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THE MECHANISM OF VINYL INTERCHANGE BY NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

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Abstract—The mechanism of the vinyl interchange reaction between benzoic acid and vinyl acetate and catalysed by mercury-II acetate and an acetic solution of the BF_3–AcOH complex has been investigated by NMR spectroscopy. For this purpose $\alpha\beta\beta'$-trideutero-vinyl acetate and deutero-O-acetic acid have been synthesized. During the course of the vinyl interchange, the vinyl group is transferred as a whole entity from one carboxylate radical to the other without any carbon-hydrogen bond scission. β-Acetoxy mercuri ethane $\alpha\alpha'$-diesters postulated as intermediates of the reaction have been prepared and characterized; these compounds are effectively reaction intermediates. The isolation and structural elucidation of some deuterated ethylidene diesters demonstrates the mechanism of side reactions of the addition of acid to vinyl esters.

Résumé—On a étudié par spectroscopie de RMN le mécanisme de la réaction de transvinylation entre l'acide benzoïque et l'acétate de vinyle catalysée par l'acétate de mercure II et une solution acétique du complexe acide acétique-fluorure de bore. A cet effet, on a préparé l'$\alpha\beta\beta'$-trideutero-acétate de vinyle et l'acide deutéro-O-acétique. On démontre qu'au cours de la réaction le groupement vinylique est tranféré intégralement d'un radical carboxylique à l'autre sans rupture de lien carbone hydrogène. D'autre part l'$\alpha\alpha'$-diester du β-acétoxy mercuri-éthane présenté comme l'intermédiaire de réaction a été synthétisé et identifié; ce composé peut effectivement agir comme intermédiaire de réaction. Enfin l'obtention et l'étude structurale de quelques diesters éthylidéniques marqués au deuterium démontrent le mécanisme des réactions secondaires d'addition d'acide à la fonction vinylique.

INTRODUCTION

VINYL interchange reactions are equilibrium reactions between a vinyl ester or ether on one hand and an organic acid or alcohol on the other hand[1–20] according to Eq. (1)

$$R_1OH + R_2O{-}CH{=}CH_2 \rightleftarrows R_1O{-}CH{=}CH_2 + R_2OH \quad (1)$$

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where R_1 and R_2 represent either acyl or alkyl groups. Apparently the reactions proceed only in the presence of catalytic amounts of mercury II-salts coupled with a strong acid. It may be accompanied by some side-reactions, e.g. the formation of ethylidene diesters (Eq. 2)

$$R_1COOH + R_2COOCH{=}CH_2 \rightarrow R_1COO{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}OOC{-}R_2 \qquad (2)$$

where R_1 and R_2 may be identical or different.

The first interpretation of the mechanism of vinyl interchange was presented by Adelman;[13] it consisted in the dissociation of the vinyl ester into the corresponding acid and acetylene which would be involved in a mercury salt complex (I).

$$\begin{array}{c} CH{=}CH \\ \diagdown\!\diagup \\ HgSO_4 \end{array} \qquad (I)$$

More recently Watanabe and Conlon[10] proposed the following mechanism in the case of vinyl ether interchange:

$$Hg(OAc)_2 \rightleftarrows {}^{(+)}HgOAc + AcO^{(-)}$$

$$AcOHg^{(+)} + RO{-}CH{=}CH_2 \underset{}{\overset{R'OH}{\rightleftharpoons}} \underset{R'O}{\overset{RO}{\diagdown\!\diagup}}CH{-}CH_2{-}HgOAc + H^{(+)}$$

$$\underset{R'O}{\overset{RO}{\diagdown\!\diagup}}CH{-}CH_2{-}HgOAc + ROCH{=}CH_2 \overset{R'OH}{\rightleftharpoons} \left[\underset{R'O}{\overset{RO}{\diagdown\!\diagup}}CH{-}CH_2\right]_2 Hg + HOAc$$

$$\underset{R'O}{\overset{RO}{\diagdown\!\diagup}}CH{-}CH_2{-}HgOAc + R'OCH{=}CH_2 + ROH$$

A similar reaction path was suggested for the vinyl transesterification. It is the purpose of the present paper to examine the nature of the reaction intermediate in the course of the vinyl transesterification using the PMR technique. In these experiments vinyl acetate and benzoic acid were mixed in the presence of mercury II-acetate as catalyst and an acetic acid solution of BF_3–AcOH complex as strong acid.

