α-Bromination of Thietan 1,1-Dioxides

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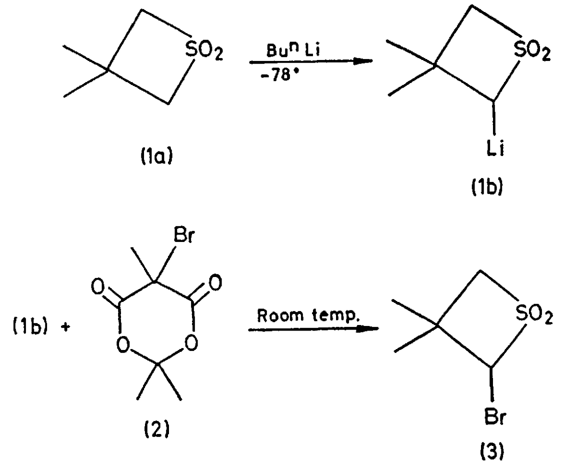
Summary The α-carbanion of 3,3-dimethylthietan 1,1-dioxide was monobrominated at room temperature and in high yield with the Meldrum's acid derivative (**2**).

DESPITE the many reports of α-halogenation of sulphides,[1] sulphoxides,[2] and sulphones,[3] none of these methods has been applied to the direct halogenation of thietan oxides. During the course of studies on base-catalysed reactions of α-halogenothietan sulphones, we required a convenient and direct method for introducing a halogen atom into the four-membered ring. The existing syntheses for α-halogenothietan sulphones, such as cycloadditions of halogenosulphenes[4] and thiocarbonyl compounds,[5] are restricted and specialized.

Since thietan sulphones are readily available from oxidations of the thietans without concomitant ring opening, we investigated the reactions of α-carbanions of these sulphones with various halogenating agents. This approach has been successfully applied to some acyclic and bicyclic sulphones,[3] although the yields have not been consistently high.

Treatment of 3,3-dimethylthietan 1,1-dioxide (**1a**) with one equivalent of Bu^{n}Li in THF at −78° readily yielded the lithio-carbanion (**1b**) in a few minutes. After many unsuccessful attempts at halogenating this carbanion with conventional reagents (Br_2, NBS, *N*-chlorobenzotriazole), the compound (**2**)[6] was employed. When a solution of (**1b**) was added very slowly to a THF solution of (**2**) (1·1 equiv.) at 0° bromination ensued. After several hours of stirring at room temperature, the lithium salt of the 5-methyl derivative of Meldrum's acid precipitated from solution. Filtration of the salt and evaporation of the THF afforded a mixture of the bromosulphone (**3**) and the starting sulphone (**1a**) in a ratio of 7:1 (87% conversion). After column chromatography on silica gel, an 85% yield of 2-bromo-3,3-dimethylthietan 1,1-dioxide (**3**) was isolated [m.p. 90—91°, δ ($CDCl_3$) 1·42 (6H, s), 3·96 (1H, s) 3·90 (1H, s), 5·52 (1H, s)]. The slow inverse addition is necessary to maximize the conversion, since the more acidic bromosulphone (**3**) is easily deprotonated by (**1b**).



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