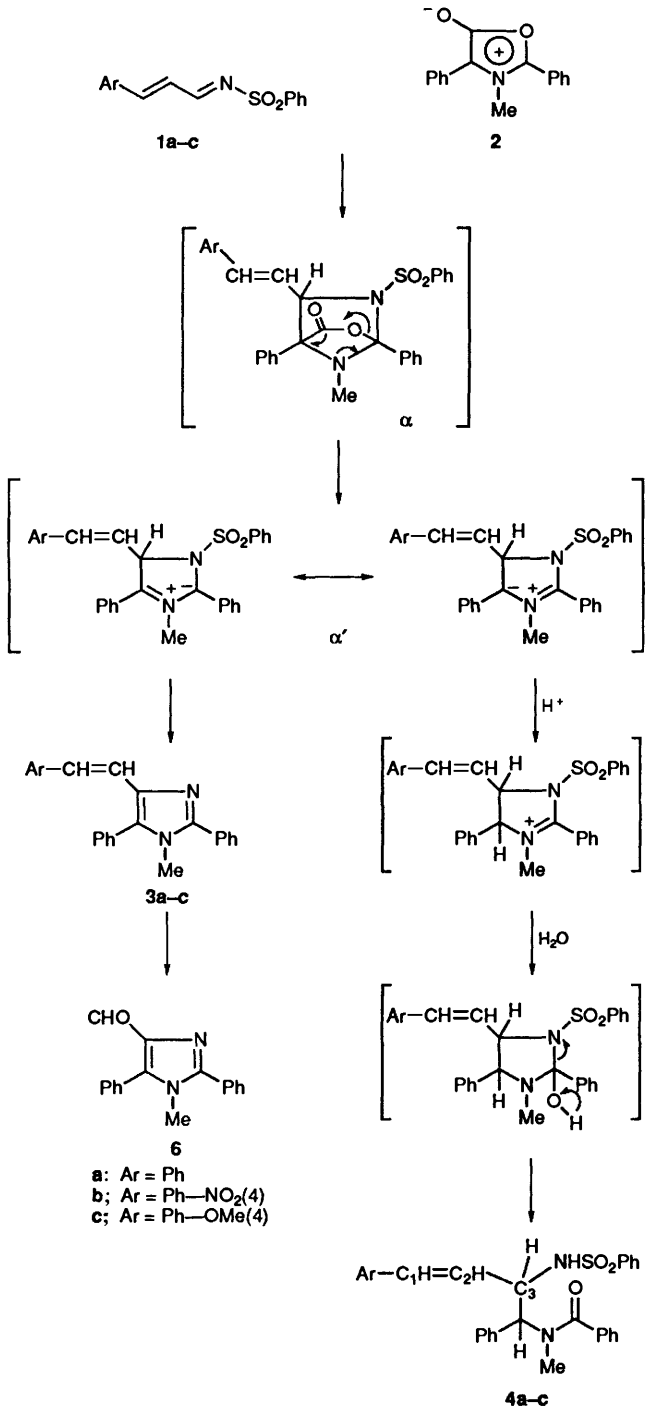
N-Phenylsulfonyl unsaturated imines (**1**) react with 2,4-diphenyl-3-methyl-1,3-oxazolium 5-oxide (**2**) giving 4-styrylimidazoles (**3**), open chain products (**4**) and pyrrol-3-ylcarboxaldehyde *N*-phenylsulfonylimines (**5**). The mechanism of formation of all the products as well as the different behaviour of imines **1** compared with those lacking the *N*-tosyl group are discussed. The structures have been assigned on the basis of ^{1}H NMR evidence and by X-ray analysis.

As part of our work concerning the use of mesoionic compounds[1] in heterocyclic synthesis we report the reaction of *N*-phenylsulfonyl α,β-unsaturated imines with 1,3-oxazolium 5-oxides. The phenylsulfonyl group is a useful functionality in organic synthesis since generally it increases the chemical reactivity and is easily removed at the end of the process giving sulfur-free derivatives. Recently *N*-sulfonyl unsaturated imines have been widely used as azadienes in Diels–Alder reactions with vinyl ethers leading to substituted tetrahydropyridines.[2] Among the examples in which unsaturated imines are employed as precursors in heterocyclic synthesis, very few deal with their use as dipolarophiles[3–5] in 1,3-dipolar cycloaddition reactions but none of them is concerned, to our knowledge, with mesoionic compounds. In this context we have set out to study the addition of 2,4-diphenyl-1-methyl-1,3-oxazolium 5-oxide (**2**) to unsaturated imines **1a–c**.

