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PREPARATION AND BASE-CATALYZED REARRANGEMENT OF THIOXANTHENIUM BISCARBOMETHOXYMETHYLIDES

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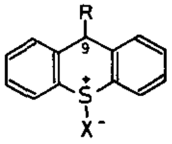
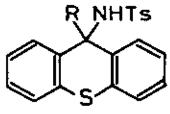
Abstract — Thioxanthenium biscarbomethoxymethylide and its trans-9-methyl derivative were prepared by thermal reaction of the corresponding thioxanthenes with dimethyl diazomalonate in the presence of copper sulfate. These sulfonium ylides underwent base-catalyzed rearrangement to the corresponding 9-(biscarbomethoxymethyl)thioxanthenes.

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 thioxanthenium biscarbomethoxymethylides (6a,b).

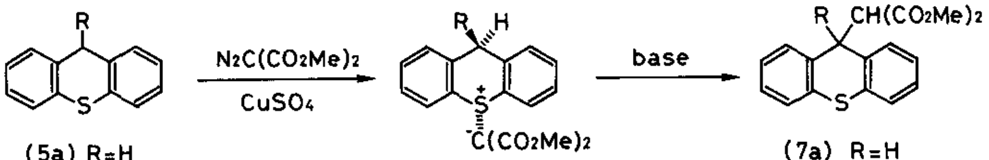


(1) X = NTs
(2) X = CR$'_2$
(3) X = O



(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 [(CHCl$_3$) 1710, 1650 cm^{-1}; δ (CDCl$_3$) 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 (CDCl$_3$) 4.39 (1H, q, *J*=7.0 Hz, C$_9$-H) and 1.51 (3H, d, *J*=7.0 Hz, C$_9$-CH$_3$)] with the corresponding sulfoxide[5] and N-(*p*-toluenesulfonyl)sulfilimine.[2]



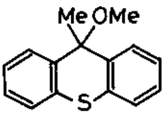
(5a) R=H
(5b) R=Me

(6a) R=H
(6b) R=Me

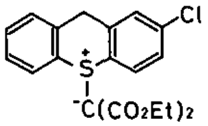
(7a) R=H
(7b) R=Me

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.

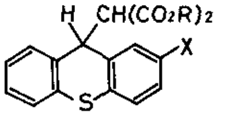
This rearrangement was found to be markedly affected by the solvent used. Thus, heating (6a) and DBU in dimethylformamide at 145°C gave (7a) and thioxanthone in 14 and 34% yields, respectively. When heated in methanol in the presence of DBU at 150°C in a sealed tube (6b) gave exclusively 9-methoxy-9-methylthioxanthene (8) in 61% yield. If the reaction was carried out on a mixture of (6a) and 2-chlorothio-*xanthenium 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.



(8)

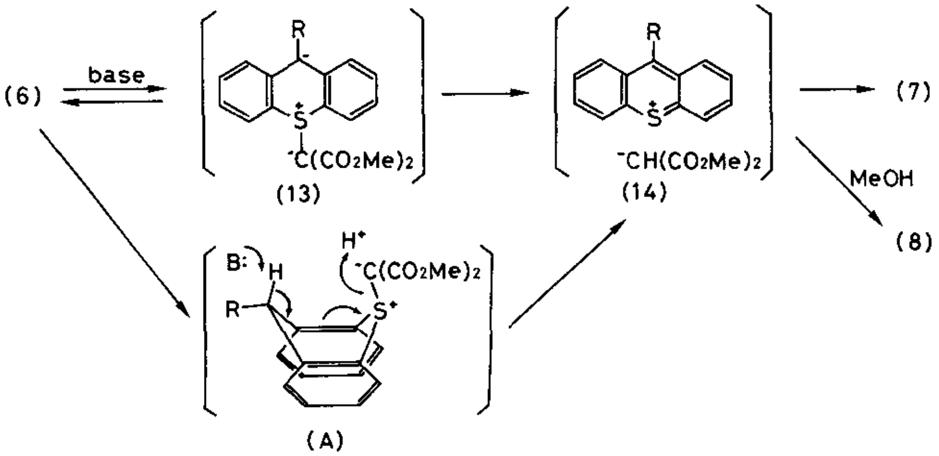


(9)



(10) R=Et, X=H
(11) R=Et, X=Cl
(12) R=Me, X=Cl

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-d_1 containing DBU at room temperature. However, the possibility of a concerted *syn* elimination mechanism[2,10] for the formation of thioxanthylium 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.
3. All new compounds gave satisfactory elemental and spectral analyses.
4. W. Ando, T. Yagihara, S. Tozune, I. Imai, J. Suzuki, T. Toyama, S. Nakaido, and T. Migita, *J. Org. Chem.*, 1972, **37**, 172.
5. A.L. Ternay, Jr. and S.A. Evans, *J. Org. Chem.*, 1974, **39**, 2941.
6. No rearrangement took place in the absence of DBU.
7. This compound, mp 164-166°C, was prepared by the reaction of 2-chlorothioxanthene with diethyl diazomalonate in 77% yield.
8. I. Okabayashi and K. Okochi, *J. Pharm. Soc. Japan*, 1966, **86**, 828.
9. Compound (**12**) has mp 118-119°C.
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