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THE VINYL-INTERCHANGE REACTION—II

VINYL ACETATE WITH CARBOXYLIC ACIDS WEAKER THAN ACETIC ACID

H. HOPFF and MAGED A. OSMAN

Department of Organic Technology, Swiss Federal Institute of Technology, Zürich

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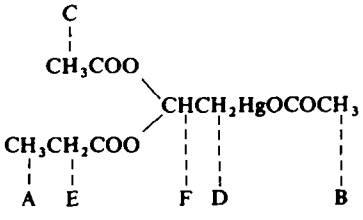
Abstract—Some new organo-mercurial compounds have been synthesized and examined by NMR. It has been shown by NMR spectroscopy that a unified mechanism can be applied to the vinyl-interchange reaction of vinyl acetate with carboxylic acids which are either stronger or weaker than acetic. The effect of the electron donating character of R in RCOOH on the formation and decomposition of the mercurial intermediate has been discussed.

INTRODUCTION

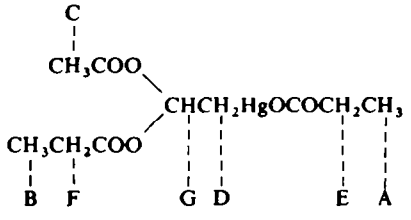
IN A previous publication,[1] the vinyl-interchange reaction of vinyl acetate with carboxylic acids stronger than acetic acid was described. A mechanism for this reaction was proposed and the mercurial intermediate isolated. The aim of the present study is to investigate whether the proposed mechanism can also be applied to the reaction with acids weaker than acetic.

RESULTS AND DISCUSSION

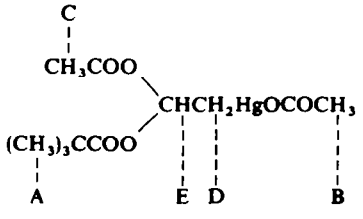
2-Acetoxymercury-1,1-diacetoxy ethane (I) was reported to react with acids stronger than acetic acid but not with weaker acids, viz. propionic and pivalic. Compounds (II–V) were synthesized and their structure established by NMR



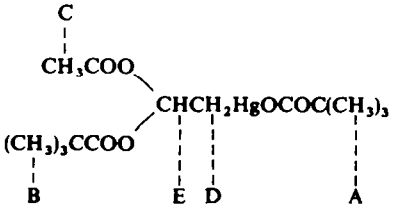
II



III



IV



V

spectroscopy (Table 1). They are stable only for short periods at room temperatures. A mixture of 1 mole propionic acid and 1 mole mercuric acetate was warmed and shaken till complete dissolution in vinyl acetate. The produced mercurial compound

TABLE 1. NMR SPECTRAL DATA TAKEN IN $CDCl_3$*

	A	B	C	D†	E	F	G	$J_{^{199}Hg-H^{\alpha}}$
II	1·15/T J = 7·5 c/s	2·03/S	2·08/S	2·27/D 4·8 c/s	2·36/Quart 7·5 c/s	7·01/T 4·8 c/s		216·8
III	1·14/T J = 7·5 c/s	1·15/T 7·5 c/s	2·10/S	2·26/D 4·8 c/s	2·32/Quart 7·5 c/s	2·36/Quart 7·5 c/s	7·03/T 4·8 c/s	216·8
IV	1·20/S	2·05/S	2·08/S	2·28/D J = 4·8 c/s	6·96/T 4·8 c/s			217·6
V	1·20/S	1·23/S	2·08/S	2·27/D J = 4·8 c/s	6·98/T 4·8 c/s			217·6

* The NMR spectra were determined on a spectrometer at 60 Mc/s, temp ca. 40°, conc ~0·25 molar. The chemical shifts given are δ values (ppm downfield from TMS).

† The protons of these doublets were found to be magnetically equivalent.

was precipitated with petroleum ether, washed thoroughly until it solidified, and then dried in a rotatory evaporator under oil pump vacuum. The NMR spectrum of the remaining solid (Fig. 1) shows that compound (I) is the main product formed together with some 2-acetoxymercury-1-acetoxy-1-propionoxy ethane (II) and

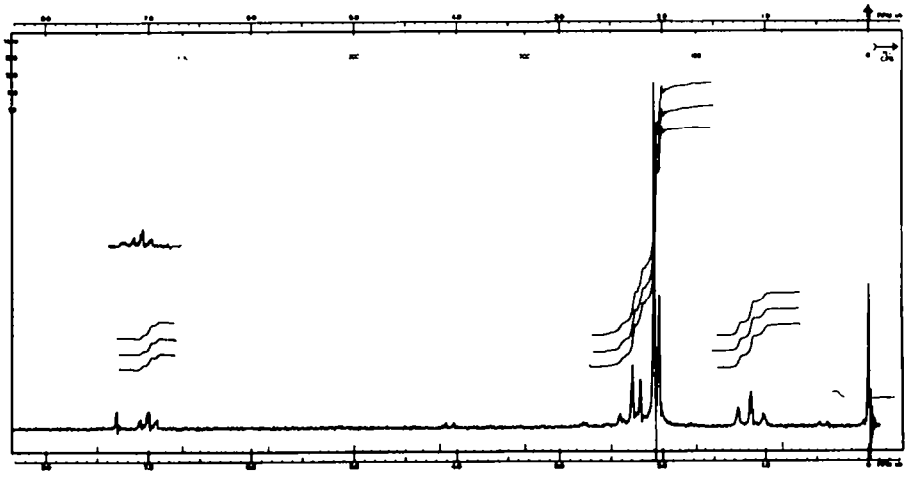
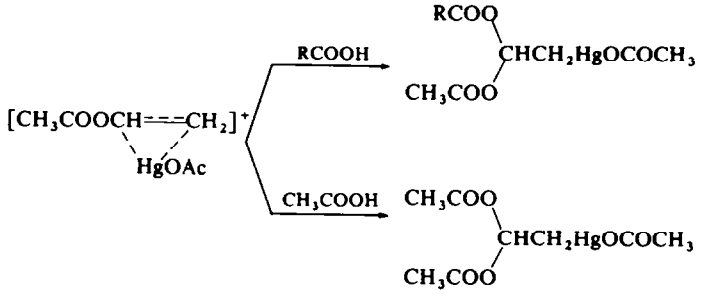