Results and Discussion

Owing to its high reactivity the munchnone **2** was prepared *in situ* starting from the corresponding *N*-benzoyl-*N*-methylphenylglycine and *N,N'*-dicyclohexylcarbodiimide and was reacted with the imines **1a–c**. The reactions were performed in toluene solution at room temperature and under nitrogen atmosphere for 12 h. Filtration of dicyclohexylurea and evaporation of the solvent gave a mixture of products **3–5** which were separated by column chromatography and further purified by crystallization. Analytical, physical and spectroscopic data for products **3**, **4** and **5** are summarized in Table 1. The structures of 4-styrylimidazole and of pyrrol-3-ylcarboxaldehyde *N*-phenylsulfonylimine were easily assigned to compounds **3** and **5** on the basis of their characteristic analytical and spectral data. Moreover the chemical behaviour of **3** and **5** agrees with their structures: treatment of **3a** with sodium periodate and a catalytic amount of osmium tetroxide and of **5a** with 20% aqueous sulfuric acid gave imidazol-4-ylcarboxaldehyde **6** and pyrrol-3-ylcarboxaldehyde **7** respectively. From a synthetic point of view compounds **3** and **5** could be considered useful precursors for these heterocycles. The assignment of a structure to compound **4** was based on elemental as well as spectral data. The IR spectrum ($CHCl_3$) showed bands at ν/cm^{-1} 3250 and 1605 indicating the presence of NH and amido carbonyl groups. The 300 MHz ^{1}H NMR spectrum showed five sets of signals in the range 5.0–6.6 ppm corresponding to five protons (see Table 1 product **4a**). The coupling constants between 1-H, 2-H, 3-H and 4-H were confirmed by suitable spin–spin decoupling experiments. On the basis of chemical shift values for the five protons and relative coupling constants it was possible to establish the sequence of connectivity in the unexpected open chain products. The proposed structure of 4-(*N*-methylbenzoylamino)-1,4-diphenyl-3-phenylsulfonylamino-but-1-ene (**4a**) was further confirmed by an X-ray single-crystal analysis. Fig. 1 shows an ORTEP II[6] diagram of the molecule with the numbering scheme. Bond distances and angles of the structure do not present any particular features, all being compatible with the values found in the literature (see for example ref. 7). The structure presents a couple of molecules lying on a centre of symmetry, linked by the strong couple of hydrogen bonds N(1)···O(3) 2.934(2) Å, N(1)–H(1)···O(3) 153(2)°. Crystallographic details are given in the Experimental section. The reaction between imines **1a–c** and munchnone **2** involves a typical 1,3-dipolar cycloaddition to C=C and C=N double bonds followed by cycloreversion of carbon dioxide from the primary adducts [α] and [β] respectively. Afterwards the cyclic azomethine ylide [α'] loses benzenesulfinic acid giving imidazole derivatives **3** and the intermediate [β'] gives rise to pyrrole derivatives **5** as a result of a spontaneous oxidative aromatisation of the initially formed dihydropyrrole.

