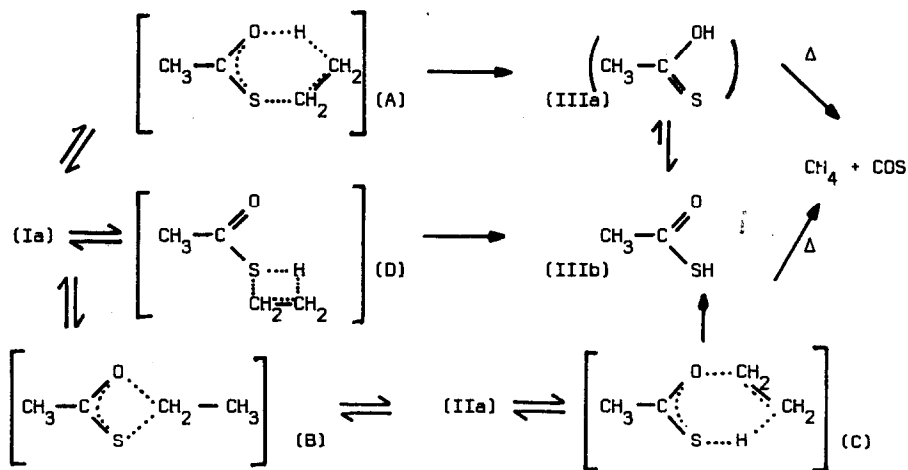


SCHEME (1)



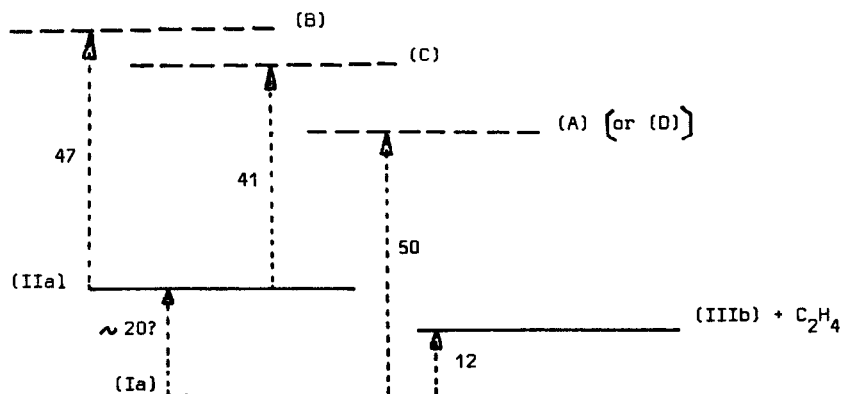
By analogy an (A) like six-centre transition state (cf. Scheme (1), outlined for $R = C_2H_5$) suggests itself. This, however, would lead to - energetically unfavourable - (IIIa) rather than (IIIb).

Both the acid (III) formed from (I) and authentic (IIIb) are found to decompose to a large extent under the prevailing conditions (cf. Table), giving $CH_4 + COS$ together with small amounts of H_2S and ketene.

When (I) is thermolyzed ($310 - 360^\circ$, $\log k = 13.0 - 39.6 (\theta)^7$, (III) - once formed - remains largely intact. Now the decomposition occurs ca. 3 times faster than that of authentic (IIIb). Presumably, (IIIa), when formed as intermediate, gives $CH_4 + COS$ directly in competition with equilibration (IIIa) \rightleftharpoons (IIIb)⁹. We therefore consider route (Ia) \rightarrow (D) \rightarrow (IIIb), involving a four-centre transition state, less likely than that via (A).

Another alternative route may be considered, viz. isomerization (I) \rightarrow (B) \rightarrow (II) prior to elimination via (C). In our hands, authentic (IIa) and (IIg) isomerize with comparable rates to give (Ia) and (Ig), the latter reaction having $\log k \sim 13.3 - 46.5/\theta^{10}$. The predominant reaction of (IIa), however, is elimination (IIa) \rightarrow (III), $\log k = 12.5 - 41.2/\theta$. It is therefore concluded - cf. the energy diagram of Scheme (ii) - that (II) is not an intermediate in pyrolytic alkene formation from thiol esters (I).

SCHEME (11)



NOTES and REFERENCES

1. A.Tinkelenberg, E.C.Kooyman and R.Louw, *Rec.Trav.Chim.* **91**, 3 (1972) and references cited there.
2. G.L.O'Connor and H.R.Nace, *J.Am.Chem.Soc.* **74**, 5454 (1952).
3. More detailed information - also on other substituted thiolacetates - will be given in a forthcoming paper and in: P.C.Dels, Thesis, Leiden (1972).
4. We used a micro-flowreactor/ g.l.c. combination as described by A.Tinkelenberg, *J. of Chromatographic Science*, **8**, 721 (1970); helium served as the carrier gas and cyclohexane, toluene or m-xylene as diluents.
5. S.W.Benson and H.E.O'Neil, "Kinetic Data on Gas Phase Unimolecular Reactions", NSRDS - NBS 21 (1970).
6. H.E.O'Neil and S.W.Benson, *J.Phys.Chem.* **71**, 2903 (1967).
7. As with chlorides⁸ and acetates³, α -OCH₃ enormously enhances the rate of elimination.
8. R.I.Failes and V.R. Stimson, *Austr. J.Chem.* **20**, 1553 (1967).
9. Proton transfer (tautomerization) is not necessarily a rapid reaction in the vapour-phase; cf. R.Louw, *Rec.Trav.Chim.* **90**, 1119 (1971).
10. This type of reaction - very probably via a transition state like (B) - has hitherto only been described for aryl esters¹¹; the isomerization of allylic thionoacetates involves a six-centre type transition state¹².

11. a) H.Kwart and R.Evans, *J.Org.Chem.* 31, 410 (1966),
b) K.Miyazaki, *Tetrah. Letters*, 2793 (1968).
12. S.G.Smith, *J.Am.Chem.Soc.* 83, 4285 (1961).