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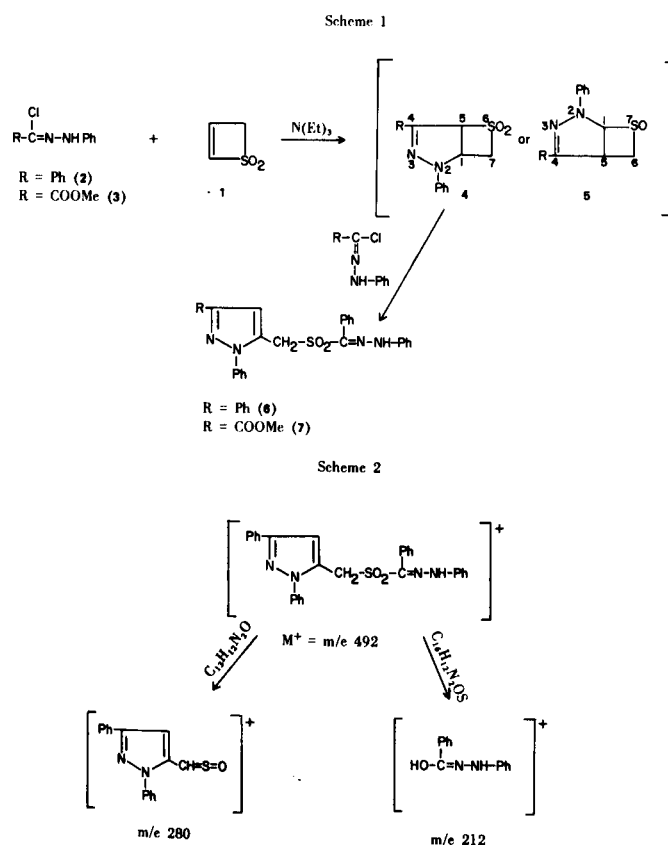
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Thiete 1,1-dioxide reacts with 2 moles of  $\alpha$ -chlorobenzalphenylhydrazine and methyl phenylhydrazonochloroacetate in the presence of triethylamine leading to the pyrazole derivatives **6** and **7** whose structure and mechanism of formation are discussed.

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The cycloadditive propensity of thiete 1,1-dioxide has been investigated in a number of cases, namely in reactions with electron rich olefins (1) and diazoalcanes (2). The latter reaction yields crystalline 1-pyrazolines with the exception of the adduct obtained from ethyl diazoacetate which forms a 2-pyrazoline. We now describe the reaction of thiete sulphone with nitrilimines which appeared of interest since the initial conceivable strained cycloadducts **4** or **5** seemed structurally disposed to undergo further transformations particularly in basic medium. In fact, relief of strain through a C-C bond breaking in the thietan dioxide moiety of the adduct, could in principle result in the formation of particularly substituted pyrazole derivatives (C<sub>1</sub>-C<sub>7</sub> or C<sub>5</sub>-C<sub>6</sub> bond breaking) or of seven membered heterocyclic systems (C<sub>1</sub>-C<sub>5</sub> bond breaking). Moreover, the cycloaddition of nitrilimines to thiete sulphone could lead both to 1 or 2-pyrazolines. Reaction between thiete sulphone **1** and halohydrazone **2** and **3** in the presence of an almost equimolar amount of triethylamine in acetonitrile solution leads to products **6** and **7** as the only isolable ones.

Structure **6** was assigned on the basis of its analytical and spectroscopic data and chemical behaviour. The ir and <sup>1</sup>H nmr spectra of **6** support the proposed structure (see Experimental). The mass spectrum (3) is reported in Figure 1 and confirms the molecular weight. Peaks at m/e 280 and 212 correspond to the kind of fragmentation reported in the literature for arylsulphones (4) (see Scheme 2).



The chemical behaviour of **6** is in accord with the proposed structure in fact: i) acidic hydrolysis with