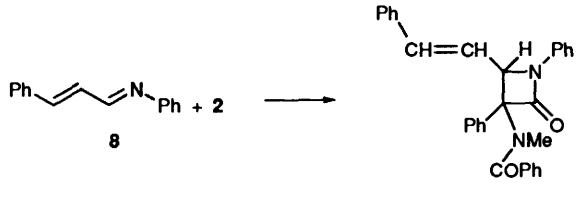
A possible mechanism that rationalizes the formation of open chain compounds **4** might follow: (i) proton transfer from benzenesulfinic acid to [α], (ii) nucleophilic attack of water with ring opening of imidazole system during the usual work-up of the reaction mixture. With the aim to verify the effect of a 4-nitro and 4-methoxyphenyl substituents on the site-selectivity of the reaction, imines **1b**, **c** were reacted with munchnone **2**. The results, summarized in Table 1, indicate a scant effect of these groups on the ratio of the products deriving from C=N (major) *vs.* C=C (minor) addition. In the 1,3-dipolar cycloaddition between munchnone **2**, a highly polar system[8,9] and the dipolarophiles **1a–c** we can hypothesize that the electrostatic interaction between the molecular charge distributions plays an important role. We may assume that the phenylsulfonyl group, a strong electron withdrawing substituent, further increases the polarization of C=N with respect to the C=C double bond. Therefore the formation of an α-adduct as well as the corresponding imidazole could result in being more favoured. On the basis of these results we expected that a solvent with a high relative permittivity affects C=C/C=N ratio. In fact the reaction of **1a** with **2**, carried out in *N,N*-dimethylformamide gave almost exclusively the imidazole derivative. Moreover, the phenylsulfonyl group on a nitrogen atom modifies the electronic distribution of the unsaturated system enhancing the inherent electron deficient character of 1-azabuta-1,3-diene. This arises from the comparison between the FMO energy levels of unsubstituted 1-azabuta-1,3-diene (HOMO: −10.1 eV; LUMO: 0.4 eV) and the *N*-phenylsulfonyl



Scheme 1

derivative (HOMO: −11.1 eV; LUMO: −0.9 eV).[2] From the FMO values of the munchnone (**2**) (HOMO: −7.8 eV; LUMO: −0.7 eV)[9] it follows that the 1,3-dipolar cycloaddition of **1a** with **2** is $HOMO_{dipole}$-controlled. The observed pyrrole/imidazole distribution could be explained if we consider the magnitude of LUMO coefficients[2] relative to *N*-phenylsulfonyl-1-azabuta-1,3-diene. On the basis of these values the LUMO orbital results in being more localised on the C=N (0.50; −0.58) double bond with respect to the C=C one (−0.3; 0.53). In the framework of PMO approach we can conclude that both the polar term and the overlap term account for the experimental results concerning the site-selectivity (see Fig. 2).

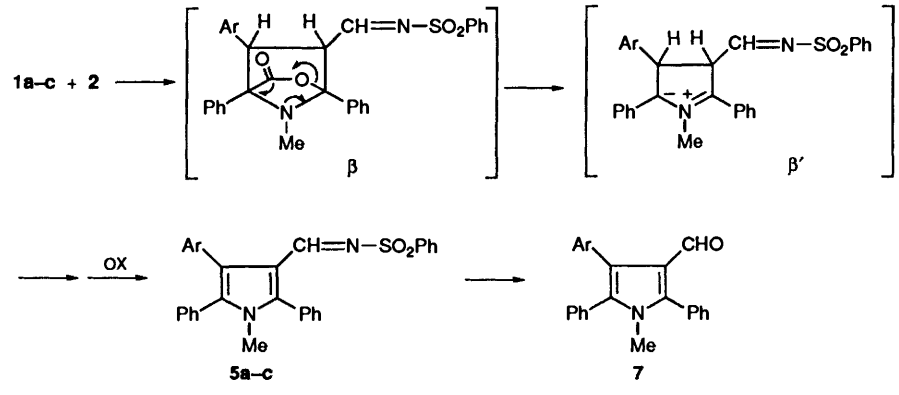
The only example of addition of munchnone **2** to imines such as *N*-(phenylmethylene)aniline and methylamine, is reported by Huisgen;[10] in this case the reaction gave β-lactam whose formation was assumed to take place *via* the valence tautomer of the starting munchnone. We extended the above reaction to 1,4-diphenyl-1-azabuta-1,3-diene (**8**) and obtained 3-(*N*-methylbenzoylamino)-1,3-diphenyl-4-phenylvinylazetidin-2-one (**9**), as the single product, deriving from a (2 + 2)π cycloaddition to C=N system. Thus the *N*-alkyl or *N*-aryl



Scheme 3

substituted imines and the corresponding α,β-unsaturated ones show the same type of reactivity with regard to munchnones. On the contrary the behaviour of *N*-phenylsulfonyl substituted 1-azabuta-1,3-dienes (**1a–c**) is completely different in that their reaction with munchnone **2** gave imidazoles **3** and pyrroles **5** deriving both from a (3 + 2)π cycloaddition reaction across C=N (major product) and C=C (minor product) double bonds respectively. These results open new opportunities in the synthesis of nitrogen heterocycles because they allow the reaction to be selectively directed towards the formation of β-lactams or imidazoles simply by modifying the substituent (phenyl or tosyl groups) on the nitrogen atom of the starting unsaturated imines.

