

proportional to gallium ion concentrations up to at least  $4 \times 10^{-4} M$  in chloride solutions.

Diffusion current data for  $2.23 \times 10^{-4} M$  gallium(III) chloride solutions  $0.05 M$  in potassium chloride and containing varying quantities of added alkali, as corrected for dilution effects, are summarized in Table I. It is clear that as the quantity of hydroxyl ion increases, more and more gallium ion is tied up in solution. It may be concluded, therefore, that gallium-hydroxyl ion aggregates are built up in these solutions, thereby reducing the speed of diffusion of gallium ions to the electrode, and that peptization is not a factor of appreciable importance. It seems very reasonable to conclude that similar aggregation processes would characterize bromide and nitrate solutions under comparable conditions.

TABLE I

EFFECT OF ADDED HYDROXYL ION ON CORRECTED DIFFUSION CURRENT IN GALLIUM(III) ION REDUCTION

Mole ratio OH <sup>-</sup> /Ga <sup>3+</sup>	pH	Corrected current, microamperes
0.0	3.45	1.39
1.0	3.56	1.12
2.0	4.00	0.77
3.0 <sup>a</sup>	5.40	0.00

<sup>a</sup> Flocculated.

Unfortunately, the data reported do not permit postulations as to the exact natures of the aggregates. Supplementary studies on the variations of the diffusion current with drop time and on the temperature coefficient of the current might permit such postulations.

#### Experimental

All materials used were chemically pure. Polarographic data were obtained with a Sargent Recording Polarograph. Polarographic reductions were run with samples thermostated to  $25 \pm 0.5^\circ$  and freed of oxygen by bubbling nitrogen. All samples were  $0.05 M$  in potassium chloride.

Initial studies were made upon gallium(III) chloride solutions of varying concentrations. To determine the effects of added alkali, solutions obtained by adding varying quantities of sodium hydroxide to fixed quantities of gallium chloride solution and adding sufficient potassium chloride were reduced polarographically. To ensure proper functioning of the dropping mercury cathode, control solutions containing no added hydroxyl ion were run immediately before and immediately after those containing alkali.

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### 5-Nitro-2-thiophenealdehyde

By TRACY M. PATRICK, JR., AND WILLIAM S. EMERSON

Although the several nitrobenzaldehydes are well known, no mention has been made of their thiophene analogs. We have found that nitration of 2-thiophenealdehyde diacetate gives 72% of 5-nitro-2-thiophenealdehyde diacetate. This diacetate has been cleaved (76% yield) by steam distillation from dilute hydrochloric acid. The 5-nitro-2-thiophenealdehyde has been characterized as the semicarbazone and oxidized to 5-nitro-2-thiophenecarboxylic acid. The methyl ester of this acid melted at  $76^\circ$ , the recorded value for methyl 5-nitro-2-thiophenecarboxylate,<sup>1</sup> rather than at  $99^\circ$ ,

(1) I. J. Rinken, *Rec. Trav. Chim.*, [4] 81, 1134 (1932).

which is the recorded value for methyl 4-nitro-2-thiophenecarboxylate.<sup>1</sup> The 5-nitro-2-thiophenealdehyde also reacted with malononitrile in the presence of piperidine to give 93% of 5-nitro-2-thienalmalononitrile.

**2-Thiophenealdehyde Diacetate.**—To a mixture of 127 g. of acetic anhydride and 2 g. of stannous chloride dihydrate held below  $10^\circ$  by means of an ice-bath there was added over a forty-five-minute period 112 g. of 2-thiophenealdehyde. When the ice-bath was removed at the close of the addition, the temperature rose rapidly to  $24^\circ$  and reapplication of the ice-bath did not prevent a continuing rise in temperature. Therefore, the mixture was treated immediately with ice, water and then sodium bicarbonate. The copious precipitate was separated by filtration, washed with aqueous sodium bicarbonate and then with water and dried *in vacuo* at  $30$ – $40^\circ$  for eight hours. After this precipitate was dissolved in benzene, the solution was filtered and evaporated to dryness. The residue was dried *in vacuo* at  $40$ – $50^\circ$  for 5.5 hours to yield 167.5 g. (78%) of 2-thiophenealdehyde diacetate. An analytical sample was crystallized from a mixture of benzene and hexane, m.p.  $66$ – $68^\circ$ .<sup>2</sup>

*Anal.*<sup>3</sup> Calcd. for  $C_9H_{10}O_4S$ : C, 50.5; H, 4.68. Found: C, 50.7; H, 4.91.

