

### CYCLOADDITION REACTIONS OF THIIRANIMINES

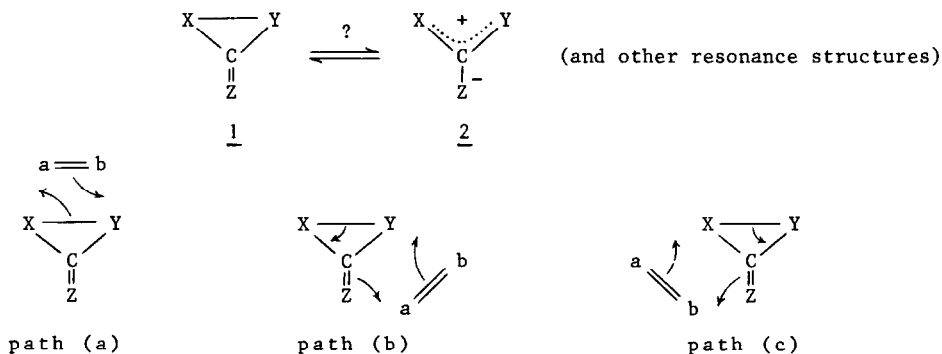
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ABSTRACT. Thiiranimines have been found to cycloadd by the three pathways shown in Scheme 1. The reactions are exemplified with enamines (path a), ynaminines (path b) and aldehydes (path c).

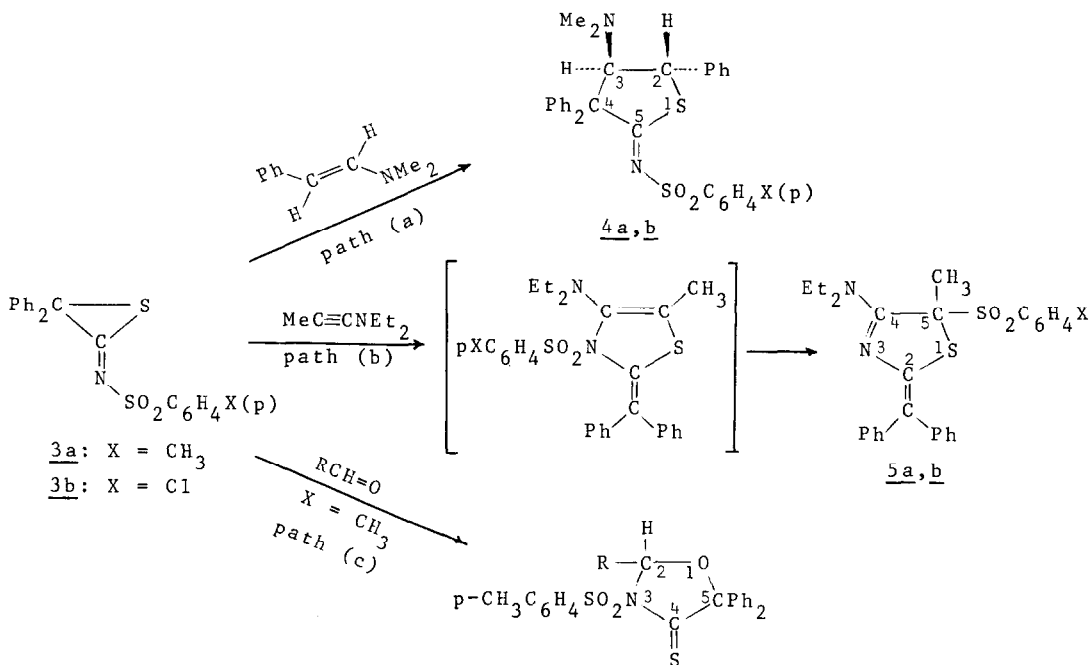
For three-membered heterocycles of type 1 ( $Z \neq C$ ) three different cycloaddition pathways can a priori be envisaged as shown in Scheme 1.<sup>1</sup> Mechanistically, these pathways can proceed by a concerted or two-step process, or via the ring-opened isomer 2 formed by cleavage of the X-Y bond.<sup>2</sup>

SCHEME 1



From the scarce literature on this topic, it is known that  $\alpha$ -lactams react by path (a),<sup>3</sup> whereas diaziridinimines fall into the category of path (b).<sup>4</sup> In other cases where the three-membered heterocycles 1 or their dipolar forms 2 have been postulated as elusive intermediates, cycloadducts were obtained which are interpretable in terms of path (a).<sup>5</sup> We now report the first examples of a small ring heterocycle undergoing cycloaddition reactions by all three pathways.

