Stability of Phenyl Oxalate.—A quantity of 83 mg of phenyl oxalate was heated at 350° for 0.5 hr. A weight loss of only 1 mg occurred, and the infrared spectrum of the reaction mixture was identical with that of starting material.

Registry No.—4,4′-Dichlorobenzhydryl oxalate, 13131-54-9; benzhydryl oxalate, 13144-28-0; benzhydryl-α-d_1 oxalate, 13144-29-1; benzhydryl ether, 575-42-5; benzhydryl diphenylacetate, 13144-31-5; *t*-butylperoxy diphenylacetate, 13144-32-6; 4,4′,4″,4‴-tetrachloro-*sym*-tetraphenylethane, 13144-33-7; 4,4′-dichlorobenzhydryl 4,4′-dichlorodiphenylacetate, 13144-34-8; tetraphenylethane, 632-50-8.

Acknowledgment.—We thank Professors G. A. Russell and P. D. Bartlett for helpful discussions and Professor J. Warkentin for sending us information concerning his work with oxalates before publication.

Imidazole-Catalyzed Hydrolysis of Vinyl Acetate

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Received June 20, 1966

Imidazole-catalyzed hydrolysis of vinyl acetate using nuclear magnetic resonance (nmr) as the monitoring technique was studied. As soon as imidazole was added to the aqueous solution of vinyl acetate, N-acetylimidazole was formed which attained a steady-state concentration in about 3 min and disappeared when the vinyl acetate was completely consumed. However, the final products of this reaction were not the expected acetaldehyde and acetic acid; instead, an addition product between the imidazole and acetaldehyde followed by acetylation was isolated whose structure is shown to be that of I by nmr, infrared, and mass spectra data. The mechanism of the formation of this product is discussed and the supporting evidence presented.

The catalytic activity of imidazole in the hydrolysis of esters is well known, especially those of substituted phenyl acetates.[2-6] Both Bruice[3] and Bender[2] proposed a mechanism for the hydrolysis of *p*-nitrophenyl acetate catalyzed by imidazole. This proposed mechanism involves a preliminary equilibrium of the imidazole and the ester to form a tetrahedral intermediate where the alkoxide ion is the preferred leaving group. The acetylated imidazole is then quickly hydrolyzed so that the net effect is an apparent imidazole-catalyzed hydrolysis as described in the text. This seems to be most probable in light of the highly labile nature of the NH hydrogen in imidazole.[7,8]

No one had investigated the imidazole-catalyzed hydrolysis of vinyl acetate. It was thought that by using nuclear magnetic resonance (nmr) to monitor the hydrolysis, it should be possible to observe and identify any long-lived intermediates formed during the course of the reaction.

Experimental Section

All the materials used are commercially available samples purified by fractional distillation. N-Acetylimidazole was prepared by the method of Reddy, Mandell, and Goldstein[8] and only freshly prepared samples were used. All the spectra were recorded on a Varian A-60 analytical spectrometer. The chemical shifts are expressed in cycles per second (cps) relative to tetramethylsilane as internal reference.

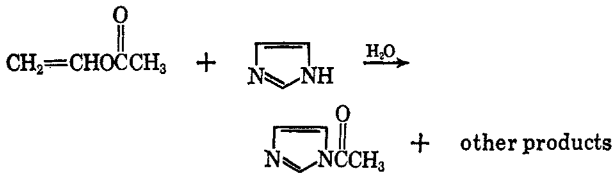
Preparation of the Final Product.—A mixture of 43 g (0.5 mole) of vinyl acetate, 34 g (0.5 mole) of imidazole, and 18 g (1 mole) of water was shaken periodically for about 2 hr. Initially, the reaction mixture became warm and was kept cool in a water bath. After 2 hr the mixture was extracted with chloroform and the extract was distilled under reduced pressure. The fraction distilling at 90° (0.6 mm) was collected. The distillate was a colorless viscous liquid. The yield was 60 g, equivalent to 80% of the theoretical yield based on the amount of imidazole taken. The nmr spectrum is given in Figure 1 and the infrared spectrum in Figure 2.

Anal. Calcd for $C_7H_{10}N_2O_2$: C, 54.50; H, 6.49; N, 18.18; O, 20.78; mol wt, 154. Found: C, 54.00; H, 6.47; N, 18.90; O, 20.63; mol wt, 154 (by mass spectrometry).

A small amount of imidazole was found to be present in the distillate which can account for the slightly higher value for nitrogen and lower value for oxygen found in the elemental analysis.