The peculiar behaviour of imines **1** compared with those lacking the *N*-phenylsulfonyl group mainly depends on the effect exerted by this group. Also stereoelectronic factors (bulky substituents on the nitrogen atom and the different nucleophilicity of imines **1** and **8**) can explain the selectivity towards the formation of a (3 + 2)π rather than a (2 + 2)π



Scheme 2

Table 1 Physical, analytical and ^{1}H NMR data of products **3**, **4** and **5**

Compound	M.p./°C	Solvent	Yield (%)[a]	NMR data	Found (%)			Formula	Required (%)		
3a	130–132	Pr^{i}OH	38	3.6 (s, 3 H, NCH_3), 6.95 (d, 1 H, *J* 16, CH=), 7.2–7.3 (3 H, m, aromatic), 7.4–7.6 (11 H, m, aromatic, =CH), 7.7 (2 H, m, aromatic).	85.6	5.9	8.3	$C_{24}H_{20}N_2$	85.7	6.0	8.3
4a	210–212	Pr^{i}OH	7	2.7 (3 H, s, NCH_3), 4.95–5.0 (1 H, m, 3-H), 5.65 (1 H, dd, *J* 15 and 7, 2-H) 5.95 (1 H, d, *J* 11, 4-H), 6.15 (1 H, d, *J* 6, NH), 6.25 (1 H, d, *J* 15, 1-H) 6.85–6.95 (2-H, m, aromatic), 7.1–7.45 (16 H, m, aromatic), 7.8–7.9 (2 H, m, aromatic).	72.4	5.7	5.5	$C_{30}H_{28}N_2O_3S$	72.6	5.7	5.6
5a	175–177	$(Pr^i)_2O$	11	3.4 (3 H, s, NCH_3, 7.1–7.7 (20 H, m, aromatic), 8.7 (1 H, s, CH=N)	75.5	5.2	5.7	$C_{30}H_{24}N_2O_2S$	75.6	5.1	5.9
3b	207–208	AcOEt	30	3.6 (3 H, s, NCH_3), 7.1 (1 H, d, *J* 16, CH=), 7.4–7.6 (11 H, m, aromatic and =CH), 7.7 (2 H, m, aromatic), 8.15 (2 H, d, *J* 9, aromatic).	75.45	4.95	10.9	$C_{24}H_{19}N_3O_2$	75.6	5.0	11.0
4b	197–198	AcOEt	6	2.6 (3 H, s, NCH_3), 4.9–5.0 (1 H, m, 3-H), 5.88 (1 H, dd, *J* 15 and 7.5, 2-H) 5.95 (1 H, d, *J* 12, 4-H), 6.35 (1 H, d, *J* 15, 1-H), 6.5 (1 H, d, *J* 8, NH), 7.0 (2 H, d, *J* 9, aromatic), 7.3–7.5 (13 H, m, aromatic), 7.8 (2 H, m, aromatic), 8.0 (2 H, d, *J* 9, aromatic).	66.6	5.1	7.95	$C_{30}H_{27}N_3O_5S$	66.5	5.0	·7.8
5b	214–215	AcOEt	8	3.4 (3 H, s, NCH_3), 7.1–7.6 (17 H, m, aromatic), 7.9 (2 H, d, *J* 8, aromatic), 8.7 (1 H, s, CH=N)	68.9	4.4	8.0	$C_{30}H_{23}N_3O_4S$	69.1	4.45	8.1
3c	158–160	Pr^{i}OH	35	3.6 (3 H, s, NCH_3), 3.8 (3 H, s, OCH_3), 6.8–6.85 (3 H, m, aromatic, CH=), 7.35–7.55 (11 H, m, aromatic, =CH), 7.7–7.8 (2 H, m, aromatic).	81.8	6.0	7.55	$C_{25}H_{22}N_2O$	81.9	6.05	7.65
4c	175–177	Pr^{i}OH	9	2.7 (3 H, s, NCH_3), 3.8 (3 H, s, OCH_3), 4.9–5.0 (1 H, m, 3-H), 5.55 (1 H, dd, *J* 16 and 7, 2-H), 5.94–5.97 (2 H, m, 4-H, NH), 6.2 (1 H, d, *J* 16, 1-H), 6.7 (2 H, d, *J* 8, aromatic), 6.9 (2 H, d, *J* 8, aromatic), 7.3–7.5 (13 H, m, aromatic), 7.85 (2 H, d, *J* 8, aromatic).	70.6	5.7	5.4	$C_{31}H_{30}N_2O_4S$	70.7	5.7	5.3
5c	156–158	Pr^{i}OH	13	3.35 (3 H, s, NCH_3), 3.85 (3 H, s, OCH_3), 6.68 (2 H, d, *J* 9, aromatic), 7.03 (2 H, d, *J* 9, aromatic), 7.2–7.6 (15 H, m, aromatic), 8.7 (1 H, s, CH=N).	73.45	5.1	5.5	$C_{31}H_{26}N_2O_3S$	73.5	5.2	5.5

