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-thenalmalononitrile.—A solution of 15.7 g. (0.10 mole) of 5-nitro-2-thiophenealdehyde 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-thenalmalononitrile 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 $C_8H_3O_2N_3S$: C, 46.8; H, 1.47; N, 20.5. Found: C, 47.2; H, 1.66; N, 20.2.

CENTRAL RESEARCH DEPT.
MONSANTO CHEMICAL CO.
DAYTON 7, OHIO
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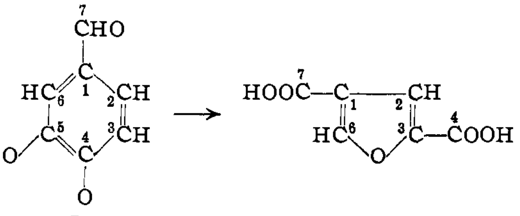
Reactions of Vanillin and its Derived Compounds. XIV.[1] 2,4-Furanedicarboxylic Acid from Vanillin

BY IRWIN A. PEARL AND JOHN S. BARTON[2]

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 *p*H 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[4] 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.



I II

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 *p*H 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[4] also recorded this characteristic for his compound, for which he recorded a melting point of 266°.

Anal. Calcd. for $C_6H_4O_5$: C, 46.15: H, 25. 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°.

THE INSTITUTE OF PAPER CHEMISTRY
APPLETON, WISCONSIN
RECEIVED OCTOBER 26, 1951

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[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).

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 Pr_2O_3, 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-

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

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

rine trifluoride was shut off and the system was flushed with nitrogen in order to eliminate all of the chlorine trifluoride before opening the tube. All the reactions were carried out at room temperature.

In all attempts, praseodymium sesquioxide yielded the trifluoride as the reaction product. Higher oxides of praseodymium, Pr_6O_{11} and PrO_2, were treated with chlorine trifluoride but, likewise, the trifluoride was the only product obtained. Neodymium sesquioxide, under similar conditions, also yielded only the trifluoride.

Bromine Trifluoride.—Bromine trifluoride was obtained likewise from the Harshaw Chemical Company. It was of technical grade and probably contained bromine pentafluoride and hydrogen fluoride as impurities.

About 5 ml. of the bromine trifluoride was poured into a platinum crucible and the rare earth compound was slowly added. The reaction mixture was allowed to stand in the hood until the excess of the bromine trifluoride had evaporated and its last traces were removed by placing the crucible in a vacuum desiccator over barium oxide for a few hours.

Freshly ignited oxides did not react noticeably with bromine trifluoride. When the oxides were exposed to the air for some time so that they absorbed some moisture, the reaction was very vigorous and was accompanied by evolution of heat and light. Small amounts of the rare earth trifluoride were formed, but usually the reaction was not complete even with excess of the bromine trifluoride.

Hydrated oxalates reacted very violently giving a mixture of the trifluoride and some carbon. No reaction was observed between the rare earth trifluorides and the bromine trifluoride. An attempt was made to facilitate the reaction by heating the bromine trifluoride–rare earth oxide mixture to about 100–150°. The reaction was somewhat more vigorous, but the products were contaminated by a brown residue which was the product of the attack of bromine trifluoride on the platinum crucible. This result contradicts the observation of Sharp and Emeleus[3] that bromine trifluoride does not attack platinum.

About 20 ml. of bromine trifluoride was distilled at room temperature, under vacuum, in a Vycor apparatus. The distillate, which had a much lighter color than the original material, was allowed to react with platinum foil. Slow reaction was observed at room temperature and the platinum was dissolved when the mixture was heated to approximately 50°. The reaction product was a brown compound containing platinum, bromine and fluorine. Its exact composition could not be determined.

In the course of this investigation, it was necessary to prepare rare earth trifluorides by a precipitation reaction. Addition of equimolar amount of fluoride ion to rare earth ion in solution produced only a highly dispersed gelatinous precipitate which was impossible to filter or centrifuge. A crystalline, easily filtrable precipitate was, however, obtained by dissolving the rare earth nitrate in 95% alcohol and slowly adding to it a 40% solution of hydrofluoric acid until the precipitation was complete. Analysis of the resulting product showed that it was the anhydrous salt rather than the monohydrate which is the usual form of the rare earth trifluoride obtained under similar conditions.

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(3) A. G. Sharp and H. J. Emeleus, *J. Chem. Soc.*, 2135 (1948).

DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING
STATE UNIVERSITY OF IOWA
IOWA CITY, IOWA

RECEIVED AUGUST 23, 1951

Addition Compound of Dicyclohexylamine and Hydrogen Peroxide

BY THEODORE WAGNER-JAUREGG

It is known that dicyclohexylamine forms a crystalline monohydrate and monoalcoholate, melting at 23 and 28°, respectively. We have found that by treating the base with 30% H_2O_2 at room temperature, a stable addition compound can be obtained, with a melting point of 88–90°. The empirical formula of this complex was found to be $2(C_6H_{11})_2NH\cdot H_2O_2$, which indicates that each of the two hydroxyl groups of hydrogen peroxide is coordinated with one $>$NH group.

The analytical values for such a complex are close to those for dicyclohexylhydroxylamine, $(C_6H_{11})_2NOH$. That the new substance is not this hydroxylamine derivative but the addition compound mentioned above has been established by the following facts: Free dicyclohexylamine can be liberated from the addition compound by gently warming with diluted sodium hydroxide. Upon the reaction of the H_2O_2 base complex with oxalic, hydrochloric or hydroiodic acid the corresponding dicyclohexylamine salts are obtained; in the latter case the expected amount of iodine is liberated.

No similar hydrogen peroxide complexes could be obtained with cyclohexylamine, dodecylamine or di-*n*-heptylamine.

The new substance might be useful for technical applications, where an oxidant is needed in the presence of a strong base, to neutralize formed acids. It further could be of value for analytical or preparative purposes as a source of hydrogen peroxide in solid form.

Twenty ml. of dicyclohexylamine was mixed with 40 ml. of 30% hydrogen peroxide. Immediate reaction with slight rise of temperature took place yielding a solid mass. Next morning the material was filtered with suction, washed with a very small amount of water, and dried over P_2O_5 in a vacuum desiccator. The yield was almost quantitative.

The product was soluble in alcohol or ether at room temperature, or in boiling petroleum ether, insoluble in water. For purification it was dissolved in a small amount of warm alcohol and precipitated by the addition of water. After recrystallization from boiling petroleum ether fine needles with a melting point of 88–90° were obtained.

Anal. Calcd. for $(C_{12}H_{23}N)_2\cdot H_2O_2$ (396.6): C, 72.8; H, 12.2; N, 7.1; equiv. wt., 396.6; H_2O_2, 8.6. Found: C, 73.0; H, 12.2; N, 7.1; equiv. wt., 404; H_2O_2, 8.1.

On boiling with 20% HCl the substance yielded dicyclohexylamine hydrochloride; m.p. 326° (uncorrected, with decomposition).

Anal. Calcd. for $C_{12}H_{23}N\cdot HCl$ (217.6): C, 66.3; H, 11.12; Cl, 16.3. Found: C, 66.24; H, 10.96; Cl, 16.7.

Dicyclohexylamine oxalate was formed by precipitation of the substance with oxalic acid in ether; m.p. 206° (uncorrected).

Anal. Calcd. for $C_{12}H_{23}N\cdot C_2H_2O_4$ (271.2): N, 5.17. Found: N, 5.23.

By dissolving the substance in diluted H_2SO_4 and addition of KI, iodine was liberated and a salt precipitated, which after several recrystallizations from hot water formed colorless flat prisms, decomposing about 300°.

Anal. Calcd. for $C_{12}H_{23}N\cdot HI$ (309.1): I, 41.1. Found: 41.3.

Acknowledgments.—A sample of dicyclohexylamine was kindly supplied by Monsanto Chemical Co., Organic Chemicals Division, St. Louis, Mo. I wish to thank Mr. B. Hackley, Jr., and Mr. R. Proper for technical assistance.

CHEMICAL CORPS MEDICAL LABORATORIES
ARMY CHEMICAL CENTER, MARYLAND

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Derivatives of β-Hydroxypropyl Sulfides. II. Alkylthioalkoxypropanols

BY EDWARD G. RIETZ, THOMAS K. TODSEN, ARTHUR S. LEON AND C. B. POLLARD

In the course of an investigation of the reactions of 1-alkylthio-2,3-epoxypropanes,[1] it was found

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(1) T. K. Todsen, C. B. Pollard and E. G. Rietz, THIS JOURNAL, **72**, 4000 (1950).