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THERMOLYTIC α-ELIMINATION OF ACETIC ACID FROM METHYLACETATE DERIVATIVES

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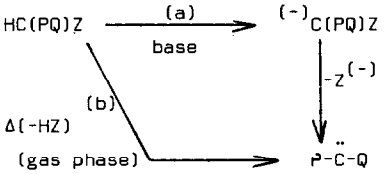
Thermolytic β-elimination - a counterpart of the solvolytic E2-type reaction - has been widely investigated [1].Ionic α-elimination (a), a carbene forming reaction, is also well known.[2] Its thermolytic analogue (b), however, has only been proposed to occur with some chloromethane derivatives (e.g., $CHCl_3$ [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) $CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{P}{\underset{Q}{\overset{|}{\underset{|}{C}}}}-H$

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: $CH_3COO.$ radicals would instantaneously have given CO_2 [5]. We suggest that a cyclic five-membered

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

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