A NOVEL SYNTHESIS OF VINYL ESTERS FROM VINYLVERSATATE-10

M. A. S. MONDAL, R. VAN DER MEER, A. L. GERMAN* and D. HEIKENS

Laboratory of Polymer Technology, Eindhoven University of Technology, Eindhoven, The Netherlands

Abstract—Vinylversatate-10 (VV10)[1] has successfully been used to synthesise a large number of lower vinyl esters by transvinylation in presence of mercuric acetate and sulfuric acid. The synthesis of vinylhalo esters proceeds with more difficulty. It has been observed that neither Hg(OAc)₂ nor H₂SO₄ alone is capable of initiating the transvinylation. Furthermore, it has been found that a molar ratio 2:1 of VV10 to carboxylic acid is sufficient to drive the reaction to the right by continuous distillation of the vinyl ester formed, and as a result a high yield of vinyl ester is obtained. A mechanism for this reaction and for the formation of side products has been proposed.

INTRODUCTION

Although the synthesis of vinyl esters has been known since 1912, most of the methods are useful in specific cases only, and as laboratory methods the yields are poor.

The classical method is the direct vinylation using acetylene and carboxylic acid. This reaction has only been used to produce the esters on an industrial scale. In spite of engineering problems (e.g. corrosion) it appears that for vinyl acetate the ethylene based process may replace the acetylene process. Most of the vinyl esters other than vinyl acetate, vinyl propionate and vinyl versatates, used today, are not produced on a large scale. The transvinylation or vinyl interchange method is commonly and conveniently used in the laboratory, but also in industry, especially when purification by distillation is difficult.

The transvinylation reaction using vinyl acetate in presence of catalytic amounts of mercuric salts was first described by Herrmann and Haehnel[2] in 1941 and by Toussaint and Mc-Dowell[3] in 1943. The main side reaction, the formation of ethylidene diacetate, was controlled by running the reaction at a low temperature for a long time.[4] Chatterjee et al.[5] used HF in combination with mercuric acetate to shorten the reaction time and improved the overall yield. Use of PdCl₂ instead of mercuric salts also gave higher yields.[6] Warson et al.[7] described the preparation of vinyl esters by vinyl interchange of C₃-C₂₆ acids with vinyl acetate using mercuric salts of aromatic sulfonic acids as catalyst.

In many cases, the synthesis of vinyl esters from vinyl acetate by the transvinylation method requires refluxing for a long time and the formation of ethylidene diacetate is very high. Consequently the yield of vinyl ester is very low.

Shell Chemical Company produces a number of vinyl esters of branched carboxylic acids. These vinyl esters (called vinyl versatates) are easily available, cheap and have relatively high boiling points. A new procedure has, therefore, been obtained, which is applicable to the synthesis of lower vinyl esters starting from vinyl versatate-10 (VV10). Advantage was taken of the fact that the desired vinyl ester is directly distilled from a solution containing catalyst, vinylating agent and carboxylic acid. This is feasible since vinyl esters generally have b.ps about 40–50° below those of the acids from which they are derived. Thus changing the vinylating agent from vinyl acetate to VV10 improves the overall yield and produces vinyl esters easily.

EXPERIMENTAL

General experimental procedure. The transvinylation reaction was carried out in a 3-necked one litre flask fitted with a glass stirrer, N₂ inlet tube and a distillation column. A mixture of two moles of VV10 and one mole of carboxylic acid together with 2% mercuric acetate by weight of acid, 0·005 mole of H₂SO₄ and 2–4 g of p-t-butylcatechol (inhibitor) was introduced into the flask. Before heating and during the reaction N₂ gas was passed through the mixture and the contents was stirred. The temp was controlled by using a constant temp silicone oil bath. The vinyl ester formed was collected directly from the flask during the reaction by continuous distillation.

It has been observed by GLC in every synthesis that the product obtained by continuous distillation contained some acetaldehyde and vinyl acetate. Traces of metallic mercury were also found inside the cooler. Finally, the product obtained was distilled once more using a fractionating column. The purity of the synthesised vinyl esters was checked by b.p, refractive index, IR spectrum and GLC. The reaction conditions, percentage conversion and physical constants of the vinyl esters are shown in Table 1.

DISCUSSION

It will be evident from the results shown in Table 1 that the yields of vinyl esters are very high as compared with the literature values, where vinyl acetate was used.[8] Heating for 3 hr was also found to be sufficient to obtain vinyl esters in good yields from VV10 instead of 8–12 or more hr[4,9] when starting from vinyl acetate. This is possible because of the fact that the desired vinyl ester was continuously distilled from a solution of catalyst, a high boiling vinylating agent (VV10) and carboxylic acid, thus shifting the equilibrium to the right.

$$VV10 + RCOOH \rightleftharpoons RCOOH = CH_2 + V10\,acid$$

Table 1. Synthesis of vinylesters from vinylversatate (VV10)

