Thermolysis of *S*-Methoxymethyl Thioacetates and Derivatives; A Novel β-Elimination Reaction in the Vapour Phase

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Summary *S*-Methoxymethyl thioacetates are cleaved into ester and (thio)aldehyde in the vapour phase, apparently *via* a four-centre transition state.

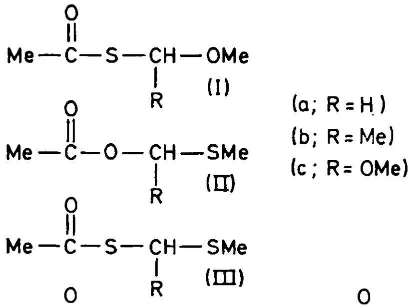
ACETATES[1] and thioacetates[2] with reactive β-H atoms form acid and alkene(s) upon thermolysis. We have now investigated[3] analogues (I)—(III) carrying OMe or SMe at the α-position in the alcohol portion of the ester, which show a novel mode of β-elimination [*A* in reactions (1)]. The ester (IIa) gives (V) rather than (IV),‡ showing that step *A*

TABLE

Arrhenius parameters

Substrate	log (A/s^{-1})	E_a/(kcal mol^{-1})	Temperature (°C)
(Ia)[a]	12·6	48·5	488—538
(IIIa)[a]	12·1	41·8	390—465
(IIIb)[a]	12·3	40·8	367—425
(IIIb)[b]	13·3	45·8	367—425
(Ib)[b]	13·0	39·6	311—358

[a] Path *A*. [b] Path *B*.

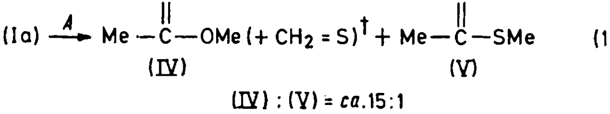


$\mathrm{Me{-}C({=}O){-}S{-}CH(R){-}OMe}$ (I)

$\mathrm{Me{-}C({=}O){-}O{-}CH(R){-}SMe}$ (II)

$\mathrm{Me{-}C({=}O){-}S{-}CH(R){-}SMe}$ (III)

(a; R = H)
(b; R = Me)
(c; R = OMe)



$$\text{(Ia)} \xrightarrow{A} \underset{\text{(IV)}}{\mathrm{Me{-}C({=}O){-}OMe}}\ (+\ \mathrm{CH_2{=}S})^{\dagger} + \underset{\text{(V)}}{\mathrm{Me{-}C({=}O){-}SMe}} \qquad (1)$$

(IV) : (V) = *ca.* 15:1

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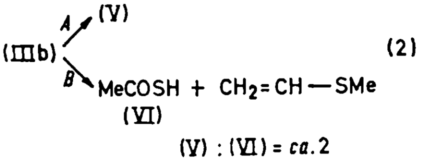
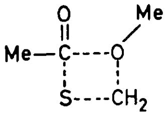
† Thioaldehydes were identified by mass spectrometry after trapping at the outlet of the katharometer system in a tube cooled with liquid nitrogen; at room temperature, insoluble polymeric materials (*cf.* ref. 4) were formed.

‡ The main reaction, however, is α-elimination of acetic acid; this phenomenon, which is the sole reaction with $MeC(O)OCH_2OMe$, will be described elsewhere.[5]

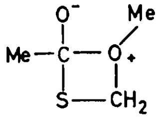
involves [MeO(MeS) + acyl] elimination rather than removal of [Me + $MeCO_2$(MeCOS)]. Furthermore, (IIIa) cleanly gives (V); by analogy, we suggest that this reaction also proceeds *via* step *A*. (IIIb) shows two modes of reaction (2); apparently, the 'ester from ester' elimination *A* effectively competes with the 'normal' olefin-forming elimination of acid *B*. (Ib) only reacts *via* step *B* (*cf.* Table).



(*i*)



(*ii*)



All reactions were homogeneous first-order processes. An increased surface-to-volume ratio (20×) had little, if any, effect on rates and product composition.

In our opinion *A* involves a transition state similar to (i), which may have some of the polar characteristics of (ii). The perhaps concerted reaction may be a nucleophilic attack on the acyl carbon atom.§ Elimination *A* is not restricted to esters carrying *one* α-OR′ or -SR′ group. Thus, (Ic) also forms (IV) rather than (V) in the vapour phase. These reactions may (but need not) be mechanistically related to some liquid-phase decompositions observed with (di)alkoxyalkyl carboxylates.[7] It is expected that *A* constitutes part of a family of thermolytic processes involving intramolecular nucleophilic attack on acyl[8] and other electrophilic carbon atoms; these possibilities are being further explored.

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§ Note that (IIIa) reacts considerably faster than (Ia) (Table), in line with the larger *C*-nucleophilicity of bivalent sulphur compared with oxygen analogues.[6] Interestingly, the reaction of the former ester is estimated to be much more endothermic (25 kcal) than that of the latter (15 kcal).

[1] A. Tinkelenberg, E. C. Kooyman, and R. Louw, *Rec. Trav. chim.*, 1972, **91**, 3. and refs. cited therein.
[2] P. C. Oele, A. Tinkelenberg, and R. Louw, *Tetrahedron Letters*, 1972, 2375.
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[4] R. Mayer, J. Morgenstern, and J. Fabian, *Angew. Chem.* 1964, **76**, 157.
[5] P. C. Oele and R. Louw, *Tetrahedron Letters*, to be published.
[6] R. E. Davis in 'Survey of Progress in Chemistry,' ed. A. E. Scott, Academic Press, vol. 2, 1964, p. 189; R. G. Pearson, H. Sobel, and J. Songstad, *J. Amer. Chem. Soc.*, 1968, **90**, 319.
[7] J. W. Scheeren, A. P. M. van der Veek, and W. Stevens, *Rec. Trav. chim.*, 1969, **88**, 195; A. P. M. van der Veek and F. H. van Putten, *Tetrahedron Letters*, 1970, 3951; P. E. Newallis and P. Lombardo, *J. Org. Chem.*, 1965, **30**, 3834.
[8] S. Searles, jun., and S. Nukina, *J. Amer. Chem. Soc.*, 1965, **87**, 5656.

† Satisfactory analyses were obtained for all new compounds.