Tetrahedron Letters No. 50, pp 5159 - 5160, 1972. Pergamon Press. Printed in Great Britain.

THERMOLYSIS OF 2-CHLORO-1-METHOXYETHYL ACETATE AND -THIOLACETATE: HCl ELIMINATION WITH REARRANGEMENT IN THE VAPOUR PHASE.▲

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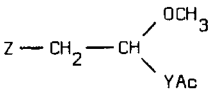
(Received in UK 7 November 1972; accepted for publication 15 November 1972)

As part of our studies[1-4] on thermolytic reactions of esters, including "coupled" substituent effects on the β-elimination of acid[1], we wished to compare the behaviour of (Ia)[3] and (Ib)[5,6].

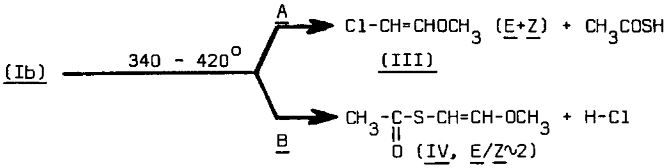
(I)



a Y = S, Z = H
b Y = S, Z = Cl
c Y = O, Z = Cl

Between 340 and 420°, (Ib) partly eliminates thioacetic acid to give (III) (Scheme I, A). The more rapid reaction, however, is loss of HCl (path B) leading to rearranged product (IV) :

SCHEME I



(IV)/(III) ∿ 4

The homogeneous, first-order character of these reactions is shown by the absence of wall[7], scavenger and/or concentration effects. Activation parameters for (Ib) → (IV) are $\log k\ (s^{-1}) = 13.4 - 42.5/\Theta\ (340 - 375^{\circ})$[9]. Optimal (g.l.c.) yields of 66% (IV) — 46% E-, 20% Z- — were recorded at 420°, with >95% conversion of (Ib).

(III) and (IV) were identified by mass spectrometry, n.m.r. and infrared spectroscopy; Pure E - (IV) — b.p. 84°/15 mm, $n_D^{20} = 1.5060$ — was obtained through fractionation using a spinning-band column[10].

Thus, the present thermolytic gas phase reaction constitutes a useful method for the preparation of E-(IV) and, presumably, of analogues as well.

The acetate (Ic) also shows elimination of both HCl and CH_3COOH, with (V)/(III) ∿ 0.4 and

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▲ Thermolytic Reactions of Esters, Part X, Part IX: Cf. ref. 4.

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$$CH_3CO_2 - CH = CH - OCH_3 \quad (Z+E)$$

(V)

E–(V)/Z – (V) $\sim$ 0.8. Although here, a considerable wall effect will adversely affect mechanistic studies, this process constitutes a simple method for the preparation of vinylic acetates (V), which have, to our knowledge, not been described earlier.

Compared with the thermolysis of (II)[6], the conversions (Ib) → (IV) and (Ic) → (V) occur at very mild conditions[5]. Apparently, the 1-methoxyl group has a pronounced accelerating effect[11]. This indicates that the transition state has considerable carbonium ion character.

Further experiments aiming at determining the synthetic utility and a more detailed mechanism of this novel type of elimination are in progress.

NOTES AND REFERENCES

1. A.Tinkelenberg, E.C.Kooyman and R.Louw, Rec. Trav. Chim. 91, 3 (1972).
2. P.C.Oele, A.Tinkelenberg and R.Louw, Tetrah. Letters, 2375 (1972).
3. P.C.Oele and R.Louw, Chem.Comm., 848 (1972).
4. P.C.Oele and R.Louw, Tetrah. Letters, 3623 (1972).
5. The synthesis of (Ib) and analogues — from thioacetic acid and the corresponding aldehyde dimethylacetal — will be published separately. (P.C.Oele and A.P.M. van der Veek, manuscript in preparation).
6. After the completion of this work we learned that Robinson (Diss. Abstracts Int. B., 31 (8), 4591 (1971) has observed rearrangements in the thermolysis of 2,2-dichloroalkyl acetates such as $Cl_2CH\text{-}CH(OAc)\text{-}CH_3$ (II) at $\sim 530^{\circ}$. In addition to normal products of β-elimination the major product was 2-chloropropanal.
7. A 20-fold increase in the surface - to - volume ratio of the "micro" reactor system[8] had little, if any effect on rate or product composition.
8. A.Tinkelenberg, J.Chromatog. Science 8, 721 (1970).
9. For (Ib) → (III), $\log k \sim 13.3 - 44.0/\theta$. For (Ia) → $CH_2{=}CHOCH_3$, $\log k = 13.0 - 39.6/\theta$,[3] thus substantiating a retarding effect by β-chloro, as is also the case for acetates (J.C.Scheer, E.C.Kooyman and F.L.J.Sixma, Rec. Trav. Chim. 82, 1123 (1963)).
10. For more details: P.C.Oele, Thesis Leiden, in preparation.
11. 1-Chloro-2-propyl thiolacetate shows only regular β-elimination without B-like rearrangements.