Results and Discussion

An aqueous solution (5–10% by volume) of vinyl acetate gave the same nmr spectrum as the solution in usual organic solvents indicating that no reaction took place within a reasonable length of time. The methyl group resonance of vinyl acetate was at −124 cps relative to tetramethylsilane. When imidazole was added to this solution and the spectrum recorded immediately, an additional methyl group resonance was observed. The frequency of this peak is at −151 cps and corresponded to the acetyl methyl group resonance of N-acetylimidazole.[8] The intensity of the new peak increased to a maximum in about 3 min and remained constant until most of the vinyl acetate reacted. Simultaneously, additional peaks were observed in the general region of the ring protons of imidazole and corresponded to the three protons of N-acetylimidazole.[8] This clearly suggested that the first and relatively fast step in this reaction is the formation of N-acetylimidazole from the reaction of vinyl acetate with imidazole.



During the initial periods of the reaction, no spectra belonging to either vinyl alcohol or acetaldehyde were

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[2] M. L. Bender and B. W. Turnquest, *J. Am. Chem. Soc.*, **79**, 1652, 1656 (1957).

[3] T. C. Bruice and G. L. Schmir, *ibid.*, **79**, 1663 (1957).

[4] T. C. Bruice and G. L. Schmir, *ibid.*, **80**, 148 (1958).

[5] J. F. Kirsch and W. P. Jencks, *ibid.*, **86**, 837 (1964).

[6] W. P. Jencks and Mary Gilchrist, *ibid.*, 4651 (1964).

[7] G. S. Reddy and J. H. Goldstein, presented at the 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1961.

[8] G. S. Reddy, L. Mandell, and J. H. Goldstein, *J. Chem. Soc.*, 1414 (1963).

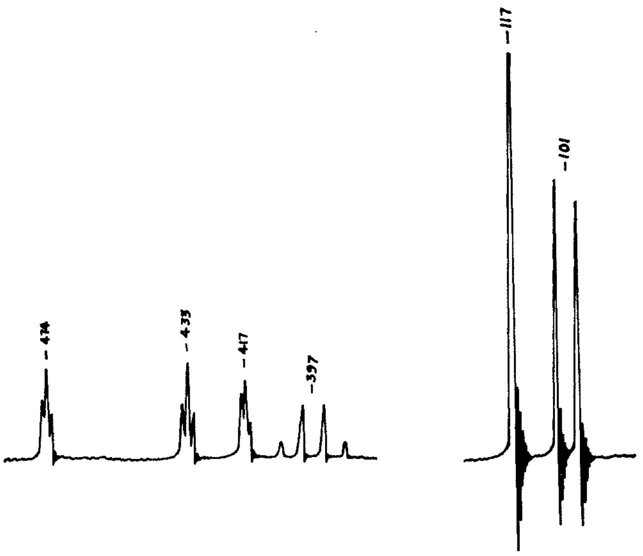


Figure 1.—Nmr spectrum of the product in deuteriochloroform.

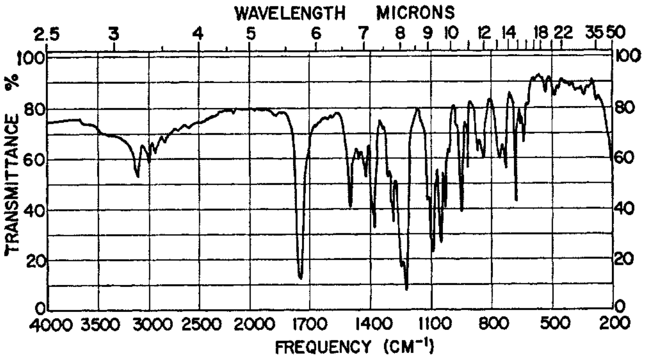
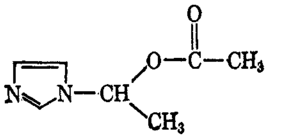


Figure 2.—Infrared spectrum of the product with structure



observed. However, as the reaction proceeded, the peak assigned to the methyl group of vinyl acetate gradually decreased in intensity while the peaks belonging to N-acetylimidazole remained constant until most of the vinyl acetate was consumed. By the time the vinyl acetate peaks disappeared, the N-acetylimidazole peaks also have disappeared. This clearly suggested that the N-acetylimidazole existed in a steady-state concentration during the reaction. Meanwhile several new peaks, both in the methyl and lower field regions, appeared and their intensities increased as the reaction proceeded. No peaks due to acetaldehyde were observed at any time during the reaction. The nmr spectrum of the mixture after all the peaks assigned to vinyl acetate have disappeared is shown in Figure 3. In the spectrum there is a small peak at −116 cps which corresponds to the methyl group of acetic acid, but the intensity of this peak is much smaller than the stoichiometric amount if the reaction were simple hydrolysis. The doublet at −102 cps is three times the intensity of the quartet at −397 cps and the spacing in both sets is 7 cps which is a typical $CHCH_3$ coupling. Although this pattern is typical of acetaldehyde and paraldehyde, the chemical shifts as well as the coupling constant did not correspond to either of these compounds.

