

9-Oxothioxanthenium Methyldes

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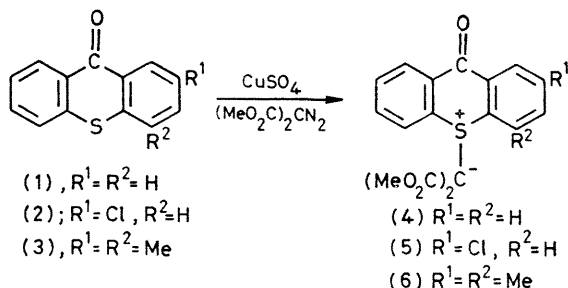
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Summary ^1H and ^{13}C N m r, i r, and X-ray data indicate that thioxanthenes react with carbenes generated from dialkyl diazomalonates to form sulphonium ylides which contain a comparatively flat heterocyclic ring

RECENTLY it has been shown^{1,2} that thioxanthenes react with carbenes, formed by decomposition of dialkyl diazomalonates, to form thioxanthenium methyldes. It has been noted, however, that this reaction may also produce 9-substituted thioxanthenes.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



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. ^1H 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 \uparrow .

\uparrow 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 thioxanthene (ref 4).

\ddagger Details of crystallographic data will be published elsewhere.

¹ Y. Tamura, C. Mukai, and M. Ikeda, *Heterocycles*, 1979, **12**, 1179.

² A. L. Ternay, Jr., D. Craig, and H. R. O'Neal, *J. Org. Chem.*, in the press.

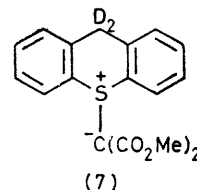
³ W. Ando, T. Yagihara, S. Tozune, I. Imai, J. Suzuki, T. Toyama, S. Nakaido, and T. Migita, *J. Org. Chem.*, 1972, **37**, 172.

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

⁵ A. L. Ternay, Jr., L. Ens, J. Herrmann and S. Evans, *J. Org. Chem.*, 1969, **34**, 940.

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

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 methyldes carbon of these ylides. This chemical shift falls within the range (δ 54–67 p p m) which we have observed⁴ for the methyldes carbon of thioxanthenium methyldes of this type [e g., 9,9-dideuteriothioxanthenium bis(methoxycarbonyl)methyldes (7)].



The similarity of the ^{13}C n m r chemical shifts of the methyldes carbons of (4)–(6) (δ 60–63 p p m) suggests that these structures have similar environments about the methyldes carbon, in spite of the C-4 methyl-group in (6) (which would be expected to force the methyldes carbon into the pseudo-axial position⁵). One explanation for this is that in solution the heterocyclic ring in thioxanthenium methyldes 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 \ddagger . Thus, the angle made between the planes containing the aryl rings is 169°. The X-ray analysis also reveals that the essentially planar malonylde 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 methyldes [e g. (4)] parallels that of thioxanthone sulphoxide,⁶ in much the same way that the thioxanthenium methyldes [e g. (7)] parallel the thioxanthene sulphoxides.⁵

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