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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[1] This research was conducted under a contract No. N8 onr 73501, between the Office of Naval Research and Oregon State College and supported in part by U.S.A.E.C.

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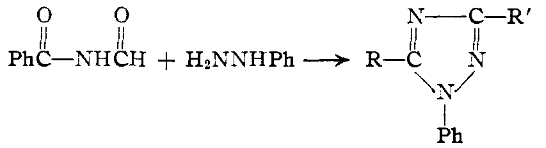
[1] Q. E. Thompson, THIS JOURNAL, **73**, 5841 (1951).

mide (II). In addition, II was insoluble in bicarbonate solution but soluble in dilute sodium hydroxide with concomitant hydrolysis to benzamide and sodium formate, thus exhibiting behavior fairly characteristic of unsymmetrical secondary amides.

Einhorn, Bischkopff and Szelinski[2] have reported the preparation of II but have described it as melting at 120° and forming a molecular compound with benzene, m.p. 84°. These characteristics do not agree with those observed by us, since our compound melted lower and was unchanged by recrystallization from benzene. In order to resolve these differences, we have repeated their synthesis of formalbenzamide; thus N-methylolbenzamide was prepared and oxidized according to their procedure. The material obtained did not correspond to the product which was previously described but melted at 112–113° and was identical in all respects with the formylbenzamide which we had obtained from I.

The previous workers reported that their formylbenzamide condensed with phenylhydrazine to give a disubstituted triazole, m.p. 96–97°, which was assumed to be 1,3-diphenyl-1,2,4-triazole (III). A picrate, m.p. 148°, was also reported for this triazole (III).



III, R = H, R′ = Ph
IV, R = Ph, R′ = H

We have found, however, that II condenses with phenylhydrazine to give a triazole, m.p. 90.5–91°, with a picrate, m.p. 138–139° (crude) and 140–141° (purified). Furthermore, we have established conclusively that this is the isomeric 1,5-diphenyl-1,2,-4-triazole (IV) by comparison with an authentic sample of IV prepared by the method of Young.[3] Both Young and Cleve[4] had prepared this triazole prior to the time of Einhorn, *et al.*, and had found the m.p. 91°, and picrate, m.p. 139° (crude).

Apparently the anomalous results reported by the earlier workers can be explained partly on the basis of incorrect melting point data, since their values were all 6–7° higher than those observed by us or by Cleve and Young. It was largely on the basis of these differences that they assumed their triazole to be III rather than the known compound IV. The formation of an addition compound with benzene is still unexplained.

Experimental

N-Formylbenzamide (II).—A solution of 8 g. of N-formyldibenzamide hydrate, m.p. 78–80°, in 100 ml. of xylene was refluxed for 2 hours, cooled, and shaken with four 50-ml. portions of saturated sodium bicarbonate solution to remove benzoic acid. After washing with 50 ml. of distilled water, the xylene solution was concentrated to about 25 ml., cooled, and the needles of N-formalbenzamide which separated were collected by filtration. Addition of petroleum ether to the filtrate caused the separation of more crystals making a total of 4.2 g. (95%), m.p. 108–111°. Recrystallization from petroleum ether gave pure needles, m.p. 112–113°. A mixed melting point with N-formylbenzamide, m.p. 112–113°, prepared by the method of Einhorn[2] and coworkers showed no depression.

Anal. Calcd. for $C_8H_7O_2N$: C, 64.40; H, 4.73; N, 5.53. Found: C, 64.58; H, 4.63; N, 5.69.

1,5-Diphenyl-1,2,4-triazole (IV).—Phenylhydrazine (0.75 g.) in 30 ml. of 30% acetic acid was treated with 1 g. of pure N-formylbenzamide in accordance with directions.[2] This procedure yielded 1.25 g. (84%) of crude, m.p. 70–80°, triazole which after two recrystallizations from petroleum ether, melted sharply at 90.5–91°. The compound crystallized in plates from petroleum ether or needles from water or dilute alcohol.

Anal. Calcd. for $C_{14}H_{11}N_3$: C, 75.99; H, 5.01; N, 18.99. Found: C, 75.68; H, 4.88; N, 19.02.

An authentic sample of IV, m.p. 90.5–91°, prepared by the method of Young,[3] showed no depression in a mixed melting point with this material.

1,5-Diphenyl-1,2,4-triazole Picrate.—About 50 mg. of triazole was heated for 10 minutes with 100 mg. of picric acid in 10 ml. of ethanol. The tiny yellow needles which separated on cooling were removed by filtration and, when dry, melted 138–139°; reported by Cleve,[4] 139° (crude). Recrystallization from dilute ethanol gave a pure product melting at 140–141°.

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Solubilities of Quaternary Ammonium Salts in Methanol and *n*-Butanol

BY ARTHUR A. VERNON AND ROBERT E. WALCK, JR.

As part of a study of the effect of dielectric constant on solubility, the solubility of some quaternary ammonium salts was determined in two alcohols. Methanol, with a dielectric constant of 32.0, and *n*-butanol, whose dielectric constant is 17.8, were used as solvents.

Experimental

Materials.—Methanol was stored over Hydralo for several days and was then distilled over Hydralo in a fractionating column, discarding the first and last fifths. The refractive index at 14.5° was 1.3312 compared with the "International Critical Tables" value of 1.33118.

n-Butanol was purified by the method of Clarke, Robinson and Smith.[1] It was washed with dilute sulfuric acid, using 250 cc. of acid for each 800 cc. of alcohol and then with a 15% sodium bisulfite solution. The alcohol was then boiled with a 20% aqueous sodium hydroxide solution for 1.5 hours and dried, first with potassium carbonate and second with barium oxide. The *n*-butanol was then distilled in a fractionating column, discarding the first and last fifths. The refractive index at 20° was 1.3991 compared with the "International Critical Tables" value of 1.39909.

Tetramethylammonium bromide and iodide (Eastman Kodak Co.) were recrystallized from 95% ethanol and dried at 80° for 24 hours. The bromide analyzed 51.77% bromine by Volhard titration compared to the theoretical 51.87%. The iodide analyzed 62.91% iodine compared to the theoretical 63.16%.

Tetramethylammonium chloride (Eastman Kodak Co.) was recrystallized from 95% ethanol and dried at 120° in a vacuum oven for 36 hours. The product analyzed 32.35% chlorine as compared to the theoretical 32.42%.

Tetrapropylammonium iodide (Eastman Kodak Co.) was recrystallized from an ethanol–ether mixture and dried at 80° for 24 hours. Analysis showed 40.43% iodine as compared to the theoretical 40.55%.

All other salts were prepared by conventional methods of refluxing the amine with a slight excess of halide and recrystallizing the crude product from a suitable solvent or

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[2] A. Einhorn, E. Bischkopff and B. Szelinski, *Ann.*, **343**, 227 (1905).

[3] G. Young, *J. Chem. Soc.*, **67**, 1069 (1895).

[4] A. Cleve, *Ber.*, **29**, 2679 (1896).

[1] J. Clarke, R. Robinson and J. C. Smith, *J. Chem. Soc.*, 2647 (1927).