[a] Yield of pure isolated products.

cycloadduct. In this last case it is generally accepted that the first step of the reaction occurs *via* a nucleophilic attack of nitrogen atom of imine[11] to the carbonyl group of **2** whereas the 1,3-dipolar cycloaddition prevails with *N*-phenylsulfonyl substituted imines.

Experimental

M.p.s were measured with a Buchi apparatus and are uncorrected. IR spectra were obtained with a Perkin-Elmer 298 spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker WP 80-SY and a Bruker AC 300 spectrometers. All chemical shifts are expressed in δ values from tetramethylsilane as the reference. *J* values are expressed in Hz. Compounds **8**[12] and *N*-methyl-*N*-benzoyl-phenylglycine[13] were prepared following the methods reported in literature.

General Procedure[14] *for the Preparation of* α,β-*Unsaturated* N-(*Phenylsulfonyl*)*imines* **1a–c**.—A solution of the aldehyde (6.4 mmol) in dry dichloromethane (80 cm^3) was cooled to 0 °C and treated, under nitrogen, with dry triethylamine (1.94 g, 19.2 mmol) and benzenesulfonamide (1.0 g, 6.4 mmol) respectively. Titanium tetrachloride (0.61 g, 3.2 mmol) was added dropwise to the reaction solution, and the mixture was stirred for 30 min (compound **1c** required stirring at room temperature for 4 h). The titanium dioxide was removed by filtration of the reaction mixture through Celite. The Celite pad was washed with dichloromethane and the combined filtrates were evaporated. The solid residue was treated with toluene (60 cm^3) and stirred at room temperature for 20 min. The slurry was filtered through Celite and extracted a second time. The combined filtrates were evaporated off to give in all cases a solid which was purified by crystallization.

1a M.p. 105–107 °C (lit.[2], 107–109 °C); **1b**: yields 79%, m.p. 166–168 °C (from ethyl acetate) (Found: C, 56.85; H, 3.7; N, 8.7. $C_{15}H_{12}N_2O_4S$ requires C, 57.0; H, 3.8; N, 8.9%); δ_H(300 MHz; $CDCl_3$) 7.09 (1 H, dd, *J* 16 and 9, Ar–CH=*CH*), 7.5–7.72 (6 H, m, aromatic, Ar–*CH*=CH), 7.98 (2 H, d, *J* 7.4, aromatic), 8.28 (2 H, d, *J* 8.8, aromatic), 8.84 (1 H, d, *J* 9, CH=N); **1c**: yields 95%, m.p. 133–135 °C (from ethyl acetate–hexane 9 : 1) (Found: C, 63.6; H, 5.1; N, 4.6. $C_{16}H_{15}NO_3S$ requires C, 63.8; H, 5.0; N, 4.65%); δ_H(300 MHz; $CDCl_3$) 3.90 (3 H, s, MeO), 6.86–6.95 (3 H, m, aromatic, Ar–CH=C*H*), 7.5–7.6 (6-H, m, aromatic, Ar–C*H*=CH), 7.96 (2 H, d, *J* 7.2, aromatic), 8.76 (1 H, d, *J* 9.5, CH=N).

