

***In Situ* Generation of 4 π -Sulphinylaminomethanide Species from W=X=Y-ZH Systems and their Cycloaddition Reactions**

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Sulphonyl group transfer from *N*-sulphonylaniline to α -amino acids and α -amino acid esters in solution at 25–110 °C gives rise to 4 π -electron species believed to be sulphinylaminomethanide anions which can be trapped in good yield by *N*-substituted maleimides in 4 π + 2 π cycloadditions.

We have previously shown that 1,3-dipoles can be generated by a formal 1,2-H shift in X=Y-ZH systems,¹ and that azomethine ylides can be generated stereospecifically from iminium ions² or by a decarboxylative route.³ We now report the first, of what we believe will be a series, of 4 π -anions derived from substrates of the type W=X=Y-ZH (1).

Substrates of type (1), in which W is an electronegative atom, are expected to be less likely to participate in the formal 1,2-H shift, (1) \rightleftharpoons (2), analogous to that observed in X=Y-ZH systems, such as imines,¹ hydrazones,⁴ and oximes,⁵ owing to the reduced basicity of Y in (1). Conversely (1) should show an enhanced tendency to form 4 π -anions (3) in the presence of a suitable base. A similar argument applies to a decarboxylative route from (4), with (3) being more favoured than (2). However, it must be noted that (4) might be decarboxylated

via cyclisation to (5) followed by a 1,3-cycloreversion. Kauffmann has shown, in extensive studies,⁶ that aza-allylic anions (6) participate smoothly in 4 π + 2 π concerted cycloadditions and (3) would be expected to behave similarly.

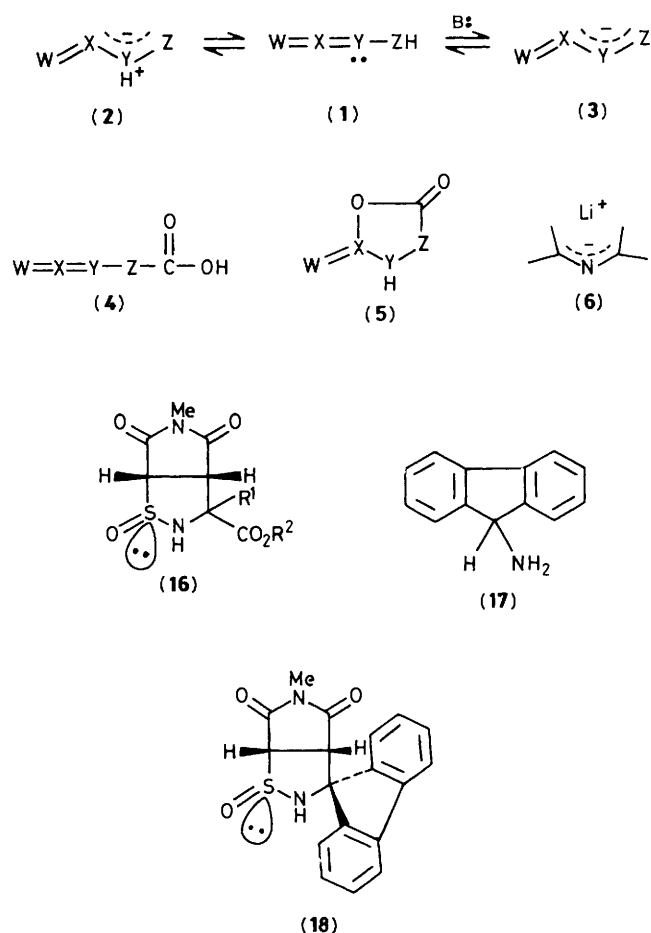
Our attention focused initially on a decarboxylative route to (3) and was encouraged by a report⁷ that *N*-sulphonylaniline (7) reacts with α -amino acids (8) at 25–80 °C in dimethyl sulphoxide (DMSO) to give aldehydes (9). An initial sulphonyl group transfer to give aniline and (10) was proposed but no mechanism was suggested for the subsequent steps leading to (9).⁷ Compounds of type (10) could give rise to either (11) or (12) by decarboxylation.

When α -amino acids are heated in DMSO with (7) and (13a) or (13b), cycloaddition occurs to give the cyclic sulphinamides (14a) or (14b) as single stereoisomers in good

Table 1. Cycloadducts (14a) or (14b) from the reaction of α -amino acids (8) with (7) and (13a) or (13b) in DMSO at 80°C.

