

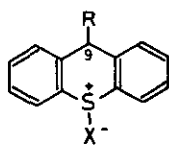
PREPARATION AND BASE-CATALYZED REARRANGEMENT OF THIOXANTHENIUM
BISCARBOMETHOXYMETHYLIDES

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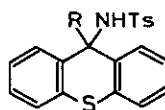
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Abstract — Thioxanthonium biscarbomethoxymethylide and its *trans*-9-methyl derivative were prepared by thermal reaction of the corresponding thioxanthenes with dimethyl diazomalonate in the presence of copper sulfate. These sulfonium ylides underwent base-catalyzed rearrangement to the corresponding 9-(biscarbomethoxymethyl)thioxanthenes.

Thioxanthene N-(*p*-toluenesulfonyl)sulfilimines (1) undergo base-catalyzed rearrangement to 9-(N-*p*-toluenesulfonamido)thioxanthenes (4).^{1,2} It appeared to be of interest to see if the isoelectronic sulfonium ylides (2) would undergo a similar rearrangement. It is known that thioxanthene 10-oxides (3) are relatively stable under basic conditions. We here report on the synthesis and base-catalyzed rearrangement of thioxanthonium biscarbomethoxymethylides (6a,b).



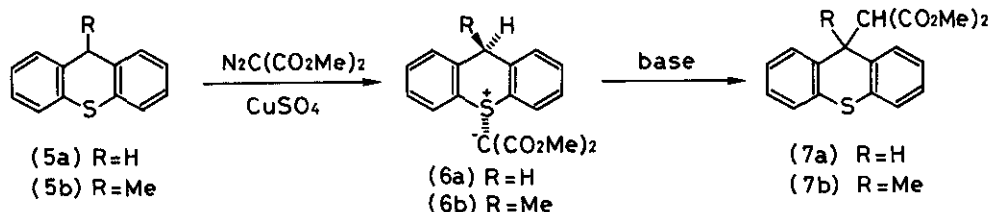
- (1) X = NTs
(2) X = CR₂⁻
(3) X = O



(4)

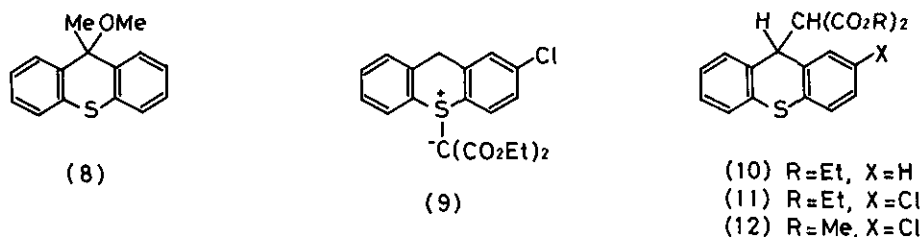
The ylide (6a), mp 199-200°C,³ was prepared in 66% yield by heating thioxanthene (5a) at 90°C for 4 hr with dimethyl diazomalonate in the presence of anhydrous copper sulfate, analogous to conditions reported by Ando et al.⁴ Spectral data and elemental analysis were in complete agreement with the assigned structure [(CHCl₃) 1710, 1650 cm⁻¹; δ (CDCl₃) 3.60 (6H, s), 4.28, 4.00 (1H each, ABq, J=17.5 Hz), 7.3-7.8 (8H, m)]. Similar reaction of 9-methylthioxanthene (5b) gave exclusively *trans*-9-methyl derivative (6b), mp 175-176°C, in 84% yield, whose stereochemistry was

assigned on the basis of nmr spectral comparison [(6b), δ (CDCl₃) 4.39 (1H, q, $J=7.0$ Hz, C₉-H) and 1.51 (3H, d, $J=7.0$ Hz, C₉-CH₃)] with the corresponding sulfoxide⁵ and N-(p-toluenesulfonyl)sulfilimine.²



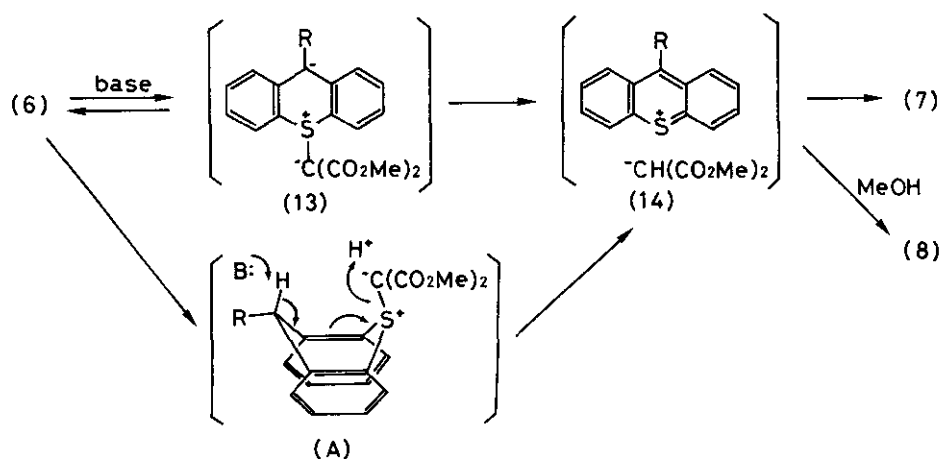
Refluxing the ylides (6a,b) in toluene in the presence of DBU (0.5 equiv)⁶ for 3-5 hr gave the rearranged products (7a), mp 110-111°C, and (7b), mp 85-86°C, in 81 and 71% yields, respectively. The structures of (7a,b) were easily confirmed by spectral evidence.

This rearrangement was found to be markedly affected by the solvent used. Thus, heating (6a) and DBU in dimethylformamide at 145°C gave (7a) and thioxanthone in 14 and 34% yields, respectively. When heated in methanol in the presence of DBU at 150°C in a sealed tube (6b) gave exclusively 9-methoxy-9-methylthioxanthene (8) in 61% yield. If the reaction was carried out on a mixture of (6a) and 2-chlorothioxanthenium biscarbethoxymethylide (9)⁷ in toluene in the presence of DBU, no cross-over products were formed; only (7a) and (11), m.p. 121.5-122°C, were obtained. However, the same mixture, upon heating with DBU in dimethylformamide at 145°C, afforded four possible products [(7a):(10)]⁸=1.5:1 and (11):(12)⁹=2:1 by nmr spectroscopy], along with thioxanthone and 2-chlorothioxanthone. These observations clearly indicate that the reaction mechanism shifts from intramolecular to intermolecular by changing the solvent from non-polar to polar.



A simple explanation would involve an initial formation of carbanions (13) which induce sulfur-carbon cleavage to give thioxanthylium ions (14), followed by an intra- or intermolecular recombination process to give (7) or (8) depending on the degree of dissociation of the ions in the solvent used. The formation of (13), at

least in methanol, was demonstrated by isolation of the 9-deuterio derivative of (6b) after stirring (6b) in methanol-d₁ containing DBU at room temperature. However, the possibility of a concerted syn elimination mechanism^{2,10} for the formation of thioxanthylum ions (14) is not ruled out, although it necessitates the postulation that (6b) must preequilibrate with the less stable conformer (A) in which the bulky biscarbomethoxymethyl group and the 9-methyl group occupy the axial and equatorial positions, respectively.



References

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2. Y. Tamura, Y. Nishikawa, C. Mukai, K. Sumoto, M. Ikeda, and M. Kise, *J. Org. Chem.*, 1979, **44**, 1684.
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6. No rearrangement took place in the absence of DBU.
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