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ERRATUM

Tetrahedron Letters No. 35, pp. 3623-3624 should have appeared as follows:

THERMOLYTIC α-ELIMINATION OF ACETIC ACID FROM METHYLACETATE DERIVATIVES

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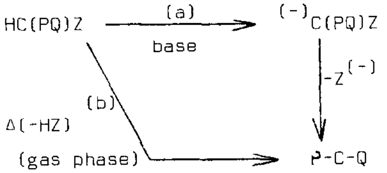
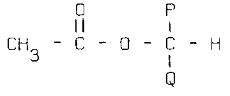
Thermolytic β-elimination - a counterpart of the solvolytic E2-type reaction - has been widely investigated[1]. Ionic α-elimination (a), a carbene forming reaction, is also well known.[2] Its thermolytic analogue (b), however, has only been proposed to occur with some chloromethane derivatives (e.g., $CHCl_3$ [3a] or $ClCH_2CN$ [3b]).



We wish to present our first results on the vapour phase thermolysis[4] of some derivatives of methylacetate (Ia-e). In all cases acetic acid was formed (50 - 80%). The reactions were homogeneous[x] and approximately first order in (I), dilution with benzene or toluene having little or no effect on the rates of decomposition.

(I)



$$CH_3-\overset{O}{\overset{\|}{C}}-O-\underset{Q}{\overset{P}{C}}-H$$

a) P = H, Q = OCH_3
b) P = H, Q = OC_6H_5
c) P = H, Q = SCH_3
d) P = Q = OCH_3
e) P = Q = OC_2H_5

These observations leave little doubt that α-elimination has taken place. In contrast with HCl elimination from halomethanes, the formation of acetic acid rules out a radical mechanism $CH_3COO\cdot$ radicals would instantaneously have given CO_2 [5]. We suggest that a cyclic five-membered

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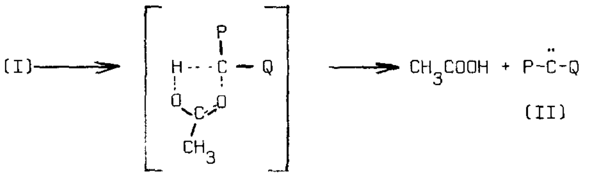
[*] Thermolytic Reactions of Esters. IX; Part VIII: P.C.Oele and R.Louw, Chem.Comm., 1972, in press

[x] An increase of the surface-to-volume ratio (20x) of the reactor affected neither rate nor product composition.

transition state is involved (eq. 1), leaving a carbene (II) which, of course, will undergo further reactions ; under the present conditions these are expected to involve only unimolecular fragmentations and/or isomerizations.



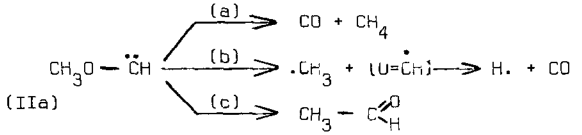
(1)

(Ia-c) : 450 - 525° C

(Id-e) : 325 - 400° C

Indeed, together with acetic acid, large amounts of gaseous products are formed. Thus, neat (Ia) gives CO, CH_4 and C_2H_6 (1 : 0.5 : 0.15), thermolysis in excess of toluene leading to a ratio 1 : 0.8 : 0.1 . In the latter case bibenzyl, benzene and ethylbenzene are also produced.

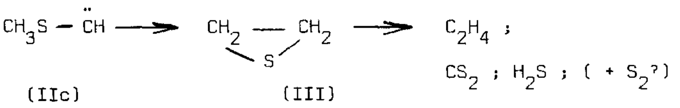
Apparently, (IIa) reacts according to (2a) and/or (2b), the formation of trace amounts of acetaldehyde indicating that (2c) occurs at best only to a minor degree [x] . The H. atoms will react with added toluene via addition - elimination to give benzene [6], or via hydrogen abstraction to give benzyl radicals and hence bibenzyl and ethylbenzene.



(2)

From (Ib) large amounts of CO and benzene (1mole/mole of acetic acid) are formed; the latter compound is free from deuteriumwhen (Ib) is thermolyzed in an excess of C_6H_5— CD_3 . Apparently, phenoxycarbene (IIb) decomposes molecularly (cf. 2a) rather than via radicals.

(Ic) leads to CH_4 - and presumably, CS - together with ethene (and a small amount of ethane). We suggest that (IIc) - apart from decomposing analogous to (2a,b) - inserts (3) and subsequently decomposes :



(3)

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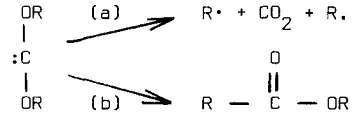
[x] Control experiments show that added acetaldehyde survives for at least 20% even at 525° .

Indeed, we have observed that the product pattern is comparable with that of *authentic* ethylene episulfide (III), thermolyzed under analogous conditions.

From the dialkoxy derivatives (Id, Ie) *CO_2 instead of CO* is formed. Further products — e.g. C_2H_4, C_2H_6 and butane from Ie; the additional production of *propane* from (Id)-(Ie)mixtures — point to (4a). The formation of methylacetate from (Id) and of *ethyl propionate* from (Ie) is interpreted via rearrangement (4b) [7] :



$$:C(OR)_2 \xrightarrow{(a)} R\cdot + CO_2 + R\cdot$$
$$:C(OR)_2 \xrightarrow{(b)} R-\overset{O}{\overset{\|}{C}}-OR$$

(4)

It appears that (resonance) stabilization of the carbene rather than the acidity of the α - proton is the determining factor [8] . For (Ia) we have obtained $\log k = 13.4 - 50.5/\theta$. From thermochemical kinetics [x] it is derived that $CH_3O\ddot{C}H$ must have a stabilization energy of roughly 40 kcal - a value close to that for $:CF_2$.

Thermolytic α-elimination of HZ is probably not restricted to Z = halogen or RCOO. We have evidence for 1,1-elimination of *alcohol* from $HC(OCH_3)_3$. Moreover, I(b) leads to *phenol* (~50%) in addition to acetic acid (~50%) already mentioned.

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[x] From current data[9] one obtains $\Delta H \approx 83$ for $CH_3COOCH_3 \rightarrow CH_3COOH + :CH_2$. By group additivity, $\Delta H^0_f(\mathrm{Ia})_g = -137$; with $\Delta H^0_f(CH_3COOH)_g = -104$, and assuming $E_a = 10$ for the back reaction (insertion of carbene in the O-H bond of acetic acid) one estimates $\Delta H^0_f(CH_3OCH)_g \approx 7$. These estimates lead to $\Delta H_{1a} \approx +40$, $\Delta H_{2a} \approx -50$ and $\Delta H_{2b} \approx +35$. Hence, (2b) — and, presumably, (2a) as well — may have $E_a \approx 35\,\mathrm{kcal.mole}^{-1}$. This order of magnitude would tally with the observation that, in the vapour phase at 250°, CH_3OCH adds to alkene rather than give fragmentation products [10] .

REFERENCES AND NOTES

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