EXPERIMENTAL

NMR spectra of the undiluted samples (Varian A 60 spectrometer; δ-scale, using TMS as internal standard.

Deutero-O-acetic acid was prepared by adding 2 g D_2O to 10·2 g (0·1 mole) fresh distilled Ac_2O in the presence of a drop anhydrous H_2SO_4; the mixture was cooled and stirred magnetically. After several hr contact, the mixture was heated at 100° for 3 hr, then anhydrous AcOK was added to neutralize the strong acid. The AcOH was then distilled neglecting the first and last mls; its isotopic purity was higher than 98%.

Dideutero-acetylene was generated from CaC_2 and heavy water. It was further purified by passing through a 10% $K_2Cr_2O_7$ solution in H_2SO_4 and then dried over conc H_2SO_4.

αββ'-Trideutero-vinyl acetate. In a 15 ml erlenmeyer flask provided with a small reflux condenser and a magnetic stirrer 0·3 g yellow HgO was dissolved in 3 ml deutero-O-acetic acid; then 0·15 ml BF_3–AcOH complex solution (see next paper) was added. The mixture was frozen, and the air of the apparatus removed under vacuum; dideutero-acetylene was then introduced slowly with vigourous stirring, the temp being kept below 30°. The mixture firstly became cloudly with formation of white precipitate, then turned grey and finally brown with partial redissolution of the precipitate. When the gas absorption stopped (after ca. 6 hr) the catalyst was destroyed by adding a small amount of AcOK. The reaction product was then washed with water, and with Na_2CO_3aq, dried ($CaCl_2$) and carefully distilled neglecting the last fraction, rich in ethylidene diacetate.

Ethylidene diacetate was prepared by reaction of AcOH with vinyl acetate at 70° for 5 hr, in the presence of small amounts of BF_3–AcOH complex. After neutralization with AcOK the excess AcOH was removed by washing with a Na_2CO_3aq; the diacetate was purified by distillation under red. press. b.p. 15 mm Hg: 75°. (Found: C, 49·75; H, 6·89%. $C_6H_{10}O_4$ requires: C, 49·31; H, 6·90%.)

The same procedure was followed in order to prepare the deuterium labelled diesters viz. *β-deuteroethylidene diacetate* from vinyl acetate and deutero-O-acetic acid (Found. C, 48·76; O, 43·33. $C_6H_9DO_4$ requires: C, 48·97; O, 43·49%) and *αββ'-trideutero ethylidene diacetate* from αββ' trideuterovinyl acetate and AcOH.

αα'-diacetoxy-β-acetoxymercuri ethane: $(AcO)_2CH–CH_2–HgOAc$ (IIa). Mercuric acetate (3 g) added to 3 ml vinyl acetate was gently heated for a moment: an exothermic reaction took place and the solid phase dissolved. The solution was filtered and compound IIa was obtained in quantitative yield after evaporation of the solution at normal temp. It was recrystallized from AcOEt m.p.: 88°. (Found: C, 23·71; H, 2·96; O, 23·71%. $C_8H_{12}HgO_8$ requires: C, 23·74; H, 2·99; O, 23·72%.)

α-benzoyloxy-α'-acetoxy-β-acetoxymercuri ethane: (BzO) (AcO)CH–CH_2–HgOAc (IIb). Mercuric acetate (3·18 g) and 1·48 g vinyl benzoate were boiled in 2 ml chf until the mercuric salt had completely dissolved. The filtered solution gave after evaporation and recrystallization compound IIb. (Found: C, 33·89; H, 3·20; O, 20·50%. $C_{13}H_{14}HgO_8$ requires: C, 33·45; H, 3·02; Hg, 42·97; O, 20·56%.)

