

[CONTRIBUTION FROM THE INSTITUTE OF PAPER CHEMISTRY]

Reactions of Vanillin and its Derived Compounds. IV.¹ The Caustic Fusion of Vanillin^{2,2a}

BY IRWIN A. PEARL

In 1874 Tiemann and Haarman³ fused vanillin with caustic potash and obtained protocatechuic acid but reported no time, temperature, reactants ratio, or yield data. More recently Lock,⁴ while studying the Cannizzaro reaction of phenolic aldehydes, reported an isolated experiment in which vanillin was fused with 8 parts of caustic potash for three hours at 150–210° and yielded a crude mixture of protocatechuic and vanillic acids melting over a range below 180° which could not be separated into its components, but which was found by methoxyl analysis to contain 20% vanillic acid. Sabalitschka and Tietz⁵ fused vanillin with 1.4 parts of caustic potash at 180–220° for forty-five minutes and obtained a mixture of protocatechuic and vanillic acids which they succeeded in separating by laborious fractional crystallizations from ether, ethanol and water. These confusing data, together with a desire to obtain protocatechuic acid from vanillin in good yields, led to the study reported herein on the caustic fusion of vanillin under controlled conditions.

Addition of vanillin to well-stirred fusions of 2.5 parts by weight of potassium hydroxide at temperatures between 140 and 240° resulted in the liberation of hydrogen and the almost quantitative transformation of vanillin to vanillic acid with no trace of protocatechuic acid. Subsequent raising of the temperature above 245° caused reaction to set in, resulting in complete demethylation of the vanillic acid to yield protocatechuic acid in almost quantitative yields. The same results were obtained when vanillin was added to the fused caustic at temperatures above 245°. The critical temperature of 245° for the demethylation of vanillic acid was found to vary somewhat with the alkali-vanillin ratio; higher alkali ratios gave slightly lower demethylation temperatures. The nature of the fusion vessel had no effect upon the course of the reaction—iron, nickel and Duriron gave equally good results. Sodium hydroxide could be substituted for potassium hydroxide with no change in critical demethylation temperature, but with slightly lower yields. The fact that sodium hydroxide does not liquefy as readily as po-

tassium hydroxide probably accounted for the lower yields with sodium hydroxide, inasmuch as mixed alkalis which fused readily at low temperatures yielded results comparable with potassium hydroxide alone.

Repetition of the reported conditions of Lock⁴ and of Sabalitschka and Tietz⁵ with accurate temperature control yielded vanillic acid with only a qualitative trace (green color with ferric chloride) of protocatechuic acid. These data indicate that, in the earlier investigators' experiments, parts of their reaction mixtures were much hotter than 210 or 220° at some time during the course of their reactions.

Treatment of vanillin with boiling 30% sodium hydroxide at 140° yielded only unchanged vanillin but when potassium hydroxide was substituted under the same conditions, a 5% yield of the Cannizzaro reaction products of vanillin¹ was obtained along with 95% vanillin recovery. Evidently there is some condition between low temperature caustic fusion and high temperature boiling at which oxidation of vanillin to vanillic acid takes place.

The caustic fusion of vanillin affords a simple process for the large scale production of either vanillic or protocatechuic acid.

Experimental⁶

Reaction of Vanillin with Fused Potassium Hydroxide below 240°.—A mixture of 165 g. of 85% potassium hydroxide and 20 g. of water was placed in a 90-mm. nickel crucible set in a deep sand-bath heated by a Bunsen burner. With vigorous mechanical agitation (Lightnin' mixer), the alkali mixture was heated to 125°, at which temperature it gelled. The sand-bath was maintained at 250°. The viscous mixture at 125° was treated with 60 g. of vanillin in small portions over a period of ten minutes. Considerable hydrogen evolution took place after each addition, the temperature rose to 140°, and the mixture became more fluid. Vanillin addition was rapid enough to keep the temperature at 140°. After all the vanillin was added, the mixture became pasty, and the temperature rose to 185°. Stirring was continued for another ten minutes at this temperature; the mixture was removed from the sand-bath, allowed to cool, and dissolved in 800 ml. of water to give a red solution. The alkaline solution was acidified with sulfur dioxide, which caused the solution to become colorless and a heavy white crystalline precipitate to separate. The precipitate was filtered, washed with water, and dried to yield 59 g. (89%) of substantially pure vanillic acid as white needles melting at 208–209°. The melting point of a mixture with authentic vanillic acid was not depressed. Ether extraction of the sulfur dioxide-saturated filtrate and washings yielded an additional 7 g. (10%) of vanillic acid as a white solid melting at 207–209°.

Hydrochloric acid and sulfuric acid gave the same results as sulfur dioxide when the fusion was made in nickel. However, when iron or Duriron vessels were employed in the fusion, hydrochloric and sulfuric acids gave slightly

(1) For paper III of this series see Pearl, *J. Org. Chem.* in press.

(2) This paper represents a portion of the results obtained in the research program sponsored by the Sulphite Pulp Manufacturers' Committee on Waste Disposal and conducted for the Committee by The Institute of Paper Chemistry. Acknowledgment is made by the Institute for permission on the part of the Committee to publish these results.

(2a) Presented before the Division of Organic Chemistry at the 110th meeting of The American Chemical Society, Chicago, Illinois, September 9–13, 1946.

