to the alcoholate titration is reached. The difference between the neutralization values by the two methods corresponds to the anhydride content.[5,6] Application of this procedure to alcoholic solutions of maleic and phthalic anhydrides yielded the results illustrated in the accompanying figure which demonstrate that alcoholysis of these anhydrides proceeds at a measurable rate. After twenty-four hours the agreement between the aqueous and alcoholate titrations was within 2%, which is evidence not only for completion of the acylation reaction but also for the absence of any appreciable hydrolysis of the acid-ester during aqueous titration.

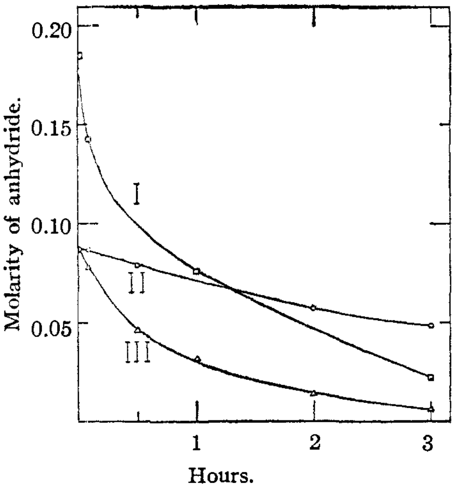

Fig. 1.—The reaction of dibasic acid anhydrides with primary alcohols at room temperature (25–27°); I, phthalic anhydride in methanol; II, maleic anhydride in ethanol; III, maleic anhydride in methanol. The solutions also contained 20% acetone by volume.

Several precautions are necessary for the quantitative application of Reaction (C) to alcohol-anhydride solutions. Because of the equilibrium between hydroxyl and alcoholate ions, either Reaction (B) or (C), or both, may ensue depending on the alcohol and its concentration. Thus, anhydrides may be titrated with aqueous alkali according to Reaction (B) if the final concentration of methanol is 70%.[2,3] Similarly, phenols and related compounds may be acylated by anhydrides in aqueous alkaline solution.[7,8] In the present instances, a 20-fold dilution with water was sufficient to eliminate the effect of alcohol on the aqueous titration. With some anhydrides (acetic and *o*-sulfobenzoic),[7] direct titration with aqueous alkali and phthaleins as indicators is not feasible because of acylation of the indicator; however, no such effect was noted with phthalic or maleic anhydrides. The possibility of hydrolysis of the ester during aqueous titration also requires consideration, although such hydrolysis is usually small under the conditions of direct titration[5] and may be evaluated when ester formation is complete.

Experimental

Titrations were carried out with 0.1 *M* sodium methylate in methanol and 0.05 *N* aqueous sodium hydroxide, with phenolphthalein as indicator. Anhydrides at hand were used without further purification. For standardization, weighed amounts were dissolved in acetone to yield 0.25 *M* solutions and 2-ml. aliquots taken for titration with (1) sodium methylate, (2) sodium hydroxide, after dilution of the sample with 20 ml. of water, and (3) sodium hydroxide, after dilution of the sample with 20 ml. of methanol. Corrections for the inherent acidity of methanol were applied in the latter titration. The results from (1), (2) − (1) and (2) − (3), respectively, were as follows: phthalic anhydride 73.9, 73.2, 73.8%; maleic anhydride 84.6, 85.4, 84.6%.

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The Esterification Rate of Dibasic Acid Anhydrides with Primary Alcohols at Room Temperature

BY I. G. ANDERSON AND J. KENYON

In a recent paper[1] it is stated that "mono-esterification of dibasic acid anhydrides with primary alcohols proceeds instantaneously and quantitatively at room temperature." This claim appeared to us so surprising that we felt impelled to examine it and to this end have carried out the following experiments:

(1) Absolute ethyl alcohol (2.3 g.) was added to a solution of freshly sublimed phthalic anhydride (3.7 g.) in dry acetone (25 cc.); after standing at 25° for one hour the solution was evaporated, also at 25°, to dryness. The residue (3.7 g.) consisted entirely of phthalic anhydride of unchanged melting point (128–130°).

(2) To a solution of absolute ethyl alcohol (1.0 g.) and phthalic anhydride (2.96 g.) in dry acetone (20 cc.) at 25° was added a solution of potassium hydroxide in *methyl* alcohol (202.0 cc. of 0.1 *N*) until neutrality—to phenolphthalein—was reached. The solution was then evaporated to small bulk at 25° and acidified with dilute hydrochloric acid. The precipitated oily material which separated rapidly crystallized and was removed by filtration washed with water and dried. It weighed 3.0 g. and had m. p. 80–83°.

After recrystallization from cyclohexane it had m. p. 83–84° alone and when mixed with an authentic specimen of methyl hydrogen phthalate.

It thus follows that phthalic anhydride does not undergo rapid mono-esterification with ethyl alcohol at 25° but does so with potassium methoxide. That the sodium and potassium derivatives of alcohols react readily with succinic and

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[1] Siegel and Moran, THIS JOURNAL, 69, 1457 (1947).

phthalic anhydrides has been known for over half a century.[2,3]

[2] Tiemann and Krüger, *Ber.*, **29**, 901 (1896).
[3] Fuller and Kenyon, *J. Chem. Soc.*, **126**, 2309 (1924).