EXPERIMENTAL RESULTS AND DISCUSSION

A. *Vinyl Interchange Reaction*

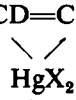
Two different reaction paths have been followed for demonstrating the reaction mechanism; they consist of the addition of a deuterium-ion or a hydrogen ion to an initially undeuterated vinyl group. Both methods will be considered.

1. *Reaction with unlabelled vinylester*

a. The NMR-spectrum of an equimolar mixture of deutero-O-acetic acid and vinyl acetate consists of one singlet at 2·03 δ (methyl group of the acetic acid), one singlet at 2·08 δ (methyl group of the vinyl acetate), the ABX pattern of the vinyl group (two doublets at 7·27 δ, for the X part of the spectrum and two doublets at 4·80 δ and two doublets at 4·52 δ for the AB part of the spectrum, and finally a small singlet due to the residual proton concentration in the deuterated carboxylic acid group at 11·38 δ. After addition of catalytic amounts of BF_3–AcOH complex this last signal is somewhat increased but it then remains constant with time, even after standing 3 days. This shows that no acid catalysed hydrogen exchange proceeds under these conditions. The vinyl interchange reaction was then repeated in the presence of $Hg^{(II)}$ acetate-BF_3 complex; no increase of the carboxylic hydrogen signal could be detected unless the mixture was heated at higher temperature (70°) for 5 hr. The vinylic absorption however disappears completely on account of the addition reaction yielding the corresponding deuterated ethylidene diacetate compound

$(CH_3–COO)_2CH–CH_2–D$: a singlet at 2·00 δ of the CH_3COO-group, a doublet at 1·41 δ J = 5·8 c/s for the CH_2D group, and a multiplet (septet) at 6·78 δ due to the CH-group.

On the basis of this first experiment a reaction intermediate such as CH=CH or CD=CH can already be excluded.



b. In a second experiment deutero-O-acetic acid and vinyl benzoate (VOBz) were allowed to react at the temperature of the magnet (ca 37°). Before addition of catalyst, the spectrum shows (Fig. 1a) a singlet at 2·02 δ (methyl group of acetic acid), two doublets at 4·93 δ (H of the $=CH_2$ group in vinyl benzoate in *trans*-position to —CH = J; *trans* = 14 c/s, *Jgem* = 1·5 c/s), two doublets at −4·57 δ (the other H of $=CH_2$ group, in *cis*-position to —CH=; *Jcis* = 6·5 c/s, *Jgem* = 1·5 c/s) a

