We have been able to show that in the Meerwein–Ponndorf–Verley reduction in a majority of cases removal of acetone is unnecessary. Compounds reduced are listed in Table I. It will be noted that in the cases of benzophenone and benzosuberone, which were reduced using varying mole ratios of aluminum isopropoxide, the quality of the product, as judged by melting point, is better with the higher mole ratios of aluminum isopropoxide.

Of particular interest is the successful reduction of benzalacetophenone, cinnamylideneacetone and cyclopentanone. As has been pointed out by Macbeth and Mills,[5] compounds of this type cannot be reduced in good yields by the normal procedure, but by the modification introduced by Macbeth and Mills of slowly adding the carbonyl compound to an excess of aluminum isopropoxide, excellent yields are realized. Apparently in our method the rate of reduction is more rapid than the rates of the competing aldol and Tischtschenko condensations.

The one failure of our method noted is in the reduction of phenyl 2-methoxy-1-naphthyl ketone, which was reduced in 95% yield by the normal method.

Experimental

Method A_1.—To 51 g. (0.25 mole) of aluminum isopropoxide in 200 ml. of boiling isopropyl alcohol was added 0.05 mole of the appropriate carbonyl compound in 50 ml. of boiling isopropyl alcohol over a period of 5 minutes. The solution was heated under reflux for one hour, poured into approximately 1.5 liters of water and sodium hydroxide solution was added until a clear solution resulted. The product was extracted with ether and the ether extract dried over magnesium sulfate. Evaporation of the dried ether extract gave the crude product.

Method A_2.—Method A_2 differs from method A_1 in that only 0.15 mole of aluminum isopropoxide and 150 ml. total volume of isopropyl alcohol was employed.

Method A_3.—Method A_3 differs from method A_1 in that only 0.05 mole of aluminum isopropoxide and 50 ml. total volume of isopropyl alcohol was employed.

Method B.—Method B differs from method A_1 only in the manner in which the product was isolated. After one hour reflux the isopropyl alcohol was evaporated to a low volume and sodium hydroxide solution was added. The liquid was filtered from the gelatinous mixture which was then washed twice with ether. The combined filtrates were dried over magnesium sulfate, decanted and distilled through a small Vigreux column.

Method C.—The normal procedure as outlined by Wilds[1] was followed.

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[5] A. K. Macbeth and J. A. Mills, *J. Chem. Soc.*, 2646 (1949).

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The Preparation of Alpha C^{14}-Labeled Pyruvic Acid and a Study of the Hydrolysis of Pyruvonitrile[1]

BY R. C. THOMAS, JR., C. H. WANG AND BERT E. CHRISTENSEN

The importance of alpha C^{14}-labeled pyruvic acid as an intermediate metabolite has made the synthesis of this acid in good yield increasingly important in tracer work. The older procedures employing aqueous hydrolysis of pyruvonitrile either give low over-all yields 20–25%[2] (based on acetate), or a product which is unsatisfactory[3] due to the incomplete removal of an acid contaminant in the pyruvic acid, probably acetic acid. For these reasons the hydrolysis of pyruvonitrile in an ethereal medium as recently described by Anker[4] has been modified and adapted to a larger scale operation for the preparation of pyruvic acid from sodium acetate. This procedure gives an over-all yield of 40% of a 98% pyruvic acid based both on radioactivity measurements and the quantity of sodium acetate used.

Experimental[5]

Hydrolysis of Pyruvonitrile in Aqueous Concentrated Hydrochloric Acid Media.—The hydrolysis of 7.12 g. (103 millimoles) of C^{14}-carbonyl labeled pyruvonitrile (specific activity of 2.1×10^4 c.p.m./millimole or a total count of 2.2×10^6 c.p.m.) at 0° with 7.4 ml. (309 millimoles based on water) of 12 *N* hydrochloric acid yielded 2.12 g. (53 millimoles) of non-radioactive formic acid, 4.08 g. (68 millimoles) of acetic acid (specific activity 2.1×10^4 c.p.m./millimole or a total count of 1.4×10^6 c.p.m.), 2.9 g. of a mixture composed of 10.5 millimoles of pyruvamide and 22.3 millimoles of pyruvic acid (specific activity of the mixture 2.1×10^4 c.p.m./millimole or a total count 0.70×10^6 c.p.m.).

Hydrolysis of Pyruvonitrile in an Ethereal Medium.—Hydrolysis of 6.6 g. of C^{14}-carbonyl labeled pyruvonitrile in an ethereal medium using dry hydrogen chloride gave 6.6 g. of pyruvamide (79% based on pyruvonitrile or 62% based on sodium acetate) m.p. 123–124° (corrected). The starting material, 14.5 mg. of sodium acetate gave 6.6×10^7 c.p.m. and the product 6.6 g. of pyruvamide gave 4.2×10^7 c.p.m. which is equivalent to a radioactivity recovery of 63%.

Conversion of the pyruvamide to pyruvic acid by hydrolysis in concentrated hydrochloric acid gave a 64% yield of pyruvic acid which was found by analysis to be 98% pure. The pyruvic acid thus obtained had a radioactivity of 2.7×10^7 c.p.m., equivalent to a radioactivity recovery of 65% based on the radioactivity of pyruvamide or 41% based on the radioactivity of the sodium acetate.

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[2] Claisen and Shadwell, *Ber.*, **11**, 620 1503 (1878); Claisen and Marasse, *ibid.*, **20**, 2196 (1887); Gould and co-workers, *J. Biol. Chem.*, **177**, 722 (1949).

[3] Hughes and Reid, Atomic Energy Commission Document number 2370.

[4] Anker, *J. Biol. Chem.*, **176**, 133 (1949).

[5] For complete details order Document 3354 from American Documentation Institute, 1719 N Street, Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.20 for photocopies (6 × 8 inches) readable without optical aid.

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Preparation and Identification of N-Formylbenzamide and its Condensation Product with Phenylhydrazine

BY QUENTIN E. THOMPSON

In connection with studies on the diacylation of amides, we have prepared N-formyldibenzamide hydrate (I).[1] This compound was observed to cleave during attempted recrystallization from nonpolar solvents giving benzoic acid and a compound, m.p. 112–113°. On the basis of analytical data, molecular weight determinations and oxidation to benzamide and carbon dioxide, this material was identified as the expected product, N-formylbenza-

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[1] Q. E. Thompson, THIS JOURNAL, **73**, 5841 (1951).