Name of acid	Quantity used for synthesis				Temp °C	Time hour	% Conversion based on acid	% Yield*	B.p of ester °C	°C n_D
	Acid mole	VV10 mole	Mercuric[c] Acetate g	Sulfuric acid mole						
Formic[a] (98%)	1	2	1·4	0·005	95	4	35	60	44–46	1·3842[20]
Acetic[a] (98·8%)	1	2	1·5	0·005	90	3	70	90	72–73	1·3942[20]
Propionic[a] (99·8%)	1	2	1·5	0·005	120	3	80	90	93·5–95	1·4005[20]
Butyric[b] (99·8%)	1	2	1·6	0·005	140	3	75	80	116–118	1·4113[20]
Isobutyric[b] (99·8%)	1	2	1·8	0·005	120	3	70	75	103·5–105	1·4056[20]
Chloroacetic[a] (99%)	1	2	2·0	0·006	150	6	60	70	135–136	1·4444[19]
Bromoacetic[b] (Purum)	1	2	2·5	0·006	160	3	25	75	145	1·4750[20]
Dichloroacetic[b] (99·5%)	2	4	6·0	0·012	125	7	35	45	48–52 (20 mm Hg)	1·4539[25]
Trichloroacetic[b] (99·6%)	1	2	3·0	0·006	150	5	No vinyl interchange reaction			
Trifluoroacetic[b] (Purum)	1	2	3·0	0·006	70	5	No vinyl interchange reaction			

*% Yield calculated from % conversion on mole basis after purification; [a]Merck; [b]Fluka; [c]Riedel-de Haën.
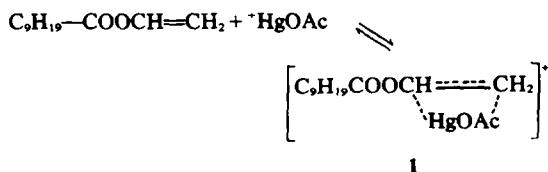
Moreover, further reaction of the newly formed vinyl ester with the added carboxylic acid to form acylal is also minimised.

Considering the mechanism reported by Slinckx and Smets[10,11] and Hopff and Osman[12,13] for the transvinylation using vinyl acetate, we propose the following scheme for the vinyl interchange with VV10.
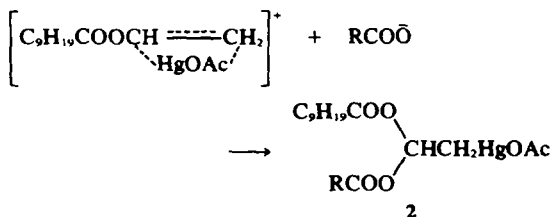
This mechanism is in agreement with our experimental results. The catalyst acts as follows:
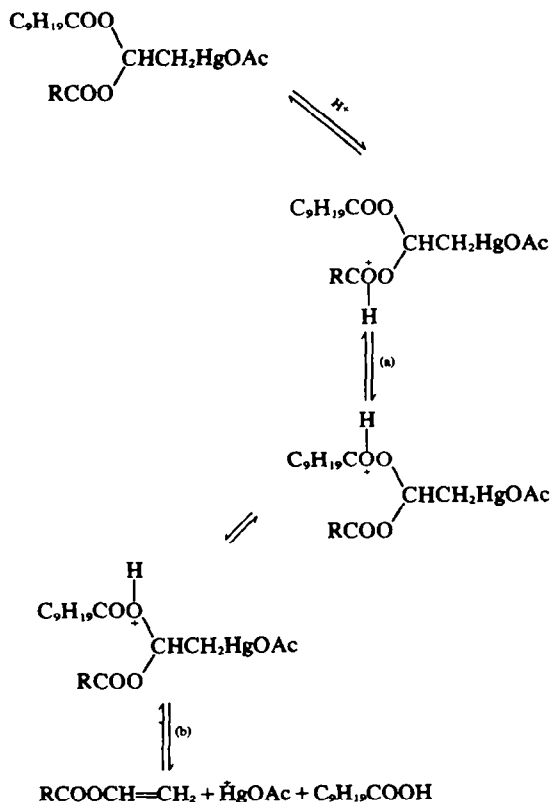
$$H(OAc)_2 + H^+ \rightleftharpoons {}^+HgOAc + HOAc$$
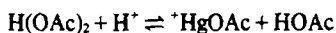
The cation formed reacts with VV10 giving a complex,

$$C_9H_{19}-COOCH{=}CH_2 + {}^+HgOAc$$

$$\left[C_9H_{19}COOCH \stackrel{\cdots}{=\!=\!=} CH_2 \atop \cdots HgOAc \right]^+$$

1

This complex ion (1) then reacts with an anion derived from the added acid giving an intermediate compound (2).

$$\left[C_9H_{19}COOCH \stackrel{\cdots}{=\!=\!=} CH_2 \atop {}_{\cdots}HgOAc \right]^+ + RCO\bar{O}$$

$$\longrightarrow \quad \begin{array}{c} C_9H_{19}COO \\ RCOO \end{array}\!\!CHCH_2HgOAc$$