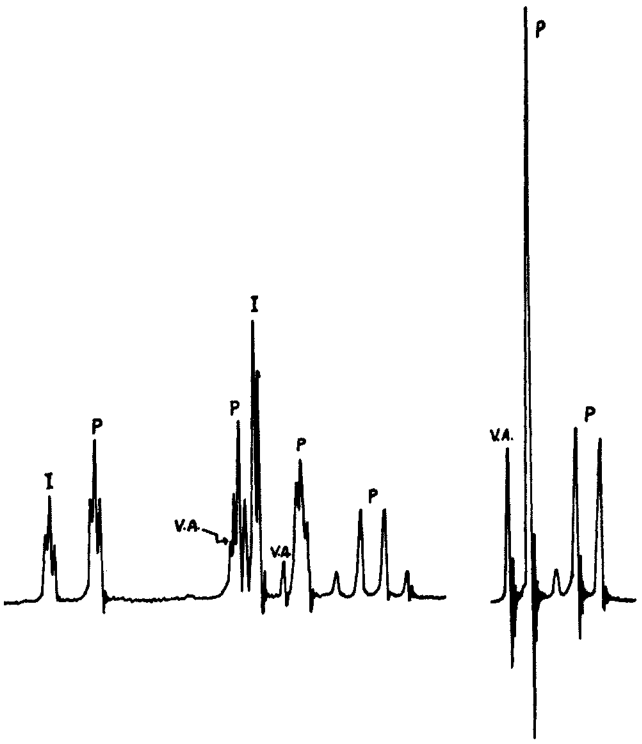
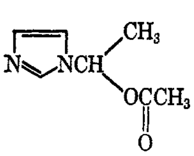


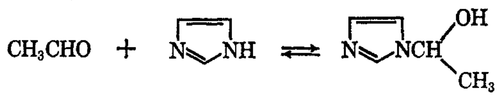
Figure 3.—Nmr spectrum of the mixture of vinyl acetate, imidazole, and water. Peaks marked P, I, and V.A. belong to the product, imidazole and vinyl acetate, respectively. Peaks due to water and the β protons of vinyl acetate are not shown. The peaks due to N-acetylimidazole are not seen owing to low concentration.

It is obvious that an unexpected product was formed in the reaction and apparently accounted for most of the vinyl acetate and imidazole initially taken.

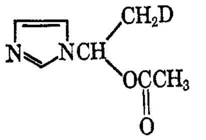
In order to identify this product, the reaction was carried out on a laboratory scale and the product obtained as described under Experimental Section. The nmr spectrum in $CDCl_3$ (Figure 1), the infrared spectrum (Figure 2), and mass spectral data as well as the elemental analysis showed the structure of the product to be



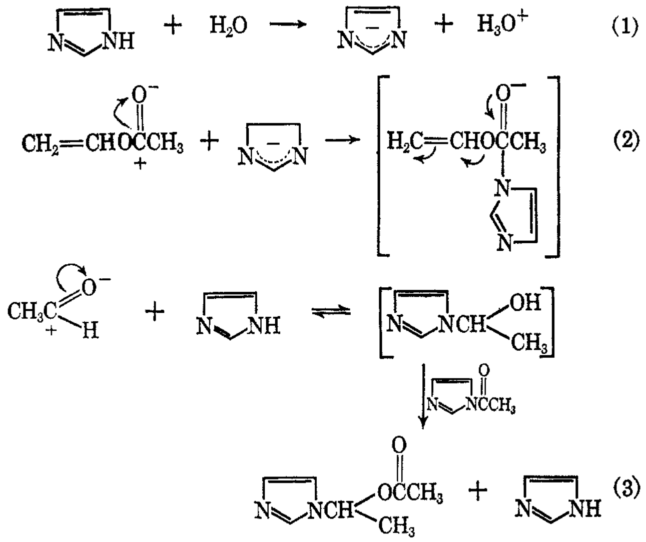
In order to formulate the reaction mechanism additional experiments were carried out with the following observations. (1) Vinyl acetate and imidazole were mixed. No apparent reaction took place within several minutes as revealed by the nmr spectrum of this mixture. However, when water was added to this mixture N-acetylimidazole was detected. This suggested that a proton acceptor like water is necessary for a reaction between vinyl acetate and imidazole. (2) When imidazole was added to acetaldehyde boiling took place apparently owing to heat of solution. The nmr spectrum of this mixture (Figure 4) showed the acetaldehyde peaks to be unusually broad. Furthermore, the peaks due to protons 4 and 5 of imidazole showed the same effect. This indicated that an equilibrium process such as



