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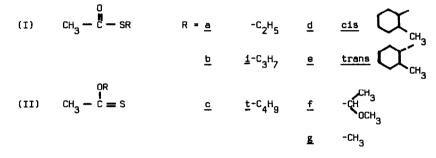
## THERMOLYSIS OF ALKYL THIOL- AND THIONOACETATES X

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Whereas  $\beta$ -elimination from alkyl acetates <sup>1</sup> and xanthates <sup>2</sup> is well characterized, that of the title compounds has, to our knowledge, not been investigated before. We have now thermolized (Ia-c) <sup>3,4</sup>, the formation of olefins appears as a clean first-order process, insensitive



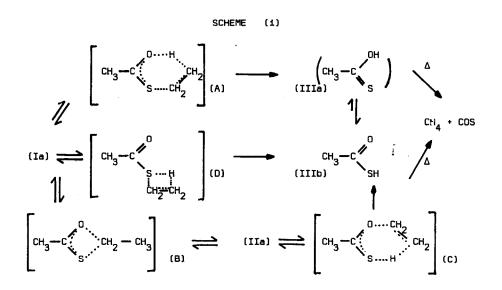
to wall effects (20 - fold increase in surface - to - volume ratio). The <u>cis</u> - character is shown by the products from (Id)(forming only 3-methylcyclohexene) and from (Ie), giving also 1-methylcyclohexene. The Arrhenius parameters (Table) show that eliminations from (Ia-c) are somewhat slower than those from the corresponding acetates. Thermolysis of thiolesters, however offers an attractive way of eliminating the components of  $H_2S$  from thiols: (RSH  $\rightarrow$  (I)  $\stackrel{\Delta}{\rightarrow}$  alkene(s)), the direct reaction (RSH  $\stackrel{\Delta}{\rightarrow}$  alkene(s)) having a much higher activation energy  $^5$ .

TABLE Arrhenius parameters for acetate and thiolacetate thermolysis

CH3 CKXR					
	x = 0 <sup>6</sup>		X = S		
R	log A	Ea	log A	Ea	temp.region ( <sup>0</sup> C)
<sup>С</sup> 2 <sup>Н</sup> 5	12.6	48.2	12.4	50.4	490 - 568
1 - C3H7	12.9	44.7	13.2	49.2	450 - 526
t C <sub>4</sub> H <sub>9</sub>	13.1	40.0	13.8	45.7	380 - 432

x Thermolytic Reactions of Esters. VII; part VI, cf. 1

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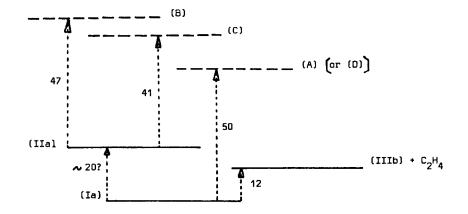
By analogy an (A) like six-centre transition state (cf. Scheme (i), outlined for  $R = C_2H_5$ ) suggests itself. This, however, would lead to - energetically unfavourable - (IIIa) rather than (IIIb).

Both the acid (III) formed from (I) and <u>authentic</u> (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 (If) is thermolyzed (310 - 360 °, log k = 13.0 - 39.6 ( $\theta$ )<sup>7</sup>, (III) - once formed remains largely in tact. Now the decomposition occurs ca. 3 times faster than that of authentic (IIIb). Presumably, (IIIa), when formed as intermediate, gives CH<sub>4</sub> + COS directly in competition with equilibration (IIIa)  $\rightleftharpoons$  (IIIb) <sup>9</sup>. 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. <u>isomerization</u> (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 - 46.5/0<sup>10</sup>. The predominant reaction of (IIa), however, is elimination (IIa)  $\rightarrow$  (III), log k = 12.5 - 41.2/0. It is therefore concluded — cf. the energy diagram of Scheme (ii) — that (II) is <u>not</u> an intermediate in pyrolytic alkene formation from thiol esters (I).





#### NOTES and REFERENCES

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- More detailed information also on other substituted thiolacetates will be given in a forthcoming paper and in: P.C.Dele, Thesis, Leiden (1972).
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- 7. As with chlorides  $^8$  and acetates  $^3$ ,  $\alpha$ -OCH $_3$  enormously enhances the rate of elimination.
- 8. R.I.Failes and V.R. Stimson, Austr. J.Chem. 20, 1553 (1967).
- 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 <u>aryl</u> esters <sup>11</sup>; the isomerization of <u>allylic</u> thionoacetates involves a six-centre type transition state <sup>12</sup>.

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