General Procedure for the Reaction Between N-(3-*Arylprop*-2-*enylidene*)*benzenesulfonamides* (**1a–c**) *and* 2,4-*Diphenyl*-3-*methyl*-1,3-*oxazolium* 5-*Oxide* (**2**).—In a typical experiment a suspension of *N*-benzoyl-*N*-methylphenylglycine (2.7 g, 10 mmol) in toluene (30 cm^3) was added dropwise to DCCI (2.5 g,

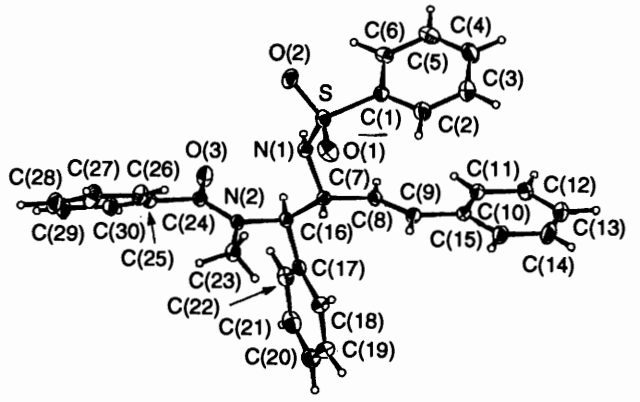


Fig. 1 ORTEP drawing of **4a** with numbering scheme. Thermal ellipsoids of non-hydrogen atoms are at 20% of probability level. H atoms not to scale.

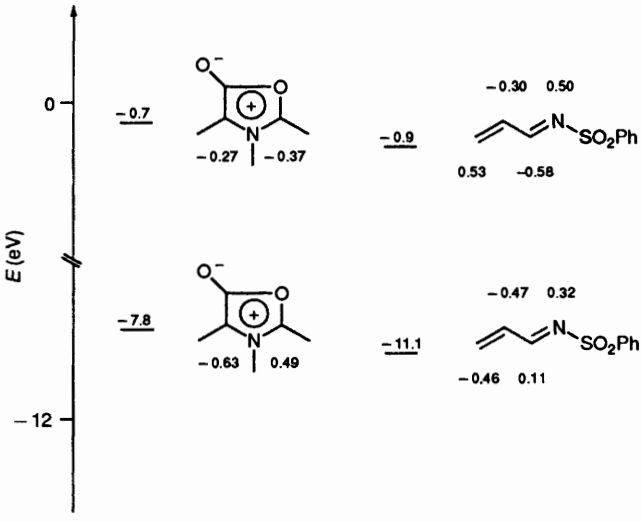


Fig. 2 Frontier orbital energies and coefficients of *N*-phenylsulfonyl-1-azabuta-1,3-diene and munchnone **2**

12 mmol) in toluene (20 cm^3) and the corresponding imine (10 mmol) in toluene (25 cm^3). The resulting mixture was stirred at room temperature under a nitrogen atmosphere for 12 h. The suspension was filtered off and the solution was evaporated at reduced pressure. The residue was taken up in CH_2Cl_2 (60 cm^3). The solution was washed with aqueous sodium hydrogen carbonate (2 × 50 cm^3) and water, dried (Na_2SO_4) and evaporated to give an oily residue. TLC analysis (toluene–ethyl acetate 9/1) revealed the presence of three major components. The mixture was separated by column chromatography (toluene–ethyl acetate 9/1). On the basis of their analytical and spectroscopic data the first component eluted from the column in each run was assigned the structure of 4-styrylimidazoles **3a–c**. The second component was identified as pyrrole derivatives **5a–c** and the third material was assigned as **4a–c**. All the three components were further crystallized.

Reaction Between N-(3-*Phenylprop*-2-*enylidene*)*benzenesulfonamide* (**1a**) *and* **2** *in DMF*.—A suspension of *N*-benzoyl-*N*-methyl-phenylglycine (1.0 g, 3.7 mmol) in DMF (15 cm^3) was treated with DCCI (0.84 g, 4.1 mmol) in DMF (10 cm^3) and with **1a** (1.0 g, 3.7 mmol) in DMF (10 cm^3). The reaction mixture was stirred under nitrogen at room temperature for 3 h. DCU was filtered off and washed with solvent. The filtrates were evaporated at reduced pressure. The residue was taken up in CH_2Cl_2 (30 cm^3). The organic phase was washed with water (150 cm^3), aqueous sodium hydrogen carbonate (2 × 15 cm^3) and water (100 cm^3), dried (Na_2SO_4) and evaporated to dryness. The residue, subjected to flash chromatography with toluene–ethyl acetate 9.5/0.5 as eluent gave compound **3a** (0.62 g, 50%).

