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ALKYL 1,1-DIALKOXY-ALKANE- AND -ARENE-CARBOXYLATES. Part IV (1).

THERMAL DECOMPOSITION REACTIONS OF 2-ACETOXY-1,3-DIOXOLANES

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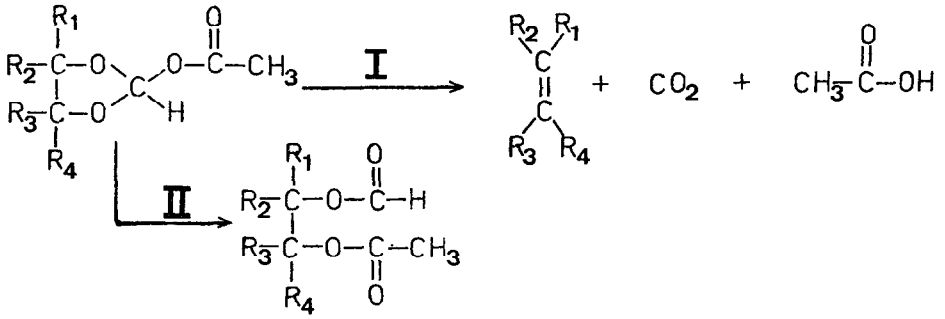
During the last decade several elimination reactions of 2-substituted-1,3-dioxolanes have been described which lead to olefinic substances, involving a stereospecific route (2-12). One of these investigations (6) led to the question whether 2-acetoxy-4,4,5,5-tetramethyl-1,3-dioxolane was an intermediate in the thermal decomposition reaction at 140-160° C of the corresponding 2-ethoxy-1,3-dioxolane in the presence of a catalytic amount of acetic acid. As we had prepared 2-acetoxy-1,3-dioxolanes (13), we were able to study their thermal behaviour.

We found that these compounds underwent decomposition when heated in the absence of either solvent or catalyst at ∿ 120° C. However, the reaction products revealed that two decomposition reactions were realised simultaneously (Reactions I and II).



Reaction I corresponds to the cited elimination reactions. Reaction II is analogous to decomposition reactions of dialkoxymethyl acetates (14,15). Which route will be preferred depends upon the substituents at carbon atoms 4 and 5. With the tetramethyl compound only reaction I is realised under these circumstances.

Table I gives a survey of the results.

TABLE I

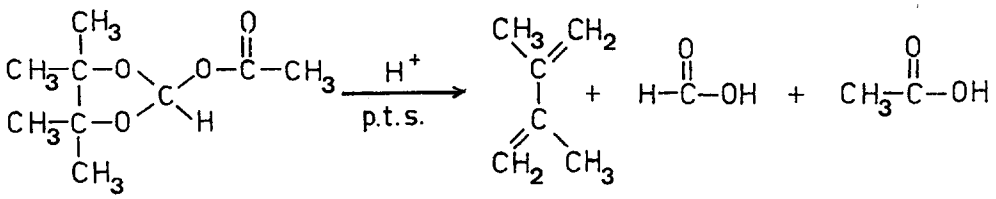
Compound	R_1	R_2	R_3	R_4	% mixed diester	% CO_2	% AcOH	% olefine	decomp. temp. (°C)
1	H	H	H	H	68	30	32	29	120-130
2	H	H	H	CH_3	55	43	46	42	110-120
3	H	CH_3	H	CH_3	34	64	68	65	120-125
4	CH_3	CH_3	CH_3	CH_3	--	96	100	93	130-140
5	H	H	H	CH_2Cl	33	66	67	65	120-140

From this table it is clear that the more methyl groups are present at carbon atoms 4 and 5 the more Reaction I is preferred. Comparison of the results obtained with compounds 2 and 5 indicated that Reaction I is also favoured by electron-withdrawal.

The detailed interpretation of these data, however, is complicated because

(a) carrying out these thermolysis reactions in o-xylene (1 molar solution) the reaction followed exclusively route I for all compounds;

(b) addition of a catalytic amount of p.toluene sulphonic acid (p.t.s.) caused the decomposition of compound 4 in o-xylene to go exclusively by a third route:



This reaction does not involve a mixed diester intermediate, as this compound was found to be stable under these conditions.

The aspects with regard to the detailed mechanism of the decomposition reactions are subject to further investigations.

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