

taining a trace of sodium hydroxide. A slight excess of saturated aqueous potassium permanganate was added dropwise to the suspension while chilling. The mixture was acidified and treated with aqueous sodium bisulfite. A nearly white solid, which remained in suspension, was removed by filtration, dried, and then dissolved in methanol. The methanol solution was saturated with dry hydrogen chloride and allowed to stand at room temperature for six hours. Evaporation of the methanol gave crude methyl 5-nitro-2-thiophenecarboxylate, m.p. 63–67°. Successive recrystallizations from benzene–hexane, hexane and 90% methanol, gave a pure product, m.p. 76° (76°).¹

5-Nitro-2-thienal malononitrile.—A solution of 15.7 g. (0.10 mole) of 5-nitro-2-thiophenecarboxylate and 6.6 g. (0.10 mole) of malononitrile in 150 cc. of absolute ethanol was heated to boiling. Two drops of piperidine was added to the amber solution causing it to change immediately to a clear dark brown. Boiling was continued for five minutes, whereupon the mixture was cooled to give a brown crystalline precipitate. The latter was separated by filtration and dried to give 17.9 g., m.p. 147–148°. Second and third crops, 0.8 g. (m.p. 145–146°) and 0.3 g. (m.p. 142–144°), obtained upon further dilution and chilling of the filtrates brought the crude yield of 5-nitro-2-thienal malononitrile to 19.0 g. (93%). A sample of the first crop was recrystallized from ethanol (Nuchar) three times to give tan crystals, m.p. 149°.

Anal. Calcd. for C₈H₅O₂N₃S: C, 46.8; H, 1.47; N, 20.5. Found: C, 47.2; H, 1.66; N, 20.2.

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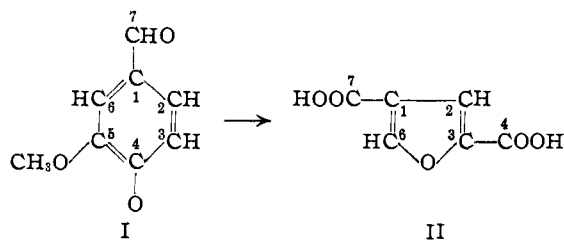
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Reactions of Vanillin and its Derived Compounds. XIV.¹ 2,4-Furanedicarboxylic Acid from Vanillin

BY IRWIN A. PEARL AND JOHN S. BARTON²

During the study of the reaction products of lignin and sodium chlorite in acid solution,³ it was desired to determine the nature of the reaction between vanillin (I) and sodium chlorite under the same conditions of reaction. Vanillin was treated with sodium chlorite in the presence of acetic acid at pH 3 at 45° for 8 hours. The reaction mixture was extracted with ether and the ether-soluble material was separated into bisulfite-, bicarbonate- and alkali-soluble fractions and neutral material. The bisulfite-soluble fraction yielded crystals of 2,4-furanedicarboxylic acid (II), a compound previously prepared by Feist⁴ by treating methyl coumalate with potassium hydroxide.

This oxidative reaction of vanillin to form 2,4-furanedicarboxylic acid, representing an interesting transformation of an aromatic compound to a furane derivative, may be pictured as follows. The numerals identify the carbon atoms involved and have no relation to the system employed in naming the compounds.



(1) For Paper XIII of this series, see *THIS JOURNAL*, **73**, 4091 (1951).

(2) Crown Zellerbach Corp., Camas, Wash.

(3) J. S. Barton, *Tappi*, **33**, 496 (1950).

(4) F. Feist, *Ber.*, **34**, 1992 (1901).

Experimental

A suspension of 76 g. of vanillin in 2 liters of water containing 5 ml. of glacial acetic acid was treated dropwise with continuous stirring with a solution of 135 g. (1.5 moles) of sodium chlorite in 300 ml. of water over a period of 8 hours. The temperature of the reaction was maintained below 45°. The pH at the start of the reaction was 3.0 and gradually dropped to 2.0 at the end. The dark red reaction mixture was cooled, filtered to remove a little dark precipitate, and extracted continuously with ether. This extract was dried and distilled to yield 37.0 g. of ether-soluble product. The entire ether extract was redissolved in ether and extracted successively with 21% sodium bisulfite, 8% sodium bicarbonate and 5% sodium hydroxide solutions. These, in turn, were acidified with sulfuric acid and re-extracted with ether, this time in separatory funnels. The yields are given in Table I.

TABLE I

FRACTIONS OBTAINED FROM ETHER EXTRACT OF VANILLIN

Fractions	Yield, g.
Bisulfite soluble	10
Bicarbonate soluble	2
Alkali soluble	1
Neutral	Trace

The high solubility of all fractions in water accounted for the low recovery of individual fractions. The bisulfite-soluble fraction was a mixture of white crystalline and brown tarry materials. The fraction was leached with cold water, which dissolved the brown tar, leaving approximately 1 g. of white crystals. These were recrystallized from 1:5 methanol–chloroform to yield 2,4-furanedicarboxylic acid as white crystals melting at 264° (Fischer–Johns block). About one half of the material sublimed before the melting point was reached. Feist⁴ also recorded this characteristic for his compound, for which he recorded a melting point of 266°.

Anal. Calcd. for C₈H₄O₅: C, 46.15; H, 2.5. Found: C, 46.20; H, 2.60.

The dimethyl ester was prepared by esterifying with methanol in the presence of dry hydrogen chloride. The product was recrystallized from absolute methanol to give crystals melting at 107°; Feist recorded 109°.

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Observations on the Fluorination of Praseodymium and Neodymium Compounds

BY ALEXANDER I. POPOV AND GEORGE GLOCKLER

In the course of study of the oxidation states of the rare earth elements^{1,2} it seemed that the higher oxidation states, if they exist, could be obtained by using fluorine as the oxidizing agent. The possibility of obtaining bromine trifluoride and chlorine trifluoride commercially, suggested the use of these powerful fluorinating agents instead of elemental fluorine.

Chloride Trifluoride.—Chlorine trifluoride was obtained from the Harshaw Chemical Company packed in steel cylinders of one pound capacity. The degree of purity could not be ascertained because of the lack, at the present time, of adequate methods for the analysis of fluoride gases. It was of technical grade and probably contained chlorine monofluoride and hydrogen fluoride as the main impurities. The source and purity of the rare earth compounds used in this investigation were reported in previous papers.^{1,2}

About 50–100 mg. of Pr₂O₃ was introduced, in a small platinum boat, into a nickel reaction chamber. A current of dry nitrogen was passed to remove the air and the moisture, and was followed by a slow stream of chlorine trifluoride. After the reaction was thought to be complete, chlo-

(1) A. I. Popov and G. Glockler, *THIS JOURNAL*, **71**, 4144 (1949).

(2) S. Rabideau and G. Glockler, *ibid.*, **73**, 488 (1951).