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β-Keto-ester Derivatives from 1-Ethoxyvinyl Carboxylates

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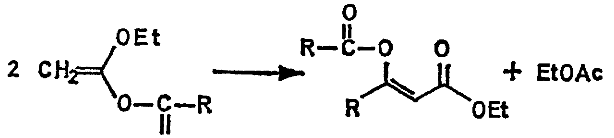
Summary Zinc salts are effective catalysts for converting 1-ethoxyvinyl esters of organic acids into β-acyloxy-αβ-unsaturated esters.

1-ETHOXYVINYL ESTERS (I) may be conveniently prepared by the addition of aliphatic and aromatic acids to ethoxyacetylene in the presence of mercuric ion.[1] We now report that these derivatives may be converted into enol-acylated β-keto-esters (II) by the action of zinc salts. The reactions may be carried out by stirring the esters in benzene solution at 25°, and are usually complete in 5—24 hr.



(I) (II)

This work complements the earlier findings of Zwanenburg[2] who described the thermal conversion of certain ethoxyvinyl esters into β-keto-ester derivatives. However, striking differences were observed between Zwanenburg's results and our own findings. As outlined in the Table, the thermal reaction appeared to be confined to esters of strong acids (containing acyl residues adjacent to electron-withdrawing groups), while[2] ethoxyvinyl acetate was found to be resistant to pyrolysis, and could be distilled without decomposition. By contrast, we have observed† that in the presence of zinc halide catalysts, ethoxyvinyl esters of weaker acids such as acetic, benzoic, and propionic acid undergo ready rearrangement, whereas the esters of strong acids such as trichloroacetic acid give poor yields of products.

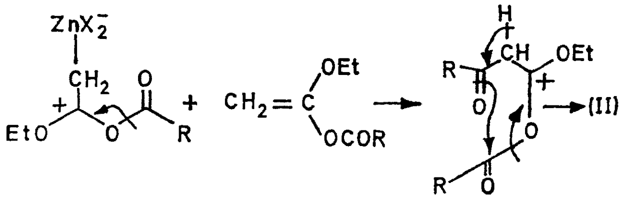
The effectiveness of zinc halides in bringing about the conversion of (I) into (II) may be explained by the following mechanism[3,4] in which the zinc salts enhance the reactivity of the alkoxyvinyl ester as an acylating agent. Transfer of an RCO^+ fragment (more highly stabilized in cases where the R group is electron-releasing) to a second molecule

Formation of O-*acyl-β-keto-esters from ethoxyvinyl carboxylates*

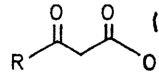
(I), (II)	Zinc salt-catalysed rearrangement	Thermal rearrangement[2]
a: R = Ph	89	0
b: R = Me	84	0
c: R = Et	75	—
d: R = CH_2Ph	79	43·5[a,b]
e: R = CH_2Cl	4	74
f: R = CCl_3	0	45

[a] β-Isomer obtained.

[b] In the thermal rearrangement of (IId), the crude material was pyrolysed in the presence of mercuric acetate, which may have acted as an acid catalyst analogous to the zinc halides.



(III)



(IV) a; R=Ph b; R=Me

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† All compounds reported herein show i.r. and n.m.r. spectra consistent with the assigned structures. The spectra of compounds (IIa), (IIb), (IVa), and (IVb) were found to be identical to those of authentic samples. Satisfactory elemental analyses were obtained for all other compounds.

of ethoxyvinyl ester leads to the intermediate (III), which, with proton loss, may rearrange to the observed product.

The reaction described above thus represents a novel, mild method for converting weaker organic acids into derivatives of β-keto-esters,‡ and may find useful application in synthetic work.

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‡ The acylated β-keto-esters (IIa) and (IIb) may be hydrolysed to the parent β-keto-esters (IVa) (87%) and (IVb) (46%) by treatment with an equimolar amount of conc. H_2SO_4, followed by brief heating of the acidic aqueous solution. Alternatively, (IIb) is converted into (IVb) (56%) by treatment with 0·5N-ethanolic HCl at 25°.

[1] H. H. Wasserman and P. S. Wharton, *Tetrahedron*, 1958, **3**, 321; H. H. Wasserman and P. S. Wharton, *J. Amer. Chem. Soc.*, 1960, **82**, 661.

[2] B. Zwanenburg, *Rec. Trav. chim.*, 1963, **82**, 593.

[3] More recently, E. S. Rothman and G. G. Moore, *Tetrahedron Letters*, 1969, 2553 have reported that isopropenyl esters of long-chain acids are converted into symmetrical β-diketones by the action of aluminium chloride in hexane solution.

[4] Analogous thermal and boron trifluoride-catalysed rearrangements of isopropenyl esters to β-diketones are described by F. G. Young, F. C. Frostick, jun., J. J. Sanderson, and C. R. Hauser, *J. Amer. Chem. Soc.*, 1950, **72**, 3635.