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AN UNUSUAL REACTION OF PHENACYLIDENEDIMETHYLSULPHURANES

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Phosphonium ylids react with aldehydes and ketones to give olefins (1). In contrast the corresponding sulphonium ylids, although less-widely investigated, normally react with aldehydes and ketones to produce epoxides. This latter reaction was first reported by Johnson and LaCount (2), and has now been well exemplified (3-7). However sulphonium ylids with strongly electron-withdrawing groups attached to the carbanionic centre are only weakly nucleophilic. Thus sulphonium phenacylids do not react with cyclohexanone (8) or aldehydes (9,10), except that phenacylidenedimethylsulphurane gives a 10% yield of epoxide with p-nitrobenzaldehyde (11). The p-bromo analogue reacts with diketene to give a furan (12).

This Letter reports an unusual reaction of sulphonium phenacylids on treatment with formaldehyde. As a potential source of the keto-epoxide (2), reaction of the ylid (1)* with formaldehyde has been investigated. However treatment of the ylid (1) with an excess of paraformaldehyde in refluxing 1,2-dimethoxyethane (DME) for 1hr. led to a crude product containing less than 1%, if any, of the required keto-epoxide, and containing methyl p-chlorobenzoate as the major (95%) volatile component. The latter was isolated in 50% yield by chromatography.

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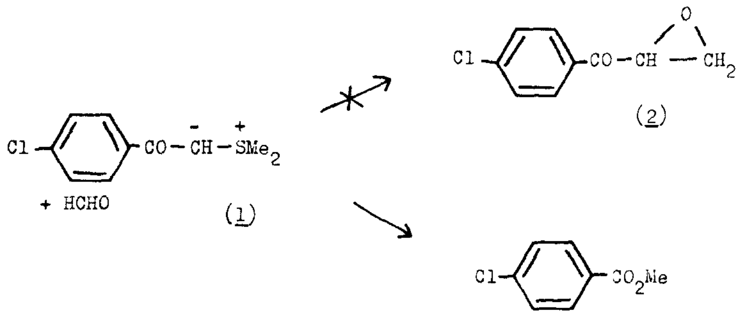
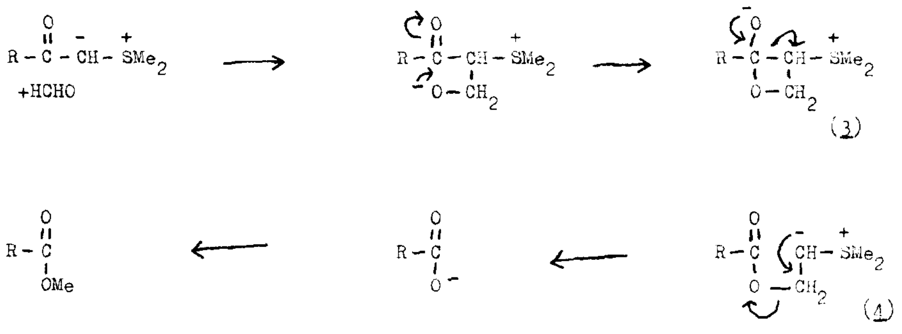
* Prepared from p-chlorophenacyl bromide by the standard method (8,9): mp 116-117°, lit. (13) 106-107°. (Found: C, 56.0; H, 5.2; Cl, 16.5; S, 14.8. $C_{10}H_{11}OClS$ requires: C, 55.94; H, 5.17; Cl, 16.51; S, 14.94%)



The reaction showed no significant solvent effect, since methyl p-chlorobenzoate was isolated in yields of 40-45% from reactions in benzene, chloroform and methanol, with no evidence of epoxide formation. In the crude product from the reaction in methanol, no α-(methylthio)methoxystyrene derivative (14) was observed (nmr). Further, phenacylidenedimethylsulphurane (8,9) and its p-phenyl analogue (9) gave methyl benzoate and methyl biphenyl-4-carboxylate respectively, in similar yields to those above, on treatment with excess of paraformaldehyde in refluxing DME.

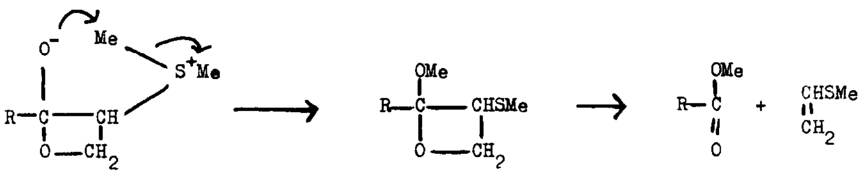
In a control experiment, the keto-epoxide (2) (see later) was shown to be stable in refluxing DME, in the presence of paraformaldehyde, thereby implying that it was not an intermediate in the formation of the benzoate ester.

Examples are known of formaldehyde forming olefins with phosphonium ylids (1,14) and epoxides with sulphonium ylids (7), but the present reaction seems to be without precedent. The following mechanism is proposed. It involves the benzoate anion as an intermediate which presumably suffers methylation by a dimethylsulphonium salt produced during the reaction. Some evidence for the feasibility of this mechanism is provided by the work of



Rydon et al. (15) who have demonstrated the extreme facility with which methiodides of β-methylthioethyl esters lose the carboxylate anion on treatment with dilute alkali, presumably *via* an ylid of type (4). Also, dimethylsulphonium salts are reported (6,11) to suffer demethylation by bromide ions.

However, an alternative mechanism, involving an intramolecular methyl transfer from the intermediate (3) followed by fragmentation of the resulting oxetane (5) cannot be ruled out.



(3) (5)

The keto-epoxide (2) was finally prepared from p-chloroacrylophenone (14) by epoxidation with hydrogen peroxide and carbonate or bicarbonate (but not hydroxide) in methanol.*

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* mp 74-76°; ν(in $CHCl_3$) 1695 cm^{-1} (C=O) (Found: C, 59.0; H, 3.7; Cl 19.2. $C_9H_7O_2Cl$ requires C, 59.20; H, 3.86; Cl, 19.42%).

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