Efficient Syntheses of Thietanes and Thiete 1,1-Dioxide using Phase-Transfer Catalysis

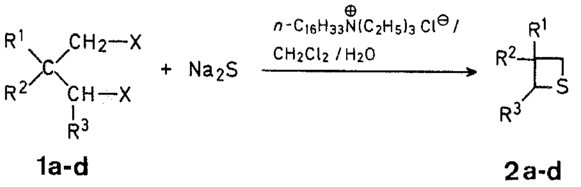
Michael LANCASTER*, David J. H. SMITH**

Chemistry Department, The University, Leicester LE1 7RH, England

In a continuation of our studies on the thermolysis and photolysis of cyclic sulphones[1], we required samples of some thietanes and thiete 1,1-dioxides. Although many synthetic routes to thietane and thiete derivatives have been described, the majority suffer from low yields or long reaction sequences. One of the more general methods of preparing thietane and its derivatives is the reaction of 1,3-dihaloalkanes with sodium or potassium sulphide[2,3]. The reactions are generally carried out in alcohol/water mixtures, at around 70 °C, over several hours. The yields in these reactions are rarely above 50%. The principle reasons for the low yields are the formation of polymeric sulphides as by-product[4].

Phase transfer catalysis has been used widely for the synthesis of sulphides[5,6]. We have recently described a simple and efficient synthesis of 1,3-dihydrobenzo[*c*]thiophene, from *α,α′*-dibromo-*o*-xylene and sodium sulphide using triethylhexadecylammonium chloride as the phase transfer catalyst[1].

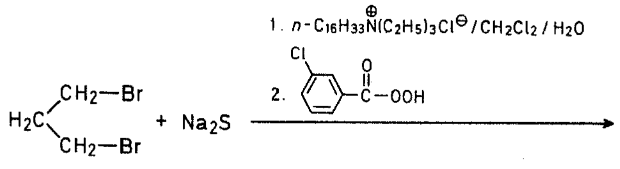
We now report the extension of this reaction to include the preparation of some thietanes **2** from 1,3-dihaloalkanes **1**.

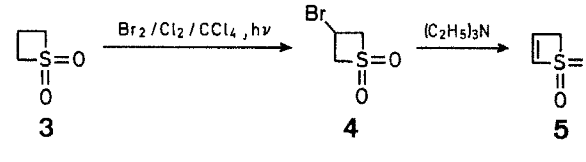


1	R¹	R²	R³	X
a	H	H	H	Br
b	OH	H	H	Cl
c	CH_3	CH_3	H	Br
d	H	H	CH_3	Br

The reaction of a dichloromethane solution of the 1,3-dihalo compound **1** (chloride or bromide) with an aqueous solution of sodium sulphide, containing hexadecyltriethylammonium chloride, as the phase-transfer catalyst, was monitored by G.L.C. Separation of the organic layer, washing, drying, and removal of solvent gave the product **2**, which could be purified by distillation. The yields from primary alkyl halides were generally excellent (Table). Secondary halides, however, proved less reactive at room temperature presumably due to steric factors.

Thietane **(2a)**, was not isolated, addition of two mol-equivalents of *m*-chloroperoxybenzoic acid to a dichloromethane solution containing crude **2a** resulted in the formation of thietane 1,1-dioxide **(3)** which was isolated in 70% overall yield by column chromatography on silica eluting with ether.





Synthetic routes to thiete 1,1-dioxide **(5)** have involved [2+2]-cycloadditions of sulphene to unstable vinylamines, these reactions necessitate the use of low temperatures and oxygen-free conditions[9]. Alternative syntheses have been based on epichlorohydrin[10], but yields are generally poor and the reaction may involve the hazardous evaporation of peracetic acid[11]. We have developed a convenient synthesis of thiete 1,1-dioxide **(5)** based on thietane-1,1-dioxide **(3)** prepared as above. Irradiation of **3** in carbon tetrachloride, containing bromine and chlorine gave **4**[12] (89%). Dehydrobromination of **4** was accomplished with triethylamine, giving thiete 1,1-dioxide **(5)** (82%) in an overall yield of over 50% from dibromopropane **(1a)**.

Thietane Derivatives 2b–d; General Procedure:

A solution of the 1,3-dihaloalkane **1** (0.4 mol) in dichloromethane (300 ml) is added to a solution of sodium sulphide nonahydrate (0.6 mol) in water (350 ml), containing hexadecyltriethylammonium chloride (20 ml of a 50% solution). The mixture is stirred rapidly. The reaction is followed by G.L.C. (3% OV 17). When the dihaloalkane **1** has been consumed or reaction has become very slow, the organic layer is separated, washed with water, and dried with magnesium sulphate. Removal of solvent gives the product which could be purified by distillation.

Thietane 1,1-Dioxide (3):

A dichloromethane solution of thietane **(2a)** is prepared as above from dibromopropane (**1a**; 0.2 mol), *m*-chloroperoxybenzoic acid (0.4 mol) is added and the solution stirred at room temperature for 4 h. The mixture is filtered and the filtrate repeatedly washed with water. Drying and removal of solvent gives a yellow solid which is purified by chromatography on silica eluting with ether; yield: 14.8 g (70%); m.p. 76–77 °C (Ref.[13], m.p. 76 °C).

3-Bromothietane 1,1-Dioxide (4):

An irradiated solution of thietane 1,1-dioxide **(3)** in carbon tetrachloride is brominated using bromine and chlorine as previously described[12]; yield: 89%; m.p. 152–155 °C (Ref.[12], m.p. 153–155 °C).

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Thiete 1,1-Dioxide (5):

Triethylamine (50 ml) is added to a solution of 3-bromothietane 1,1-dioxide (**4**; 14.8 g, 0.08 mol) in dry benzene (500 ml). The mixture is stirred for 4 h before being refrigerated overnight. The triethylamine hydrobromide is filtered off and washed with benzene. The filtrate is evaporated to dryness and the residue crystallised from ether and ethanol; yield: 6.8 g (82%); m.p. 48-50 °C (Ref.[7], m.p. 52-54 °C).

^{1}H-N.M.R. ($CDCl_3$): $\delta = 7.18$ (dt, 1 H, $J = 2$ Hz, 4 Hz); 6.80 (dt, 1 H, $J = 0.5$ Hz, 4 Hz); 4.58 ppm (dd, 2 H, $J = 0.5$ Hz, 2 Hz).

Table. Thietane Derivatives **2**

Product	Reaction time	Yield [%]	b.p. [°C]/torr	
			found	reported
2a	3 h	>70	see text	
2b	3 h	81	53°/1	51-52°/0.9[7]
2c	2 h	94	115-117°/760	115-116°/760[8]
2d	35 h	57	99-101°/760	101-102°/760[8]

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* Present address: BP Research Centre, Chertsey Road, Sunbury-on-Thames, Middlesex, TW16 7LN, England.

** Author to whom correspondence should be addressed.

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