Reaction Between N-(3-*Phenylprop*-2-*enylidene*)*aniline* (**8**) *and* **2**.—To a suspension of *N*-benzoyl-*N*-methylphenylglycine (2.7 g, 10 mmol) in toluene (30 cm^3), was added a solution of DCCI (2.5 g, 12 mmol) in toluene (40 cm^3). The mixture was kept stirring, under a nitrogen atmosphere for 30 min. The resulting yellow suspension was added to **8** (2.1 g, 10 mmol) in toluene (25 cm^3). The reaction mixture was kept stirring, at 80 °C for 12 h under a nitrogen atmosphere. The mixture was filtered off and the solution was evaporated under reduced pressure. The crude residue was chromatographed on silica gel with hexane–diethyl ether (7:3) as eluent and yielded **9** as a white solid (2.9 g, 66%), m.p. 185–187 °C (from diisopropyl alcohol) (Found: C, 81.35; H, 5.7; N, 6.1. $C_{31}H_{26}N_2O_2$ requires C, 81.2; H, 5.7; N, 6.1%); ν_{max}(nujol)/cm^{-1} 1750 (C=O), 1660 (C=C) and 1610 (CONMe); δ_H(300 MHz; $CDCl_3$) 3.15 (3 H, s, N-Me), 5.58 (1 H, d, *J* 8, 4-H), 5.86 (1 H, dd, *J* 16 and 8, Ph-CH=*CH*), 6.88 (1 H, d, *J* 16, Ph-*CH*=CH) and 7.1–7.68 (20 H, m, aromatic); δ_C(300 MHz; $CDCl_3$) 37.24 (Me), 65.35 (C-4), 80.31 (C-3), 163.05 (C=O) and 173.5 (C-2).

N-*Methyl*-2,4,5-*triphenylpyrrol*-3-*ylcarboxaldehyde* (**7**) *by Hydrolysis of* **5a**.—To a solution of **5a** (0.48 g, 1.0 mmol) in methanol (6 cm^3) was added hydrochloric acid 10% (3 cm^3). The reaction was stirred at room temperature for 12 h. The solvent was evaporated to dryness to give a residue. It was taken up in CH_2Cl_2 (15 cm^3). The organic layer was washed with water (10 cm^3) and separated, dried (Na_2SO_4) and evaporated off. The residue was purified by chromatography on silica gel (hexane–ethyl acetate 6/4 as eluent). A solid was obtained (0.26 g, 77%), m.p. 183–185 °C (from diisopropyl alcohol 9/1) (Found: C, 85.25; H, 5.55; N, 4.0. $C_{24}H_{19}NO$ requires C, 85.4; H, 5.7; N, 4.15%); δ_H(80 MHz; $CDCl_3$) 3.4 (3 H, s, N-Me), 7.0–7.5 (15 H, m, aromatic), 9.75 (1 H, s, CHO).

N-*Methyl*-2,4-*diphenylimidazol*-4-*ylcarboxaldehyde* (**6**) *by Oxidation*[15] *of* **3a**.—A mixture of water (0.5 cm^3), dioxane (5 cm^3), **3a** (0.2 g, 0.6 mmol) and osmium tetroxide (3 mg, 0.012 mmol) was stirred for five minutes, keeping the temperature at 20 °C. Then sodium periodate (0.26 g, 1.2 mmol) was added in portions and the reaction changed to pale yellow. The mixture was extracted with diethyl ether (3 × 5 cm^3) and the organic phase was dried (Na_2SO_4) and evaporated off. The residue, separated by chromatography (hexane–ethyl acetate 6/4 as eluent) gave **6** as a white solid (112 mg, 71%), m.p. 131–132 °C (from diisopropyl ether–diisopropyl alcohol 9/1) (Found: C, 77.7; H, 5.3; N, 10.6. $C_{17}H_{14}N_2O$ requires C, 77.8; H, 5.4; N, 10.7%); δ_H(80 MHz; $CDCl_3$) 3.55 (3 H, s, N-Me), 7.35–7.9 (10 H, m, aromatic) and 9.8 (1 H, s, CHO).