Cycloadduct (14)	Time/h	% Yield ^a
a; R = Ph	4	60
a; R = CH ₂ Ph	2	90
a; R = Pr ⁱ	4	74
a; R = [CH ₂] ₂ SMe	4	75
a; R = Bu ^s	4	68
a; R = Bu ⁱ	4	72
a; R = CH ₂ -Ind ^b	4	78
b; R = CH ₂ Ph	1	68
b; R = Pr ⁱ	4	68
b; R = [CH ₂] ₂ SMe	4	71
b; R = CH ₂ -Ind ^b	4	70

^a Isolated yields. All new compounds give satisfactory analytical and spectral data. ^b Ind = indol-3-yl.

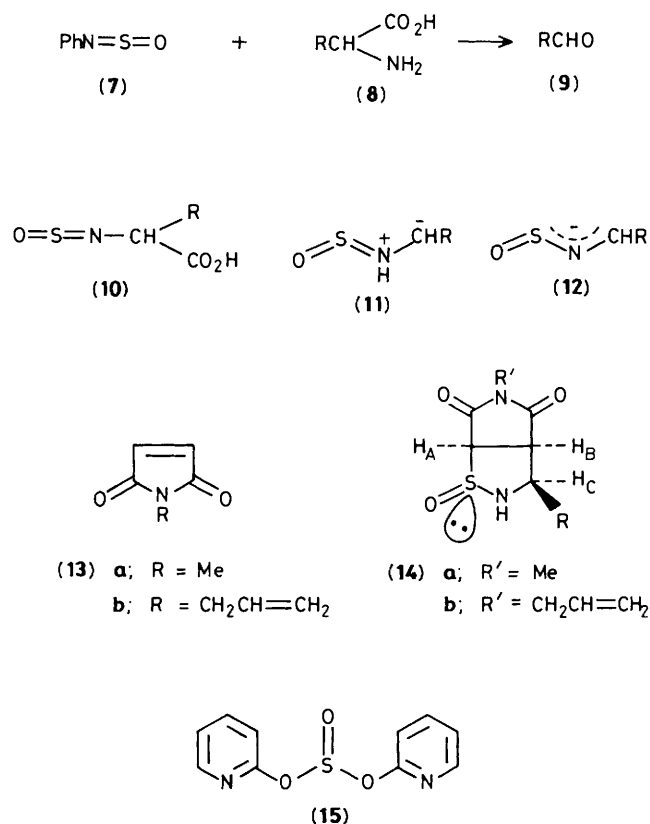


yield (Table 1). The relative stereochemistry of (14) at C(3), C(4), and C(5) is readily established by nuclear Overhauser enhancement (n.O.e.) difference spectroscopy whilst the stereochemistry at sulphur remains to be defined by X-ray crystallography. A typical n.O.e. study (CDCl₃) on (14a, R = Buⁱ) illustrates the magnitude of enhancements that are observed. Irradiation of the signal for H_A (d, δ 4.25) results in an 8.5% enhancement of the signal for H_B, whilst irradiation of H_B (t, δ 3.49) causes enhancement of the signals for H_A

Table 2. Cycloadducts from the reaction of α -amino acid esters with (7) and (13a) in toluene at 110°C.

Cycloadduct (16)	Time/h	% Yield ^a	Isomer ratio ^b
R ¹ = R ² = Me	7	70	1:2:3:3
R ¹ = Ph, R ² = Me	3	91	1:2:2
R ¹ = CH ₂ -Ind, R ² = Me	10	90	1:1.7 ^c
R ¹ = CO ₂ Et, R ² = Et	2	70	Single isomer ^d

^a Isolated yield. ^b Estimated by n.m.r. spectroscopy. ^c Ind = indol-3-yl. ^d Reaction carried out at 80°C in benzene in the presence of 1 mol. equiv. of triethylamine.



(9.5%) and H_C (8.5%). The signal for H_C appears as a multiplet at δ 4.67. Attempts to utilise (15) as a sulphonyl transfer agent⁸ in place of (7) resulted in low yields of (14). The by-product of sulphonyl transfer from (15) is the non-basic 2-pyridone which suggests a possible role for the aniline liberated from (7) in the cycloaddition process.

α -Amino acid esters also react with (7) and (13a) in toluene at 110°C to give the cycloadducts (16) as a mixture of stereoisomers (Table 2).

The beneficial influence of base is illustrated by the last entry in Table 2 and the observation that (17) reacts with (7) and (13a) in benzene (room temp.; 24 h), in the presence of 1 mol. equiv. of triethylamine, to give (18) (45%) as a single stereoisomer.

Speculation on the stereospecificity observed in the case of (14) and the general lack of stereospecificity in the case of (16) is deferred pending assignment of stereochemistry at sulphur in (14) and (16). The poor yields encountered using (15) as the sulphonyl transfer agent and the beneficial effects of added base suggest the reactive intermediate in the cycloaddition reactions is (12) rather than the 1,3-dipole (11).

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