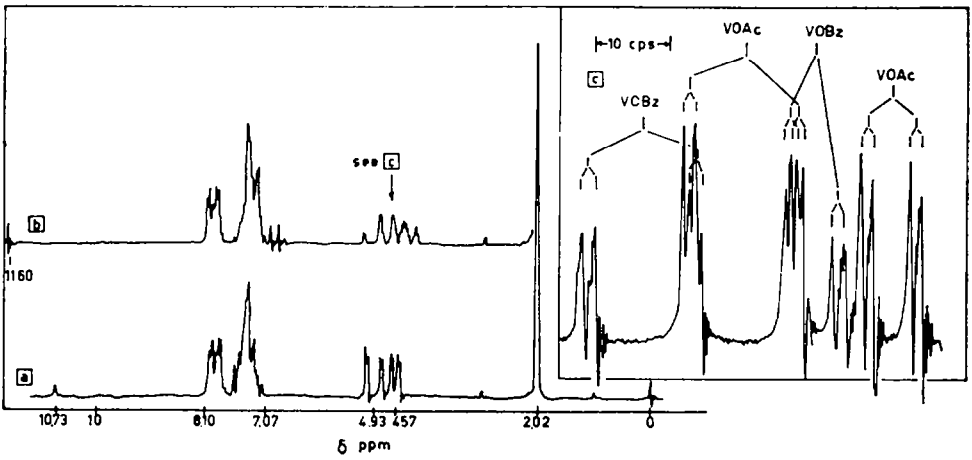


FIG. 1. 60 Mc NMR Spectra of
(a) an equimolecular mixture of vinyl benzoate andO-deuterated acetic acid before reaction.
(b) solution (a) during vinyl interchange reaction
(c) partial expanded region of spectrum 1b (methylenic absorptions)
VOBz = vinyl benzoate
VOAc = vinyl acetate.

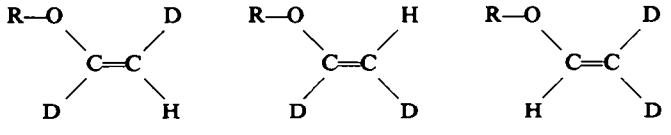
multiplet between 7·07 and 7·63 δ (—CH= proton partially superimposed on the *meta* and *para* hydrogens of the phenyl group), a multiplet between 7·80 and 8·10 δ (*ortho* hydrogens) and finally a slightly broad and weak signal at 10·73 δ (carboxyl residual hydrogens of deutero-acetic acid. After addition of the strong acid catalyst, one observes (Fig. 1b): (i) a low field shift of the carboxylic hydrogen from 10·73 to 11·61 δ, difference in hydrogen bonding due to the formation of acetic acid; (ii) decrease of the methylenic absorption and of the two low field components of the methinic proton absorption of vinyl benzoate and simultaneous increase of the vinylic absorption and appearance of two high fields components of the methinic proton of vinyl acetate. An expanded partial spectrum is represented in Fig. 1c. The important features of this experiment are that: (a) no increase of carboxylic

hydrogen is observed, and that (b) the total methylenic $=CH_2$ absorption remains constant with time; the vinyl group remains structurally unaffected during its transfer from one acid to the other.

2. *Reaction with deuterated vinylester*

A more sensitive method for detecting hydrogen scrambling during the vinyl-interchange consists of the reaction of $\alpha\beta\beta'$-trideuterovinyl acetate with benzoic acid.

The NMR-spectrum of this deuterated ester shows a sharp singlet at 2·08 δ (methyl group of the vinyl acetate) and three weak signals: (i) a triplet at 4·51 δ, J = 1 c/s for the methylenic hydrogen in P, the three components having the same intensity; (ii) a triplet with components of same intensity at 4·82 δ, J = 2·25 c/s for the methylenic hydrogen in Q; (iii) unresolved absorption at 7·27 δ (methinic proton in S).



The observed splittings of the bands into three signals of equal intensity arise from the hydrogen-deuterium coupling. By analogy with H—H couplings in vinyl compounds, the assignments were based on the values of the H—D coupling constants $J_{HDcis} = 1$ c/s and $J_{HDtrans} = 2{\cdot}25$ c/s. A nine-line multiplet corresponding to the methinic proton was however not observable.