The sulfonyliminothiiranes 3a,b, prepared from sulfonyl isothiocyanates and diphenyldiazomethane,<sup>6</sup> were allowed to react with an equimolar amount of trans- $\beta$ -dimethylamino styrene in ether at 0°C. This furnished cycloadducts which were identified as 4a (70%, mp 179-181) and 4b (70%, mp 183-185°) on the basis of



- 6a: R = CH<sub>3</sub>  
6b: R = C<sub>6</sub>H<sub>5</sub>  
6c: R = m-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>

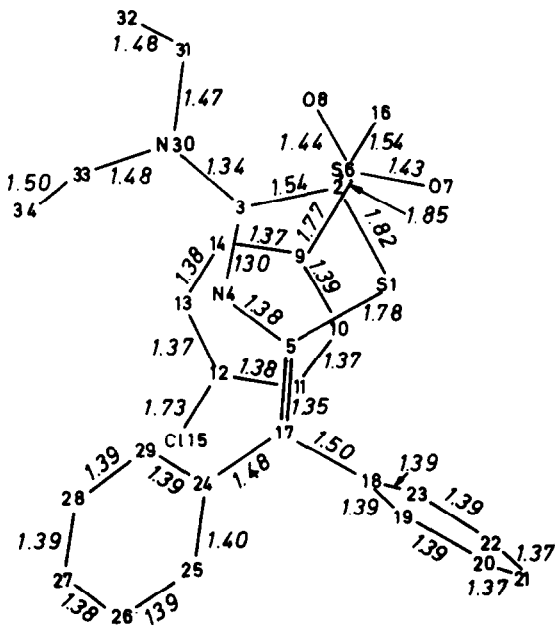
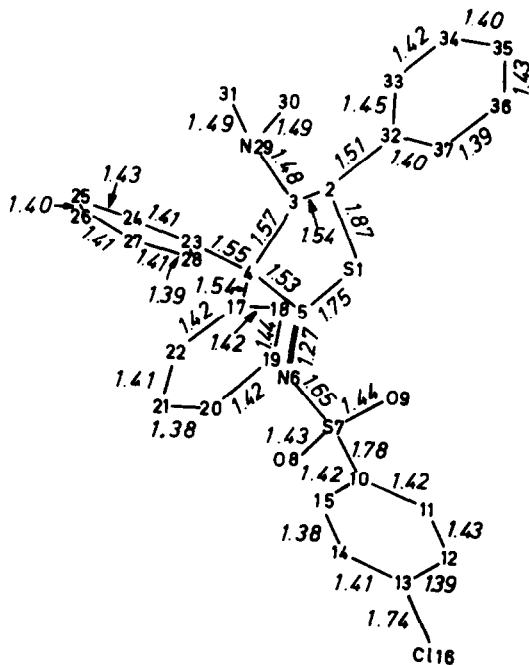
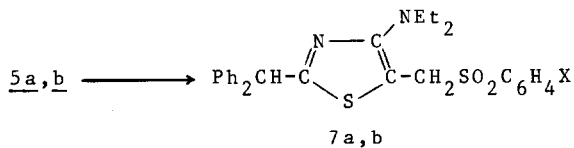


Fig 1. Structure of 4b with bond lengths (Å) and numbering scheme

Fig 2. Structure of 5b with bond lengths (Å) and numbering scheme

combustion analyses and spectral data. In particular, the IR spectra (KBr) showed strong broad absorption bands at  $1550\text{--}1570\text{ cm}^{-1}$  ( $\text{C}=\text{NSO}_2$ ),<sup>7</sup> while the  $^1\text{H}$  NMR spectra ( $\text{CDCl}_3$ ) indicated the presence of an AB system with resonances at  $\delta$  4.62 and 4.74 ( $J_{\text{AB}} = 10\text{--}11\text{ Hz}$ ). The ring carbon absorptions in the  $^{13}\text{C}$  NMR spectra ( $\text{CDCl}_3$ ) were found at  $\delta$  51.5 ( $\text{C}^2$ ), 75.8 ( $\text{C}^3$ ), 69.8 ( $\text{C}^4$ ) and 191.5–193 ppm ( $\text{C}^5$ ). The structure of 4b was further confirmed by a single crystal X-ray analysis<sup>8</sup> as shown in Fig 1. The  $\text{H}-\text{C}^2-\text{C}^3-\text{H}$  torsion angle is  $168.6^\circ$ , consistent with the high value of the coupling constant ( $J = 11\text{ Hz}$ ).

