9-Oxothioxanthenium Methylides

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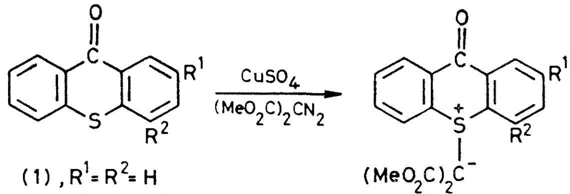
Summary ^{1}H and ^{13}C N m r , i r , and *X*-ray data indicate that thioxanthones react with carbenes generated from dialkyl diazomalonates to form sulphonium ylides which contain a comparatively flat heterocyclic ring

RECENTLY it has been shown[1,2] that thioxanthens react with carbenes, formed by decomposition of dialkyl diazomalonates, to form thioxanthenium methylides It has been noted, however, that this reaction may also produce 9-substituted thioxanthens [2] In view of this dichotomy and of the possibility that the thioxanthone (**1**) might react to produce either an epoxide or a sulphonium ylide, we now report the reaction of (**1**), 2-chlorothioxanthone (**2**), and 2,4-dimethylthioxanthone (**3**) with dimethyl diazomalonate in the presence of anhydrous copper sulphate [3]



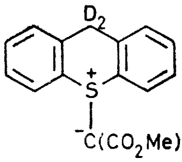
(**1**), R^1= R^2= H
(**2**); R^1= Cl , R^2=H
(**3**), R^1= R^2= Me

(**4**) R^1= R^2= H
(**5**) R^1= Cl , R^2= H
(**6**) R^1= R^2= Me

The products of the reactions [(**4**), m p 204 °C, (**5**), m p 184 °C, and (**6**), m p 203 °C, respectively] were obtained in 60—75% yield when toluene was used as a solvent' Products could be recrystallized from ethanol or benzene–ethyl acetate (1 : 1), were homogeneous on t l c (silica gel, chloroform eluant, u v or iodine visualization) and had a molecular weight (mass spectrum) consistent with the proposed structures

The i r spectra (mull) of these products suggest that they are ylides rather than epoxides For example, (**4**) exhibits three absorptions in the carbonyl region (ν 1660, 1625, and 1645 cm^{-1}) assigned to the ester carbonyl-groups and to the diaryl ketone ^{1}H N m r spectroscopy also suggests that these are ylides Thus, isomeric epoxides of (**5**) and (**6**) would possess diastereotopic methoxy-group signals, but these compounds give rise to a single absorption near δ 3 7 †

The carbon-13 n m r spectra of these compounds further supports the ylide structure for (**4**)—(**6**) Thus, the resonance corresponding to the carbonyl-carbon of (**1**) (δ 179 74) is present in (**4**) (179 62), (**5**), (176 76), and (**6**) (179 62 p p m) An absorption at approximately δ 60 p p m in all of these ylides is absent in the spectra of (**1**) and of dimethyl malonate (δ 166 42, 51 86, and 40 51 p p m) and is assigned to the methylide carbon of these ylides This chemical shift falls within the range (δ 54—67 p p m) which we have observed[4] for the methylide carbon of thioxanthenium methylides of this type [*e g* , 9,9-dideuteriothioxanthenium bis(methoxycarbonyl)methylide (**7**)]



(**7**)

The similarity of the ^{13}C n m r chemical shifts of the methylide carbons of (**4**)—(**6**) (δ 60—63 p p m) suggests that these structures have similar environments about the methylide carbon, in spite of the C-4 methyl-group in (**6**) (which would be expected to force the methylide carbon into the pseudo-axial position[5]) One explanation for this is that in solution the heterocyclic ring in thioxanthenium methylides is close to planarity, a near planar geometry would remove much of the distinction between pseudo-axial and pseudo-equatorial positions The single crystal *X*-ray analysis of (**4**) bears this out ‡ Thus, the angle made between the planes containing the aryl rings is 169° The *X*-ray analysis also reveals that the essentially planar malonylide moiety does, indeed, rest 'within' the shallow fold of the heterocycle and can, therefore, be described as being pseudo-equatorial It is concluded that the geometry of simple 9-oxothioxanthenium methylides [*e g* (**4**)] parallels that of thioxanthone sulphoxide,[6] in much the same way that the thioxanthenium methylides [*e g* (**7**)] parallel the thioxanthene sulphoxides [5]

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† The absorption is broad as are the ^{13}C n m r resonances of the methoxy-group and carbonyl-carbons This suggests a restricted rotation about the S$^+$–C$^-$ bond Broadening has yet to be reported in the n m r spectra of ylides derived from thioxanthen (ref 4)

‡ Details of crystallographic data will be published elsewhere

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[4] D Craig, A L Ternay, Jr , G E Martin, and W H Watson, *J Org Chem* , submitted for publication In thioxanthenium methylides the pseudo-axial methylide carbon absorbs near δ 67 p p m while the pseudo-equatorial absorbs near δ 54 p p m.

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[6] S S C Chu, *Acta Crystallogr* , *Ser B*, 1976, **32**, 1583