FIG. 1

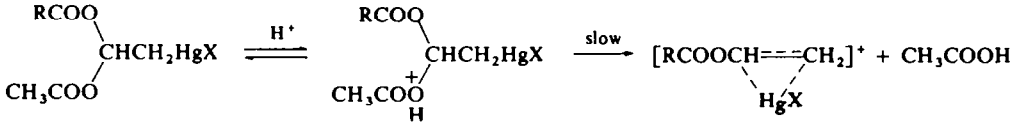
probably some 1-acetoxy-2-propionoxymercury-1-propionoxy ethane (III). A fact which is to be expected from the previously proposed mechanism for the formation of these mercurial compounds.



As weaker acids will react slower than acetic, compound I is mainly formed.

These results indicate that compounds of the type II and/or III are the mercurial intermediates responsible for the vinyl-interchange reaction of vinyl acetate with weaker acids than acetic. However, in this case the catalytic intermediates are formed in smaller quantities than in case of stronger acids, thus giving slower catalytic effect.

As mentioned before the rate determining step is the elimination reaction:



This elimination step should be faster when R is an electron donating group (compare hydrolysis of esters), i.e. the vinyl-interchange should be faster with weaker acids than with stronger acids than acetic. The overall rate of reaction will be the sum of these contradicting factors. Table 2 shows clearly that the electron donating character of R dominates the catalytic effect.

TABLE 2

Acid	p*K*	% Yield*
Chloroacetic	2·85	11·3†
Benzoic	4·19	19·5
Phenylacetic	4·28	32·7
Isobutyric	4·84	42·7†
Propionic	4·87	40·4†

* Yield of pure vinyl ester after 5 hr reaction time.

† Yield was determined by gas chromatography of an acid free sample of the reaction mixture.

EXPERIMENTAL

Reaction of compound I *with propionic and pivalic acids.* An equimolecular quantity of the acid was added to a conc soln of I in acetone. The soln was filtered and the product precipitated with petrol (30–50)

as an oil. The oil was redissolved and reprecipitated twice, then triturated with petrol until it solidified. The solid was found by NMR and mixed m.p. to be unreacted I.

Synthesis of compounds II *and* IV. Acetic acid (0·01 ml) was added to an equimolecular mixture of the corresponding vinyl ester and mercuric acetate in acetone. The reactants were slightly warmed on a water bath till complete dissolution. The soln was filtered and the product precipitated with petrol. The mercurial compound was redissolved and reprecipitated twice, then dried in a rotatory evap. under vacuum. Compound II was a crystalline solid easily soluble in acetone, alcohol, and benzene but insoluble in petrol and hexane. It was recrystallized from acetone–ether, m.p. 46·5–47°. (Found: C, 25·73; H, 3·42: Hg, 47·87. Calc: C, 25·81; H, 3·37; Hg, 47·90%). Compound IV was a glass clear sticky mass. Its solubility properties were as above. (Found: C, 29·44; H, 4·10; Hg, 44·95. Calc: C, 29·56; H, 4·06; Hg, 44·89%).

1-*Acetoxy-2-propionoxymercury-1-propionoxy ethane* (III). Mercuric-II-propionate (0·01 mole) was warmed in 20 ml vinyl acetate on a water bath till complete dissolution. The product was precipitated and purified as usual. It is a colourless oil, soluble in acetone, alcohol, and benzene but insoluble in petrol and hexane. (Found: C, 27·56; H, 3·81; Hg, 46·49. Calc: C, 27·75; H, 3·73; Hg, 46·35%).

1-*Acetoxy-2-pivaloxymercury-1-pivaloxy ethane* (V). Mercuric-II-pivalate (m.p. dec. 223·5° 0·01 mole) and 20 ml vinyl acetate were warmed till complete dissolution. The soln was filtered and the excess vinyl acetate distilled off under reduced press. The remaining oil was dissolved in petrol and the solvent evaporated several times to get rid of all traces of vinyl acetate. Finally the oil was dried in a rotatory evap. under oil pump vacuum at room temp.

The product is a glass clear sticky mass easily soluble in all known solvents even in petrol. (Found: C, 34·63; H, 5·06; Hg, 41·08. Calc: C, 34·39; H, 4·95; Hg, 41·03%).

Vinyl-interchange with acids mentioned in Table 2. Oleum (ca. 20%; 0·03 mole) was added to a mixture of 1 mole vinyl acetate, 4×10^{-4} mole mercuric acetate and 0·1 mole of the corresponding organic acid. The reactants were shaken at room temp for 5 hr. The reaction mixture was then shaken with a soln of 6 g Na_2CO_3, separated and the excess vinyl acetate distilled off under reduced press. The remaining vinyl ester in ether was washed twice with 2N Na_2CO_3, then with sat NaCl aq and finally dried over Na_2SO_4. The ether was distilled off and the yield of vinyl ester determined. The purity of the product was examined by TLC.

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REFERENCE

[1] *Tetrahedron.*