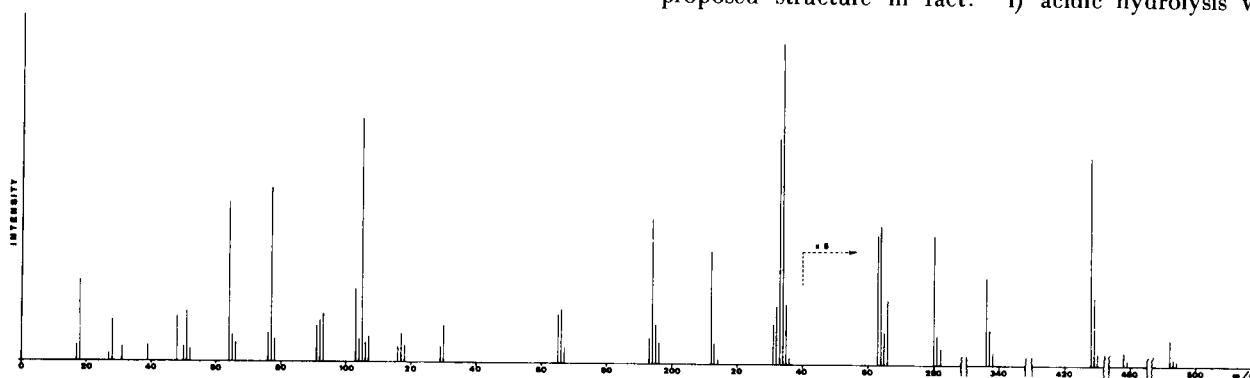
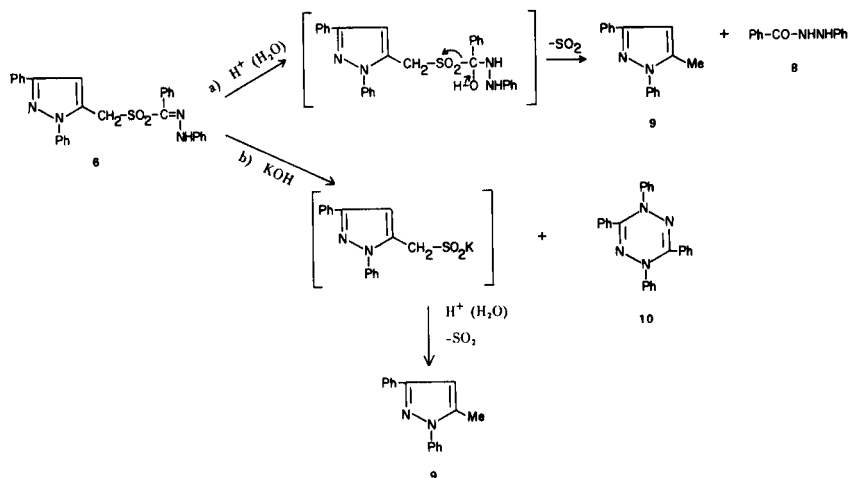


Figure 1. Mass spectrum of **6**.

Scheme 3



hydrochloric acid in acetic acid gives  $\beta$ -benzoylphenylhydrazine (**8**) and 1,3-diphenyl-5-methylpyrazole (**9**) (path *a* in the Scheme 3); ii) basic hydrolysis with potassium hydroxide in ethanol-water solution at room temperature gives the tetrazine **10** and, after acidification, the same pyrazole derivative **9** (path *b* in the Scheme 3). Compound **9** was identified by comparison with an authentic sample obtained independently (see Experimental). Presumably the formation of **6** occurs through the aromatization of the primarily formed 1-pyrazoline derivative **6**. This implies the  $\text{C}_5\text{-S}$  bond breaking (5) and concurrent (or not) reaction with a second mole of chlorobenzaldehyde. Structure **7** was assigned by analogy with **6** as well as by the analytical and spectroscopic data (see Experimental).

#### EXPERIMENTAL

The ir spectra were obtained with a Perkin-Elmer 137 instrument (solids as Nujol mulls).  $^1\text{H}$  nmr spectra were determined with a Varian A60-A spectrometer for solutions in  $[\text{2H}]$  chloroform (tetramethylsilane, as internal standard). Melting points are uncorrected.

Tosylate of 3-Thietanol 1,1-dioxide.

3-Thietanol 1,1-dioxide (5.5 g., 0.045 mole) prepared by permanganic oxidation (7) of the 3-thietanol (8) was dissolved in pyridine (4 ml.) and a solution of *p*-toluenesulphonyl chloride (9.45 g., 0.049 mole) in pyridine (14.79 g.) was added dropwise at  $0^\circ$ . The mixture was stirred for 1.5 hours at  $0^\circ$  and an additional 3 hours at room temperature, then quenched with ice water. The solid was filtered off and washed several times with water. The crude material (m.p.  $117\text{-}119^\circ$ , yield 80%) was directly used for the following step; nmr:  $\tau$  7.52 (3H, s, *Me-Ph*), 5.49-5.76 (4H, m,  $\text{CH}_2\text{-SO}_2\text{-CH}_2$ ), 4.6-5.03 (1H, m, CH), 2.1-2.75 (4H, m, *Me-Ph*).

Thiete 1,1-Dioxide (**1**).

Compound **1** was prepared from the tosylate of 3-thietanol 1,1-dioxide following the procedure given by King (9), in the case of 1,1-dioxy-3-thietanylphenylmethanesulphonate with purifica-

tion by chromatography (silica gel and chloroform as eluent) of the crude residue obtained from the reaction mixture after evaporation of the benzene.

Reaction Between  $\alpha$ -Chlorobenzaldehyde (2) and Thiete 1,1-Dioxide (1).