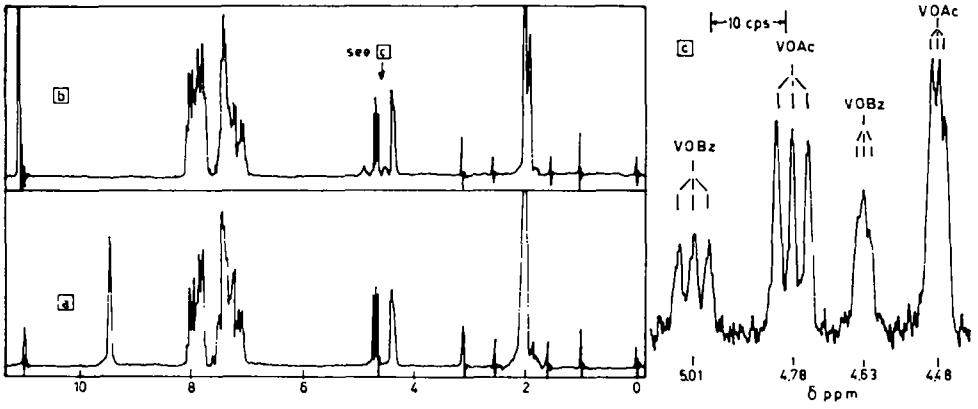


FIG. 2. 60 Mc NMR Spectra of
(a) a saturated solution of benzoic acid in trideuterovinyl acetate before reaction
(b) solution (a) during vinyl interchange reaction
(c) partial scale expanded portion of spectrum b in the methylenic region.

A saturated solution of benzoic acid in d_3-vinyl acetate was allowed to stand in the presence of mercury$^{(II)}$ acetate for one night; no spectral change was observed (Fig. 2a). However after addition of the strong acid, vinyl interchange occurs (Fig. 2b). One observes: (i) a singlet at the high field side of the methyl group in vinyl acetate (methyl group of acetic group); (ii) a triplet at 5·01 δ, J = 2·55 c/s (proton *trans* to methinic deuteron in d_3-vinyl benzoate; structure Q); (iii) a triplet at 4·63 δ;

$J = 1$ c/s (proton *cis* to methinic deuteron in d_3-vinyl benzoate, structure P). A partial scale-expanded spectrum is presented in Fig. 2c.

The solubility of benzoic acid in the reaction medium increases in such a manner that the addition of benzoic acid to the reacting solution enhances an increase of the benzoate concentration as represented in Fig. 2b. Nevertheless the relative methylenic hydrogen concentration remains constant.

In this way it is clearly demonstrated that a reaction mechanism including cleavage of a carbon-hydrogen bond in the vinyl group must be rejected; the exchange of the vinyl group as an integral unit is the only way to interpret all the experimental results.

During the course of these investigations, Rekasheva *et al.*[26] published the results of experiments on vinyl interchange with deutero acetic acid and vinyl acetate, showing by combustion analysis of the products that no deuterium was present in the vinyl group after reaction.

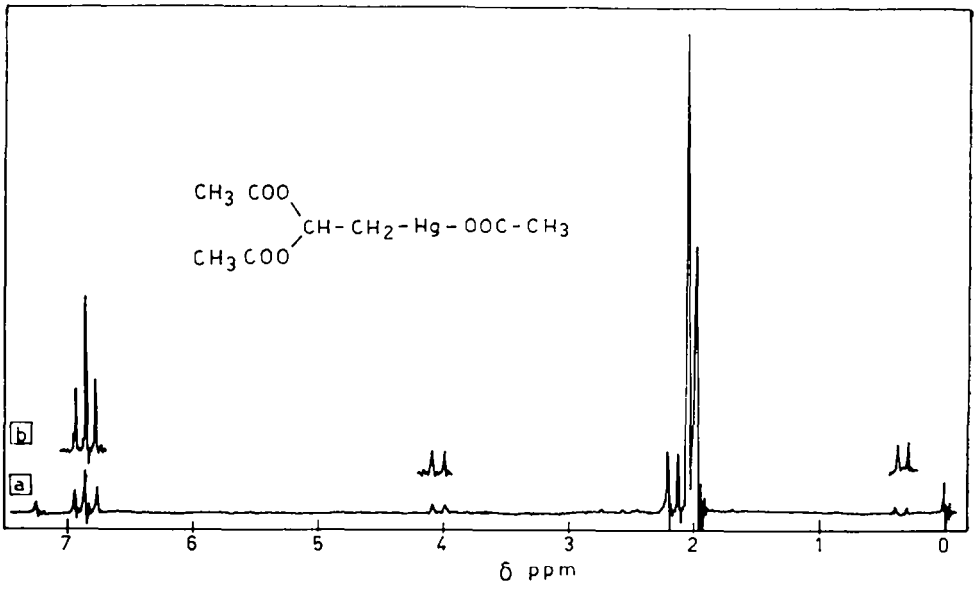


FIG. 3. 60 Mc NMR Spectra of compound IIa
(a) as a 10% WV solution in $CDCl_3$
(b) the name spectrum at higher gain