When N-diethylaminopropyne was treated with 3a,b under identical conditions, cycloadducts 5a (28%, mp  $117\text{--}120^\circ$ ) and 5b (45%, mp  $127\text{--}129^\circ$ ) were obtained. In the  $^1\text{H}$  NMR spectra ( $\text{CDCl}_3$ ) the N-methylene protons gave rise to an ABX<sub>3</sub> pattern centered at  $\delta$  3.30 (dq) and 4.05 (dq) due to the presence of an asymmetric carbon atom in the  $\gamma$ -position ( $\text{C}^5$ ). The  $^{13}\text{C}$  NMR spectra ( $\text{CDCl}_3$ ) were devoid of low field  $\text{C}=\text{NSO}_2$  absorptions (at ca  $\delta$  190 ppm), but showed resonances at  $\delta$  143 ( $\text{C}^2$ ), 161.6 ( $\text{C}^4$ ) and 86 ( $\text{C}^5$ ) besides an olefinic  $\text{CPh}_2$  carbon signal at  $\delta$  121 ppm. The mass spectra exhibited weak molecular ion peaks and significant fragments for  $\text{M}^+ - \text{ArSO}_2\text{H}$ . The structure of 5b was unambiguously established by an X-ray structure analysis<sup>9</sup> as shown in Fig 2. It is apparent that the sulfonyl group has migrated from  $\text{N}^3$  to  $\text{C}^5$  during the reaction. The yields of the pure isolated products 5a,b are rather low, but this is due to the facile isomerization of 5a,b in solution into products to which we assign structures 7a,b.<sup>10</sup> Indeed, when the reactions of 3a,b and N-diethylaminopropyne at  $0^\circ$  were monitored by  $^1\text{H}$  NMR, the cycloadducts 5a,b were formed first and quantitatively; they then aromatized slowly into 7a,b.



The thiiranimine 3a also reacted with an equimolar amount of acetaldehyde in benzene at room temperature to give 6a (mp  $166\text{--}168^\circ$ ) in 68% yield. With benzaldehyde and m-nitrobenzaldehyde, the formation of 6b (16.5%, mp  $142\text{--}144^\circ$ ) and 6c (12%, mp  $193\text{--}195^\circ$ ) was competitive with decomposition of 3a into benzthiophene.<sup>6</sup> The products 6a-c showed IR (no  $\text{C}=\text{NTs}$  absorption at ca  $1550\text{ cm}^{-1}$ ) and  $^1\text{H}$  NMR data (CH of 6a at  $\delta$  5.82,  $J = 5\text{ Hz}$ ) consistent with their structures. The  $^{13}\text{C}$  NMR spectra ( $\text{CDCl}_3$ ) enabled us confidently to establish the ring skeleton with a diagnostic  $\text{C}^4=\text{S}$  carbon resonance at  $\delta$  200 ppm<sup>11</sup> and other absorptions at  $\delta$  98 ( $\text{C}^5$ ) and 92.1–94.3 ppm ( $\text{C}^2$ ). Noteworthy were also the mass spectra which exhibited base peaks for  $\text{RHC} \begin{array}{c} \diagup \\ \text{O} \\ \diagdown \end{array} \text{CPh}_2 \cdot^+$

From the experiments described above, it is evident that the thiiranimines 3a,b have reacted by the three pathways of Scheme 1. We believe that their high and versatile reactivity stems from their propensity to undergo ring-opening by cleavage of the ( $\text{sp}^3$ )C-S bond.

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## REFERENCES AND NOTES.

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- (7) See, for instance, G. L'abbé, E. Van Loock, R. Albert, S. Toppet, G. Verhelst, and G. Smets, *J. Am. Chem. Soc.*, 96, 3973 (1974).
- (8) Compound 4b crystallizes in the triclinic space group  $P\bar{1}$  with  $a = 14.766$ ,  $b = 10.227$ ,  $c = 9.792$  Å;  $\alpha = 91.34^\circ$ ,  $\beta = 100.23^\circ$ ,  $\gamma = 73.27^\circ$ ;  $Z = 2$ . The structure was solved by the MULTAN 77 program (ref 12) and refined with the X-Ray 72 system (ref 13) to  $R = 0.089$  for 1410 reflections (Syntex diffractometer, MoK $\alpha$  radiation,  $2\theta_{\max} = 47^\circ$ ).
- (9) Compound 5b crystallizes in the triclinic space group  $P\bar{1}$  with  $a = 13.987(9)$ ,  $b = 9.610(8)$ ,  $c = 9.382(3)$  Å;  $\alpha = 94.60(5)^\circ$ ,  $\beta = 86.94(4)^\circ$ ,  $\gamma = 90.33(6)^\circ$ ;  $Z = 2$ . The structure was solved by direct methods (MULTAN) and refined to  $R = 0.036$  using 2658 independent reflections (Syntex diffractometer, MoK $\alpha$  radiation,  $2\theta_{\max} = 47^\circ$ ).
- (10) Spectral data of 7a (mp  $118^\circ$ ): IR (KBr) 1540 (m), 1450 (m), 1375 (w), 1310 (s) and 1135 (s)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.75 (t, 6H), 2.40 (s, 3H), 2.78 (q, 4H), 4.51 (s, 2H,  $\text{CH}_2$ ), 5.69 (s, 1H, CH), 7.1-7.7 (14 aromatic H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  171.5 ( $\text{C}^2$ ), 160.5 ( $\text{C}^4$ ), 111.9 ( $\text{C}^5$ ), 55.3 ( $\text{CHPh}_2$ ), 54.6 ( $\text{CH}_2\text{SO}_2$ ); mass spectrum ( $m/e$ , %) 490 (0.4,  $\text{M}^+$ ), 335 (100,  $\text{M}^+ - \text{Ts}$ ).
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