To the stirred solution of **2** (8.82 g., 0.0348 mole) and **1** (2 g., 0.0192 mole) in acetonitrile (40 ml.), triethylamine (3.88 g., 0.0384 mole) was added dropwise. After 6 hours of stirring, more triethylamine (1.94 g., 0.0192 mole) was added and the solution stirred for an additional 20 hours. The triethylamine hydrochloride was filtered off, the solvent evaporated at reduced pressure and the residue was purified by chromatography on silica gel (chloroform-ethyl acetate 95:5 as eluent). Adduct **6** was isolated in 43.2% yield, m.p.  $138\text{-}140^\circ$  (from ethanol); nmr:  $\tau$  5.2 (2H, s,  $\text{CH}_2$ ), 2 (1H, s, NH), 2.1-3.2 (21H, m, Ph and  $=\text{CH}$ ); ir:  $\nu$  max  $3333\text{ cm}^{-1}$  (NH),  $1550\text{ cm}^{-1}$  (C=C),  $1492\text{ cm}^{-1}$  (N=C),  $1317$  and  $1149\text{ cm}^{-1}$  ( $\text{SO}_2$ ).

Anal. Calcd. for  $\text{C}_{25}\text{H}_{25}\text{N}_4\text{O}_2\text{S}$ : C, 70.7; H, 4.9; N, 11.4; S, 6.5. Found: C, 71.0; H, 5.1; N, 11.4; S, 6.4.

Reaction Between Ethyl 2-Chloro-2-phenylhydrazoacetate (3) and Thiete 1,1-Dioxide (1).

Compound **7** was synthesized by analogy to **6** by reacting **1** (0.945 g., 9.1 mmoles) and **3** (3.88 g., 18.2 mmoles) in the presence of triethylamine (2.76 g., 0.027 mole) in chloroform solution at room temperature for 24 hours then heating at  $50^\circ$  for three additional hours. After washing the chloroform solution with water the product was purified by chromatography on silica gel (chloroform or ether as eluent), yield 0.930 g. (20%), m.p.  $185^\circ$  (from acetic acid); nmr:  $\tau$  6.24 and 6.09 (6H, 2s,  $\text{OCH}_3$ ) 5.3 (2H, s,  $\text{CH}_2$ ), 2.4-2.83 (11H, m, Ph and  $\text{CH}=\text{C}$ ), 4.2 (1H, s, NH).

Anal. Calcd. for  $\text{C}_{21}\text{H}_{20}\text{N}_4\text{O}_6\text{S}$ : C, 55.2; H, 4.4; N, 12.3. Found: C, 55.1; H, 4.5; N, 12.1.

Some 1,4-diphenyl-3,5-carbomethoxytetrazine was also recovered from the chromatography, m.p.  $169\text{-}170^\circ$  (from acetic acid).

#### Acidic Hydrolysis of 6

Compound **6** (0.24 g., 0.575 mmole) was refluxed for 24 hours in acetic acid (5 ml.) and hydrochloric acid (three drops). The solution was evaporated under reduced pressure and the residue was taken up with ether and washed with a solution of sodium bicarbonate. The ether was dried over anhydrous sodium sulfate,

evaporated and the residue was chromatographed on silica gel (eluent chloroform followed by chloroform and ethyl acetate 95:5).  $\beta$ -Benzoylphenylhydrazine was obtained, m.p. 165° (lit. (10) 168°) and an oil that was further purified by distillation, b.p. 155-160°/0.5 torr and identified as 1,3-diphenyl-5-methylpyrazole (9); nmr:  $\tau$  7.71 (3H, d, Me), 5.56 (1H, q, =CH), 2.78-2.06 (10H, m, Ph); ir and <sup>1</sup>H nmr spectra of 9 were superimposable with those of an authentic sample prepared through standard procedures by reaction of  $\alpha$ -chlorobenzalphenylhydrazine with ethyl acetoacetate in the presence of sodium ethoxide followed by hydrolysis and thermal decarboxylation of the resulting 1,3-diphenyl-4-carbomethoxy-5-methylpyrazole.

Anal. Calcd. for C<sub>16</sub>H<sub>14</sub>N<sub>2</sub>: C, 82.0; H, 6.0; N, 11.9. Found: C, 81.8; H, 6.0; N, 12.0.

#### Basic Hydrolysis of 6.

A solution of 6 (2.05 g., 4.3 mmoles) and of potassium hydroxide (0.45 g., 8.6 mmoles) in ethanol-water 9:1 (23 ml.) was stirred at room temperature for 3.5 hours. The solid was filtered off and crystallized from ethanol-water to give tetraphenyltetrazine (10) m.p. 200° (lit. (11) 203°). The reaction mother liquors were evaporated under reduced pressure and the residue was washed with anhydrous ether, dissolved in water, filtered from some insoluble material and acidified with hydrochloric acid. After extraction with chloroform and chromatography on silica gel (benzene as eluent) more tetrazine was collected (overall yield 37%) together with pyrazole (8) in 26% yield.

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