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Rearrangement of Phenylethynylcarbinol

BY WARREN S. MACGREGOR

Rupe[1] reported that several tertiary acetylenic alcohols containing a free acetylenic hydrogen were rearranged upon boiling with 85% formic acid to the corresponding α,β-unsaturated aldehydes. Thus, the ethynylcarbinols from tetrahydrocarvone and fenchone were reported to yield 5 - isopropyl - 2 - methylcyclohexylidene - 1 - acetaldehyde and 1,3,3-trimethylbicyclo[2,2,1]-heptylidene-2-acetaldehyde, respectively.[2] The reaction represents a special case of a Meyer–Schuster rearrangement[3] and was considered by Rupe[1] to proceed in analogous manner

$$R(R')C(OH)C{\equiv}CH \longrightarrow R(R')C{=}C{=}CHOH \longrightarrow R(R')C{=}CHCHO$$

Reinvestigation of several of the reported rearrangements by Fischer and Lowenberg,[4] Hurd and Christ[5] and others demonstrated that the principal products were unsaturated ketones presumably formed by dehydration of the carbinols followed by hydration of the triple bond.[5] Thus, 1-ethynylcyclohexanol yielded 1-acetylcyclohexene[4,5] rather than cyclohexylidene acetaldehyde. Chanley[6] showed that both the ketone and aldehyde products resulted from the rearrangement of 1-ethynyl-1-cyclohexanols although the aldehydes were formed in very low yield (0.8 to 6%).

The reaction probably involves initial elimination of the hydroxyl group to form a carbonium ion. The loss of a proton from an adjacent carbon followed by hydration of the triple bond and ketonization would yield the observed unsaturated ketone. Shifting of the carbonium ion bonds to the allenic structure followed by hydroxylation at the positive terminal carbon would yield the enolic form of the unsaturated aldehyde which is in equilibrium with the predominantly favored aldehyde.

A compound such as phenylethynylcarbinol would yield a carbonium ion that could not form an unsaturated ketone by the above mechanism and hence, barring alternative modes of reaction, should yield cinnamaldehyde as the principal rearranged product. When the carbinol was heated with 30% sulfuric acid, 85% phosphoric acid or phthalic anhydride the odor of cinnamaldehyde was evident but the material was largely polymerized to a tar. The rearrangement was achieved with less polymerization by steam distilling the carbinol through 28% sulfuric acid. The resultant crude cinnamaldehyde in two experiments was converted directly to the phenylhydrazone (35% over-all yield). In a third experiment the aldehyde was converted to α-bromocinnamaldehyde (21% over-all yield).

Experimental

Rearrangement of Phenylethynylcarbinol.—Phenylethynylcarbinol (5.4 g.) and 5 cc. of water were placed in a 25-cc. distilling flask fitted for steam distillation with the side arm extending nearly to the bottom of the 50-cc. flask of a Clark acetyl apparatus[7] containing 25 cc. of 28% sulfuric acid. The flasks were heated in oil-baths to 115°, a steam generator connected to the small flask, and steam distillation started adjusting the bath temperatures to maintain approximately constant volume in the flasks. A water-insoluble oil (3.1 g.) separated in the distillate and dissolved in 5 cc. of ethanol. A solution of 17.5 g. phenylhydrazine hydrochloride and 10.0 g. sodium acetate in 150 cc. of water then was added to the oil and the mixture warmed for fifteen minutes on a water-bath. After filtering, washing with water, ethanol and ether, and drying, 3.0 g. (33%) of crude cinnamalphenylhydrazone (m. p. 154–157°) was obtained. Two recrystallizations from ethanol raised the m. p. to 168–169° and a mixed m. p. with an authentic sample showed no depression. A second experiment yielded 1.2 g. (36%) of the crude phenylhydrazone (m. p., 161–165°) from 2.0 g. of the carbinol.

The crude cinnamaldehyde from a similar rearrangement of 6.2 g. of phenylethynylcarbinol was extracted from the distillate with ether, and upon removal of solvent the oil was taken up in 10 cc. of glacial acetic acid. A solution of 10.7 g. of bromine in 19.9 g. of acetic acid was added dropwise with stirring and cooling in an ice-bath until the bromine color remained for ten minutes (10.3 g. of the solution, corresponding to 3.0 g. cinnamaldehyde, was required.) Potassium carbonate (1.5 g.) was then added and the mixture allowed to stand overnight at room temperature. After refluxing thirty-five minutes, the mixture was cooled and poured into 30 cc. of water, whereupon an oil separated that partially crystallized upon shaking. The oil and crystals were removed and taken up in 10 cc. of warm ethanol. Upon cooling and seeding 2.1 g. (21%) of α-bromocinnamaldehyde, m. p., 71.5–72°, was obtained. Recrystallization from ethanol did not alter the m. p., and the mixed m. p. with a sample prepared following the directions of Allen and Edens[8] showed no depression.

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[1] Rupe and Kambli, *Helv. Chim. Acta*, **9**, 672 (1926).
[2] Rupe and Keunzy, *Helv. Chim. Acta*, **14**, 708 (1931).
[3] Meyer and Schuster, *Ber.*, **55**, 819 (1922).
[4] Fischer and Lowenberg, *Ann.*, **475**, 183 (1929).
[5] Hurd and Christ, THIS JOURNAL, **59**, 118 (1937).
[6] Chanley, THIS JOURNAL, **70**, 244 (1948).
[7] Clark, *Ind. Eng. Chem., Anal. Ed.*, **8**, 487 (1936).
[8] Allen and Edens, "Organic Syntheses," **25**, 92 (1945).

DEPARTMENT OF CHEMISTRY
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Indium Orthovanadate[1]

BY W. O. MILLIGAN, HENRY H. RACHFORD, JR., AND L. MERTEN WATT

Forty-seven years ago Renz[2] prepared a gel which he designated as $In(VO_3)_3 \cdot 2H_2O$ by the addition of a sodium metavanadate solution to an indium chloride solution. The supposed constitution of the gel was based merely upon a chemical analysis, and there does not exist in the literature.

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[1] Presented before the Texas Regional Meeting of the American Chemical Society held in Austin, Texas, December 7–8, 1945.
[2] Renz, *Ber.*, **34**, 2765 (1901).