**5-Nitro-2-thiophenealdehyde Diacetate.**—Two solutions (A and B) were prepared. A consisted of 107 g. (0.5 mole) of 2-thiophenealdehyde diacetate in 200 cc. of acetic anhydride, and B consisted of 30 cc. of fuming nitric acid (d. 1.49–1.50) in 250 cc. of glacial acetic acid. Half of solution B was placed in a 1-l., three-necked flask fitted with a stirrer, a thermometer and a dropping funnel. The stirred mixture was cooled to  $5$ – $10^\circ$  and then half of solution A was added dropwise over a 30-minute period. The temperature was held at  $10$ – $15^\circ$  during the addition. The remainder of solution B was then added to the flask followed by dropwise addition of the balance of solution A over 30 minutes. The cooling-bath was removed, and the amber reaction mixture was stirred at room temperature ( $30^\circ$ ) for ninety minutes longer. The mixture was next poured into 1 l. of finely crushed ice, whereupon a yellow crystalline solid separated. The product was removed by filtration, washed with cold water, and pressed as dry as possible on the filter.

The crude product was dissolved in 350 cc. of benzene, filtered, and then washed with water until neutral. Water and 2 cc. of 85% phosphoric acid were added to the benzene solution and the mixture was steam distilled in an effort to hydrolyze the crude 5-nitro-2-thiophenealdehyde diacetate to the free aldehyde. This procedure was unsuccessful. Therefore, the crude product again was dissolved in benzene, washed with water, and distilled from a Claisen flask to give 92.9 g. (72% yield) of yellow liquid, b.p.  $155$ – $165^\circ$  (1.5 mm.), which solidified in the receiver. A sample of the solid was recrystallized three times from ethanol and once from a benzene-hexane mixture to give pale yellow tablets, m.p.  $71$ – $75^\circ$ .

*Anal.* Calcd. for  $C_9H_7O_6NS$ : N, 5.41. Found: N, 5.23.

**5-Nitro-2-thiophenealdehyde.**—Ten grams of the crude distilled 5-nitro-2-thiophenealdehyde diacetate was placed in a 1-l. Claisen flask with 500 cc. of 1 *N* hydrochloric acid and steam distilled. The first 200 cc. of distillate was a cloudy liquid from which 1.7 g. of long yellow thread-like needles deposited on chilling, m.p.  $63$ – $71^\circ$ . Subsequent crops totalling 2.9 g., m.p.  $72$ – $75^\circ$ , were obtained upon further distillation of some 1200 cc. Filtrates from the separation of these crops were returned to the distilland from time to time. The total yield of 5-nitro-2-thiophenealdehyde was 76% (4.6 g.). A sample of the first crop was crystallized twice from aqueous ethanol and finally from water, m.p.  $75$ – $76^\circ$ .

*Anal.* Calcd. for  $C_8H_7O_3NS$ : C, 38.2; H, 1.92; N, 8.92. Found: C, 38.5; H, 2.02; N, 9.10.

The semicarbazone melted at  $242$ – $243^\circ$  after one crystallization from nitrobenzene.

*Anal.* Calcd. for  $C_8H_9O_3N_4S$ : C, 33.6; H, 2.80. Found: C, 33.9; H, 2.73.

**Methyl 5-Nitro-2-thiophenecarboxylate.**—A few crystals of 5-nitro-2-thiophenealdehyde were suspended in water con-

(2) All of the melting points are corrected.

(3) All of the analyses are microanalyses performed by Mr. Donald Brels of these laboratories.

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°).<sup>1</sup>

**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 C<sub>8</sub>H<sub>5</sub>O<sub>2</sub>N<sub>3</sub>S: C, 46.8; H, 1.47; N, 20.5. Found: C, 47.2; H, 1.66; N, 20.2.

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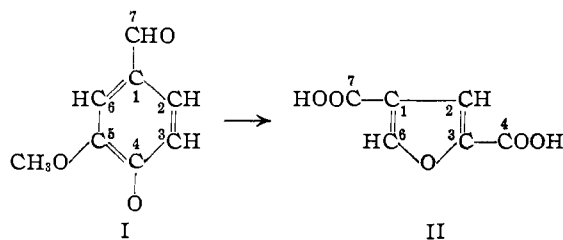
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## Reactions of Vanillin and its Derived Compounds, XIV.<sup>1</sup> 2,4-Furanedicarboxylic Acid from Vanillin

BY IRWIN A. PEARL AND JOHN S. BARTON<sup>2</sup>

During the study of the reaction products of lignin and sodium chlorite in acid solution,<sup>3</sup> 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 Feist<sup>4</sup> 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 OXIDATION

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. Feist<sup>4</sup> also recorded this characteristic for his compound, for which he recorded a melting point of 266°.

*Anal.* Calcd. for C<sub>8</sub>H<sub>4</sub>O<sub>5</sub>: 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<sup>1,2</sup> 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.<sup>1,2</sup>

About 50–100 mg. of Pr<sub>2</sub>O<sub>3</sub> 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).