2

The intermediate (2) reacts further with a strong acid,

$$\begin{array}{c} C_9H_{19}COO \\ RCOO \end{array}\!\!CHCH_2HgOAc$$

$$\begin{array}{c} C_9H_{19}COO \\ RC\overset{+}{O}O \\ H \end{array}\!\!CHCH_2HgOAc$$

(a)

$$\begin{array}{c} C_9H_{19}\overset{+}{C}OO \\ RCOO \end{array}\!\!CHCH_2HgOAc$$

$$\begin{array}{c} C_9H_{19}C\overset{+}{O}O \\ RCOO \end{array}\!\!CHCH_2HgOAc$$

(b)

$$RCOOCH{=}CH_2 + \overset{.}{H}gOAc + C_9H_{19}COOH$$

The equilibrium (a) depends on the nature of R in such a way that a more electron donating group R will shift the equilibrium backward.

Though R has influence on the equilibrium (a), it also determines the elimination equilibrium (b) which is the rate determining step. This elimination step will be faster when R is an electron donating group, i.e. the vinyl interchange will be favoured with weaker acids (RCOOH). Thus going from $-CX$ via $-CX_2$ to $-CX_3$ (X = halogen), the group R becomes more electron withdrawing, so the chance of occurrence of the elimination reaction (b) becomes increasingly smaller. This scheme is consistent with our experimental results, monochloro- and monobromoacetic acid react rather slowly, dichloroacetic acid reacts still slower, trichloro- and trifluoroacetic acid do not give vinylesters at all.

Moreover, as reported by Sandler[9], the failure of the synthesis of vinyltrichloro- and trifluoro-esters from vinylacetate by the transvinylation method may be due to the formation of acylal directly:

$$R_1COOH + R_2COOCH = CH_2 \rightarrow CH_3CH \underset{OCOR_2}{\overset{OCOR_1}{<}}$$
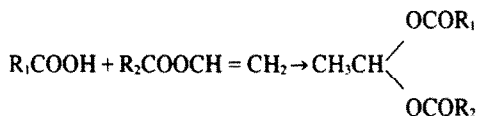
It has been observed that neither H_2SO_4 nor $Hg(OAc)_2$ alone is capable of initiating the transvinylation. The intermediate compound (2) was isolated in crystalline form during the transvinylation using a low concentration of H_2SO_4 (0·001 mole). The mechanism given for the transvinylation also explains the need for a strong acid in combination with mercuric acetate.

Furthermore, the presence of small amounts of vinyl acetate and acetaldehyde as products can now be explained. The complex cation (1) may also react with the acetate anion derived from mercuric acetate to produce vinyl acetate. This vinyl acetate may undergo hydrolysis in presence of H^+ to form vinyl alcohol, which immediately rearranges to give its tautomer-acetaldehyde.

$$CH_2\!\!=\!\!CHCOOCH_3 \xrightarrow[H^+]{H_2O} CH_3CHO + CH_3COOH$$
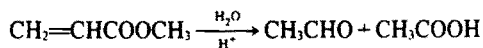
Any acylal formed during the reaction may also decompose to give anhydride and acetaldehyde.

$$CH_3CH \underset{OCOR_2}{\overset{OCOR_1}{<}} \longrightarrow \underset{R_2CO}{\overset{R_1CO}{>}} O + CH_3CHO$$
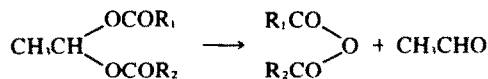
REFERENCES

[1] VV® 10 Vinyl Monomer, Development Product, Shell Chemical Company
[2] W. O. Herrmann and W. Haehnel, U.S. Pat., 2245131 (1941), Chem. Abstr. 35, 5908 (1941)
[3] W. J. Toussaint and L. G. McDowell Jr. U.S. Pat., 2299862 (1942), Chem. Abstr. 37, 1722 (1943).
[4] R. L. Adelman, J. Org. Chem. 14, 1057 (1949)
[5] P. C. Chatterjee, H. Dakshinamurti and J. S. Aggarwal, Indian J. Techn. 4, 173 (1966)
[6] A. Sabel, J. Smidt, R. Jira and H. Prigge, Chem. Ber. 102, 2939 (1969)
[7] H. Warson, J. E. O. Mayne and R. J. Parsons, Brit. Pat., 827718 (1960), Chem. Abstr. 54, 15248 (1960)
[8] S. Nozakura, M. Sumi, M. Voi, T. Okamoto and S. Murahashi, J. Pol. Sc. Chem. 11, 279 (1973)
[9] S. R. Sandler, J. Chem. Eng. Data 14, 503 (1969)
[10] G. Slinckx and G. Smets, Tetrahedron 22, 3163 (1966)
[11] G. Slinckx and G. Smets, Ibid, 23, 1395 (1967)
[12] H. Hopff and M. A. Osman, Ibid. 24, 2205 (1968)
[13] H. Hopff and M. A. Osman, Ibid. 24, 3887 (1968)