B. *Structure of the Transition Complex*

The formation of a symmetrical intermediate of structure II for vinyl interchange was previously presented by Watanabe.[10] The addition of mercury II acetate to vinyl acetate proceeds very easily and exothermally, and a quantitative yield of *αα'-diacetoxy-β-acetoxymercuri ethane* (IIa) is obtained.

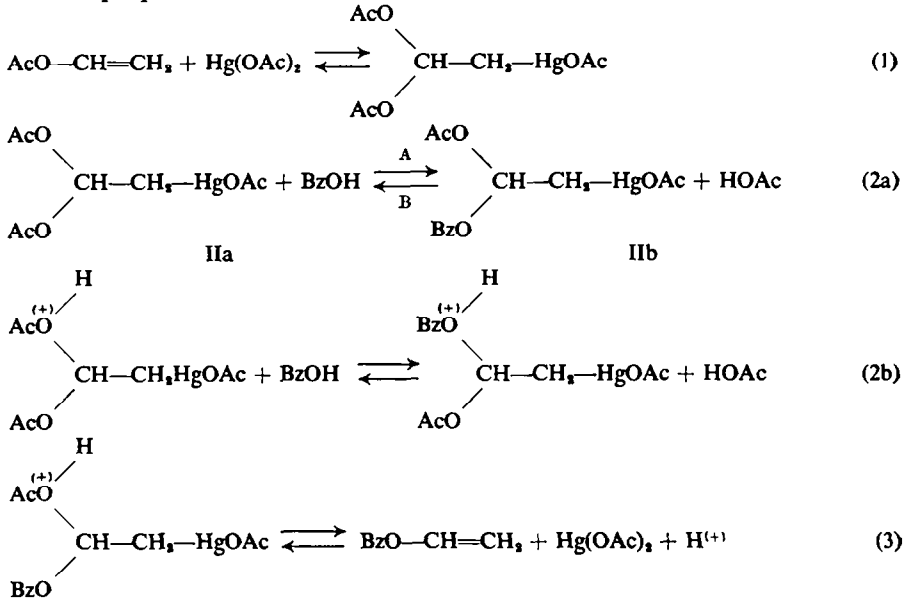
The structure of this compound $(CH_3COO)_2CH—CH_2—Hg—OOC—CH_3$ results directly from its NMR spectrum in deuterochloroform (Fig. 3): one singlet at 2·02 δ (CH_3—COO—Hg protons), a second singlet at 2·088 δ ((CH_3—COO)$_2$C protons), a doublet ($J = 5$ c/s) at 2·24 δ (methylenic protons) and a triplet ($J = 5$ c/s) at 6·96 δ (tertiary methinic hydrogen >CH—).

The formation of a mercury-carbon bond was shown by the presence of two satellite

doublets of lower intensity, J = 5 c/s, at 112 c/s up- and down-field of the absorption at 2·24 δ; they originate from the α-hydrogen coupling with the 199-mercury isotope natural abundance 16·86%). The satellite triplets in the neighbourhood of the 6·96 δ triplets were only detected in a concentrated solution of the organo mercuric compound in vinyl acetate.

