A Novel Skeletal Rearrangement During Ester Pyrolysis

By HAROLD KWART* and D. P. HOSTER

(*Department of Chemistry, University of Delaware, Newark, Delaware,* 19711)

A two-stage mechanism of pyrolytic ester elimination has been advanced[1] as the culmination of extensive rate and product studies by several groups of workers.

$$R\cdot CO_2R' \rightleftharpoons [RCO_2^-]\ [^+R'] \rightarrow R\cdot CO_2H + \text{Olefin}$$

Depuy and King[2] have stressed the factor of the incipient double-bond stability. G. G. Smith and his co-workers,[3] by contrast, have emphasized the role of carbonium-ion stability in the transition state. Emovon and Maccoll,[4] who suggested that the heterolysis of the carbon–oxygen bond is of primary importance, viewed the ester decomposition as being of the same type as thermal dehydrohalogenation of alkyl halides.[1b] Again, an observed parallelism of polar substituent and structural effects is the essential basis of this hypothesis. Whereas with pyrolytic dehydrohalogenations the occurrence of Wagner–Meerwein rearrangement has been cited[5] as evidence for a carbonium-ion mechanism, no example of gas-phase rearrangement of esters has been reported.

The results of the pyrolysis of 2-methyl-2-phenylpropyl acetate, (I), (neophyl acetate) reveal the first instance of skeletal rearrangement made to occur under normal[1b,2] reaction conditions. However, considering the carbonium-ion rearrangement which takes place in the model reaction,[1b,3] the pyrolysis products are strikingly different. Only phenyl migration products are observed, for none of the olefins found represent methyl migration. Two products of β-scission, α-methylstyrene and cumene, are formed at high temperatures as a competing pyrolysis. Furthermore, in the analogous reaction requiring much lower temperatures, neophyl methylxanthate (*ca.* 200°) and neophyl halides (*ca.* 450°) give rise *exclusively* to the same phenyl migration products, the competing fragmentation being entirely absent under these conditions.

Product compositions derived from neophyl substrates may afford a basis for choice between a heterolytic and a homolytic mechanism.[6] In gathering the data (see Table) conditions were selected so as to achieve a small extent of reaction and avoid extensive isomerization of the least stable olefin product. However, at least part of the more stable conjugated product, 1-phenyl-2-methylpropene (II), is formed by isomerization of the unconjugated isomer, 3-phenyl-2-methylpropene (III). Moreover, the ratio of (III)/(II) is within small limits relatively constant (1·5 → 3·3) and in line with the same product ratio (2·2 → 4·8) observed by Ruchardt and Trautwein[6] and by Kharasch and Urry[7] for free-radical elimination of the elements of HCl (by means of RMgBr + $CoCl_2$). On the other hand, the solvolysis of neophyl esters results[8] in a decided predominance of isomer (II); [(III)/(II) ratio = 0·5 → 0·1]. Furthermore, neat liquid-phase pyrolysis, allowed to occur with free evolution of HCl at 275°, affords a similar (III)/(II) ratio = 0·1.

The addition of up to one mole % of di-butyl

TABLE

Product composition data[a] *as a function of temperature and additives in the pyrolysis of neophyl acetate phenyl migration products*

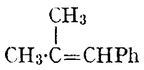
Column temperature	Additive	(III)	(II)	Ratio (III)/(II)	Unreacted % acetate[c]
550°	none	2·6	1·8	1·5	94
550°	DTBP[b]	2·0	1·1	1·8	97
575°	none	5·7	2·6	2·2	87
575°	DTBP[b]	5·3	2·1	2·5	89
600°	none	9·2	2·8	3·3	81
600°	DTBP[b]	8·8	2·7	3·3	83

[a] Essentially the same reaction conditions, apparatus and techniques were employed here as described elsewhere for eliminating the incursion of heterogeneous reaction (ref. 1b).

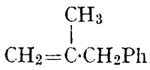
[b] Di-t-butyl peroxide in one mole percent proportion based on neophyl acetate.

[c] Residual product components identified as cumene and α-methylstyrene.

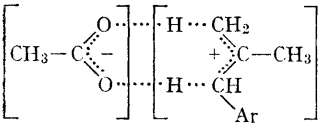
peroxide, a free radical source, has only a minor effect on either the product proportions or the rate of ester decomposition. Thus, we are not dealing with a free-radical chain-mechanism.



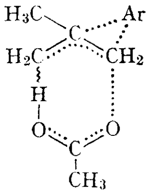
$CH_3{\cdot}\overset{CH_3}{C}{=}CHPh$ (II)



$CH_2{=}\overset{CH_3}{C}{\cdot}CH_2Ph$ (III)



(*A*)



(*B*)

If any significant amount of bond heterolysis had been accompanied by phenyl migration, or, in other words, if we can represent the transition state by analogy to the two-stage mechanism[1] as (*A*), a predominance of the more stable product (II) would be anticipated. The strong preference for formation of the unconjugated isomer (III) [particularly at the higher temperatures where some isomerization to (II) is bound to be taking place; see Table] must be correlated with a seven-membered concerted, cyclic transition state (*B*). Although this must be the first case involving a skeletal rearrangement during gas-phase ester pyrolysis, the fact that a seven-membered cycle is required apparently constitutes no real limitation. The hydrogen nucleus in (*B*) is easily accommodated between the carbon and oxygen atoms engaged in its transfer.

Any effort to account for these product composition results by assuming the intermediacy of benzyldimethylcarbinyl acetate, formed *via* a preliminary internal rearrangement, must fail on the basis of the recognized[2] pattern of pyrolytic elimination in such esters. In all known[9] cases, a large preference for formation of substituted (conjugated) styrene by ester pyrolysis is plainly manifest.

In studies of the pyrolysis of neophyl chloride and related cases found to involve Wagner–Meerwein rearrangement accompanying gas-phase pyrolysis, similar results have been obtained. These all point to the occurrence of a concerted transition state without indications of charge development therein.

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