Crystal Data of Compound **4a**.—$C_{30}H_{28}N_2O_3S$, M = 496.6, monoclinic, space group $P2_1/n$, a = 10.590(2), b = 15.627(2), c = 16.150(2) Å, β = 105.24(2)°, V = 2579(1) $Å^{-3}$, (from 2θ values of 25 reflections in the range 30 < 2θ < 36°), Z = 4, D_x = 1.279 Mg m^{-3}, F(000) = 1048, μ(Mo-Kα) = 0.15 mm^{-1}, crystal dimensions 0.28 × 0.24 × 0.20 mm, λ = 0.710 73 Å (Mo-Kα, graphite monochromator, Enraf-Nonius CAD4 diffractometer).

Data collection. Room temperature, ω-2θ scan mode, with $\omega = 0.8 + 0.35 \tan\theta$, check reflections monitored every 3 hours (maximum variation ±1.5), $2\theta \leqslant 50°$, $0 \leqslant h \leqslant 12$, $0 \leqslant k \leqslant 18$, $-19 \leqslant l \leqslant 19$, 4532 unique reflections, giving 3184 observed, with $I_0 > 2\sigma(I_0)$. No absorption correction.

Structure Analysis and Refinement.—The structure was

Table 2 Selected bond lengths (Å), angles and torsion angles (°) with e.s.d.s in parentheses for **4a**

S–O1	1.425(2)	S–O2	1.429(2)
S–N1	1.616(2)	S–C1	1.768(3)
N1–C7	1.482(2)	N2–C16	1.480(3)
N2–C23	1.461(3)	N2–C24	1.349(3)
C7–C8	1.500(3)	C7–C16	1.534(2)
C8–C9	1.315(3)	C9–C10	1.468(3)
C16–C17	1.513(3)	C24–C25	1.508(3)
O3–C24	1.232(3)		
O1–S–O2	120.6(1)	O1–S–N1	106.70(9)
O1–S–C1	108.2(1)	O2–S–N1	105.8(1)
O2–S–C1	105.9(1)	N1–S–C1	109.3(1)
S–N1–C7	122.9(1)	C23–N2–C24	124.3(2)
C16–N2–C24	118.9(2)	C16–N2–C23	116.8(2)
N1–C7–C16	104.9(1)	N1–C7–C8	112.1(1)
C8–C7–C16	112.9(2)	C7–C8–C9	124.7(2)
C8–C9–C10	127.1(2)	N2–C16–C7	110.7(2)
C7–C16–C17	116.5(1)	N2–C16–C17	109.8(2)
O3–C24–N2	121.8(2)	N2–C24–C25	119.8(2)
O3–C24–C25	118.4(2)		
N1–S–C1–C2	−106.2(2)	C1–S–N1–C7	78.8(2)
S–N1–C7–C8	−75.6(2)	S–N1–C7–C16	161.5(1)
N1–C7–C8–C9	114.9(2)	N1–C7–C16–N2	−61.4(2)
C8–C9–C10–C11	0.2(4)	C7–C8–C9–C10	−176.4(2)
C16–C7–C8–C9	−126.8(2)	N2–C16–C7–C8	176.2(2)
C7–C16–N2–C24	120.3(2)	C16–N2–C24–C25	180.0(2)
N2–C24–C25–C26	−137.9(2)		

solved by direct method (MULTAN[16] routine) and refined by full matrix least squares with anisotropic thermal parameters for non-hydrogen atoms and isotropic ones for the H atoms. Atomic scattering factors were those given by Enraf-Nonius SDP[17] system of computing programs. The final refinement gave $R = 0.045$ and $R_w = 0.044$; $w^{-1} = [\sigma^2(I_0) + 0.009I_0^2]/4I_0Lp^2$, 438 parameters; max $\Delta/\sigma = 0.02$, $\Delta\rho_{max} = 0.014$ e Å^{-3} on final difference Fourier map. Table 2 reports selected bond distances, bond angles and torsion angles. Details of coordinates of non-hydrogen atoms have been deposited at CCDC, along with supplementary materials.*

* Details of the deposition Scheme can be found in 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 2*, 1993, issue 1.

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