The measured H_β-coupling constants $J_{^{199}Hg-H\beta}$ was 165 c/s. The values of the Hg–H coupling constants reported in the literature show that the $J_{^{199}Hg-H\beta}$ is higher than $J_{^{199}Hg-H\alpha}$ excepted when mercury is directly bound to an oxygen atom where the reverse is true.[21–25]

The NMR spectrum of IIb prepared by the addition of vinyl benzoate to mercuric acetate, exhibited features analogous to those of IIa: two singlets of equal intensities at 2·00–) ϱ Hg—COO—CH_3 group) and at 2·09 δ (CH_3COO—C—group), a doublet at 2·35 δ (J = 4·7; methylenic group), a triplet at 7·27 δ (CH-proton) partially superimposed on the phenyl absorption separated into two groups from 7·20 to about 7·75 δ and from 7·9 to 8·2 δ. The experimental intensity ratios agree with the calculated values. Furthermore the high- and low field satellite doublets (J_{HH} = 4·7 c/s) arising from ^{199}Hg–H coupling were clearly observed with a coupling constant identical to that measured in compound IIa ($J_{^{199}Hg-H\alpha}$ = 224 c/s). Thus the following mechanism is proposed:



Experiments have demonstrated that reaction (1) proceeds very rapidly and that no acid is required for it. The occurrence of step 2a has been indicated in both directions: when a mixture of benzoic acid and compound IIa is allowed to stand in vinyl acetate

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solution, reaction A can be observed with NMR spectroscopy on the basis of the decrease of concentration of IIa (triplet at 7·00 δ and doublet at 2·22 δ) and the increase of IIb (doublet at 2·38 δ). Inversely the reaction of acetic acid with compound IIb in vinyl acetate solution was observed; it is however limited by the equilibrium. The observation of the peaks due to mercury coupling also confirmed these results. Reaction (2) is catalysed by strong acid; in the absence of it (reaction 2a) the reaction proceeds slowly in spite of the relatively high concentration of the reactants. In contrast, at low acid concentration the reaction progresses rapidly (reaction 2b), even when the concentrations of reactants were much lower than in the uncatalysed reaction (see next paper). In reaction (3) an elimination reaction with a vinyl-oxygen scission occurs, as shown previously by Rekasheva;[26] indeed the vinyl interchange between vinyl acetate and oxygen-18 labelled acetic acid (Me–$C^{18}O^{18}OH$) in the presence of mercury-II-sulphate gives at equilibrium an isotopic distribution that can only be interpreted on the basis of a vinyl–oxygen breakage.

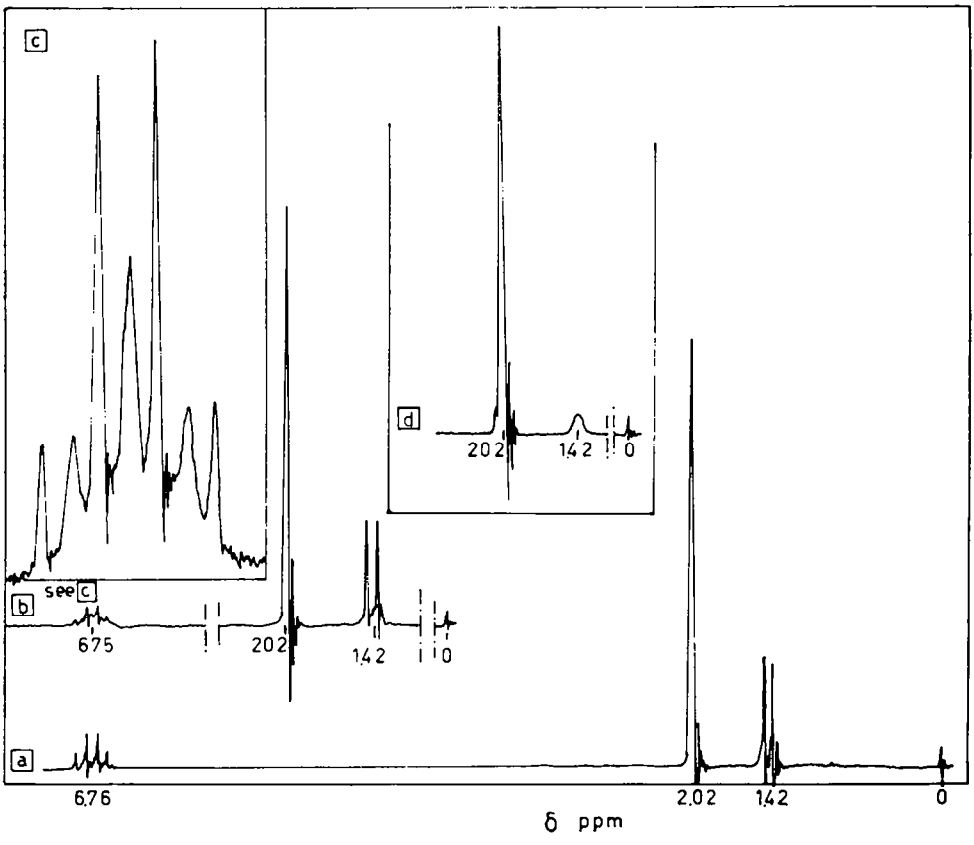
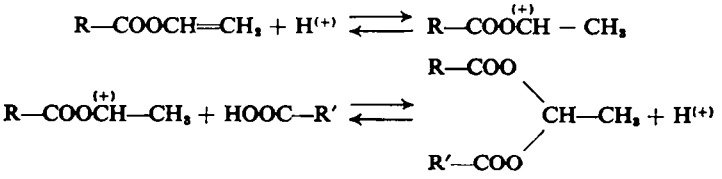