(3) Tiemann and Haarman, *Ber.*, **7**, 617 (1874).

(4) Lock, *ibid.*, **62**, 1187 (1929).

(5) Sabalitschka and Tietz, *Arch. Pharm.*, **269**, 554 (1931).

(6) All melting points given are uncorrected.

colored vanillic acid, whereas sulfur dioxide gave a white product in all cases.

Reaction of Vanillin with Fused Potassium Hydroxide above 240°.—The same apparatus was used. A mixture of 165 g. of potassium hydroxide and 20 g. of water was heated to 225° and with vigorous stirring was treated with 60 g. of vanillin in small portions at such a rate as to keep the resulting vigorous reaction from effervescing out of the crucible and to maintain the temperature at 225°. Vanillin addition required approximately twenty minutes. The temperature was maintained at 225° for another five minutes, at which time all effervescence had ceased. A sample dissolved in water and acidified with hydrochloric acid gave only crystals of vanillic acid melting sharply at 207–208°. The mixture was heated to 240° for five minutes, which caused the fused mass to become more fluid. A sample at this point indicated only vanillic acid. No test for protocatechuic acid could be obtained by the very sensitive ferric chloride reaction. The temperature was then raised to 245–250°, at which temperature effervescence again took place. After five minutes at 250°, a sample no longer gave a precipitate of vanillic acid when dissolved in water and acidified with hydrochloric acid. The fusion mixture was allowed to cool somewhat and was dissolved in 600 ml. of water. The alkaline solution was acidified with 6 *N* hydrochloric acid, giving an effervescent yellow solution which, upon standing, deposited colorless crystals. The crystals were filtered, washed with water, and dried

at 105° to yield 36 g. (59%) of protocatechuic acid melting at 199–200° and not depressing the melting point of a mixture with authentic protocatechuic acid. Saturation of the acid filtrate with sodium chloride and extraction with ether yielded an additional 24 g. (40%) of protocatechuic acid melting at 195–200°.

This experiment was repeated, the temperature being maintained just below 245° for thirty minutes. At that point no protocatechuic acid could be found. Raising the temperature to 245° caused reaction to set in and the temperature to rise to 255°. The mixture was worked up as above to yield 99% protocatechuic acid.

Summary

Caustic fusion of vanillin below 240–245° results in very high yields of vanillic acid free from protocatechuic acid. Fusion of vanillin above 240–245° yields protocatechuic acid free from vanillic acid. The critical demethylation temperature varies somewhat with the alkali–vanillin ratio. Reaction of vanillin with strong alkali solution at elevated temperatures does not yield either of the acids.

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Absorption Spectra of Heterocyclic Compounds. I. Quinolinols and Isoquinolinols¹

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An examination of the literature shows that very few of the simple derivatives of quinoline and isoquinoline have been studied from the standpoint of their absorption spectra. It seems desirable, both from theoretical considerations and with the object of discovering criteria for the identification of isomers, to investigate the spectroscopic properties of various isomeric series differing from one member to the next only in the position of the substituent groups. The present paper deals with the mono-hydroxy derivatives² of quinoline and isoquinoline. A subsequent paper is planned to consider the monoamino derivatives.

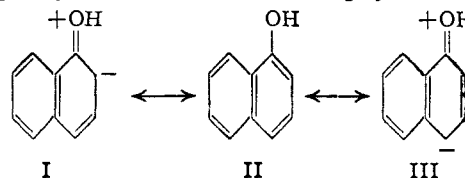
It is convenient for present purposes to classify the quinolinols and isoquinolinols into three groups—those which bear formal analogy to (1) α -naphthol, (2) β -naphthol, and (3) those which can be written as derivatives of 2- and 4-pyridones.

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(2) The following spectra have been reported, though many with insufficient precision according to modern standards: 2-Quinolinol—(a) Hartley and Dobbie, *J. Chem. Soc.*, **75**, 640 (1899); (b) Morton and Rogers, *ibid.*, **127**, 2698 (1925); (c) Ley and Specker, *Ber.*, **72**, 192 (1939); (d) Morton and Stubbs, *J. Chem. Soc.*, 1321 (1939); 6-Quinolinol—(e) Dobbie and Fox, *ibid.*, **101**, 77 (1912); 8-Quinolinol—(f) Dabrowski and Marchlewski, *Bull. int. acad. polon. sci. lett., Cl. sci. math. nat.*, **A**, 479 (1935); (g) Bednarczyk and Marchlewski, *ibid.*, **A**, 187 (1937); (h) Kiss, Bacskai and Csokan, *J. prakt. Chem.*, [2] **160**, 1 (1942).

I. α -Naphthol Analogs.—In the prototype of this class, α -naphthol itself (II), the absorption of light by a neutral solution is largely due to con-



tributing structures such as I and III which resonate with II. The contribution to resonance of these forms, however, is relatively slight, since their formation involves the separation of charges and hence is not favored. However in basic solution where the phenol is completely ionized, V, the formation of the corresponding quinonoidal forms IV and VI is much more probable, and hence contribute more strongly to the resonance. Since these quinonoidal forms absorb light more strongly than the purely aromatic forms, a bathochromic shift is expected in passing from neutral to basic solution. That this is borne out by experiment can be seen from Fig. 1.