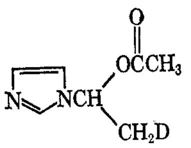
may be in operation. (3) The spectrum of a mixture of acetaldehyde and vinyl acetate showed no obvious reaction between these two reagents. (4) The spectrum of a mixture of freshly prepared N-acetylimidazole and acetaldehyde showed no reaction. However, when water was added to this mixture the peaks due to the product appeared in the spectrum within a few minutes. In addition peaks due to imidazole and acetic acid were also detected. (5) When D_2O was used instead of H_2O in the reaction the product obtained showed the structure



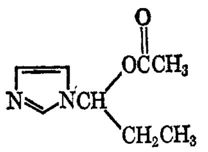
Based on these observations, the following steps are proposed for the formation of the product (eq 1–3).



When deuterium oxide was used instead of the water the product obtained showed the structure to be



The reaction was repeated with propionaldehyde, imidazole, and N-acetylimidazole. The product obtained has the structure



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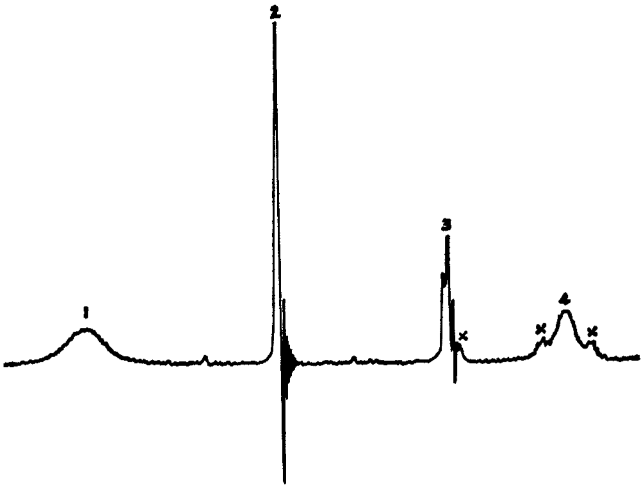
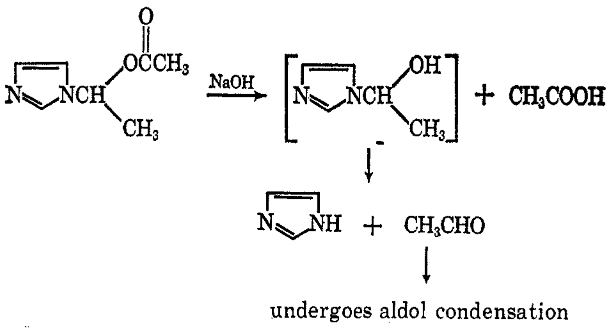


Figure 4.—Low-field nmr spectrum of a mixture of acetaldehyde and imidazole: peak 1, the aldehydic hydrogen of acetaldehyde; peak 2, the NH and the OH hydrogens of imidazole and the proposed complex; peak 3, the 2 hydrogen of imidazole; peak 4, 4 and 5 hydrogens of imidazole; peaks X, which seem to belong to the imidazole ring hydrogens in the complex. In addition to these, peaks due to $CH<^{O}_{CH_3}$ hydrogens were observed (not shown in the spectrum).

These results are consistent with the postulation that the product was formed as a result of the reaction between acetaldehyde and imidazole followed by acetylation with N-acetylimidazole. In the proposed reaction sequence no formation of acetic acid is anticipated. However, a small amount of acetic acid was observed in the reaction mixture which is believed to be due to hydrolysis of N-acetylimidazole as a side reaction.

The product was found to be stable on storing in a glass container for several weeks, but hydrolyzes very slowly in presence of water. When aqueous solution of sodium hydroxide was added, the mixture warmed rapidly and a series of color changes were observed. This may be due to the decomposition of the product to give imidazole, acetic acid, and acetaldehyde, the last one undergoing aldol condensation.



Registry No.—Imidazole, 288-32-4; vinyl acetate, 108-05-4; product $C_7H_{10}O_2N_2$, 10464-67-2.