FIG. 4. 60 Mc NMR Spectra of
(a) ethylidene diacetate as a pure liquid
(b) β-deuteroethylidene diacetate as a pure liquid
(c) partial scale expanded portion of spectrum b in the methinic region
(d) $\alpha\beta\beta'$-trideuteroethylidene diacetate as a 10% WV solution in $CDCl_3$.

C. *Addition reaction with vinyl group*

Using deuterated and undeuterated compounds, it is possible to prepare various ethylidene esters by addition of acids to a vinyl ester. The NMR spectra confirm the structure of these addition products and therefore establish the mechanism of these catalysed additions:



1. Ethylidene diacetate $(CH_3COO)_2CH—CH_3$ was obtained by addition of normal acetic acid to vinyl acetate. The NMR spectrum (Fig. 4a) of the pure liquid sample shows (i) a doublet at 1·42 δ (J = 5·5 c/s) corresponding to the methyl group, (ii) a singlet at 2·02 δ for the acetoxy group, (iii) a quadruplet at 6·76 δ (J = 5·5 c/s) of the —CH group. The intensities were found as expected in the ratio 3/6/1.

2. *β-deutero ethylidene diacetate* $(CH_3COO)_2CH—CH_2D$ was prepared by addition of deutero-O-acetic acid to vinyl acetate. The NMR spectrum (Fig. 4b) of the pure liquid sample shows as for the preceding compound a doublet at 1·41 δ (J = 5·5 c/s), and a singlet at 2·02 δ. A multiplet (septet) at 6·75 δ is also present with equally spaced components in intensity ratio 1–1–3–2–3–1–1. This septet is due to vicinal coupling of the tertiary hydrogen with two hydrogens of the methyl group (J_{HH} = 5·7 c/s), this triplet being itself further split by coupling with the deuteron, J_{HD} (2·85 c/s) being exactly one half of J_{HH} Fig. 4c.

3. *αββ′-trideutero ethylidene diacetate* $(CH_3COO)_2CD—CD_2H$ was prepared by addition of acetic acid to αββ′-trideutero-vinyl acetate. Its NMR spectrum (Fig. 4d) shows again a broad absorption at 1·42 δ and a singlet at 2·02 δ. The ratio of intensities was consistent with the structure of this compound (6/1); the highfield unresolved absorption is due to the coupling of the hydrogen with two deuterium nuclei, which also broaden the line on account of their electrical quadrupole moment.

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