liter at 25°. Ultraviolet absorption E_{max} in 2% aqueous dimethylformamide 16500 at 366.0 mμ.

Anal. Calcd. for $C_9H_9N_3O_5$: C, 45.19; H, 3.79; N, 17.57. Found: C, 45.13; H, 3.80; N, 17.33.

EATON LABORATORIES
DIV., NORWICH PHARMACAL CO.
NORWICH, NEW YORK

The Hydrolytic Rearrangement of α-Cyanoisopropyl Mesitoate[1]

BY JEREMIAH P. FREEMAN AND GEORGE B. LUCAS

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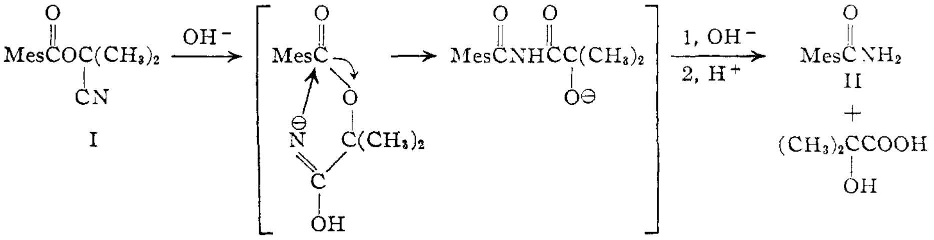
In connection with other work, the action of ethanolic sodium hydroxide on α-cyanoisopropyl mesitoate (I) has been examined. From this reaction, mesitamide (II) and α-hydroxyisobutyric acid were isolated. It is suggested that this reaction involves an intramolecular rearrangement which probably proceeds in the manner



Mes = 2,4,6-trimethylphenyl

Steric hindrance around the ester carbonyl group prevents attack of the hydroxide ion at that site so that the less reactive but unhindered nitrile function is attacked. Attack of the strongly nucleophilic intermediate imide ion on the carbonyl group is followed by tautomerization to the hydroxy imide which undergoes hydrolysis in the alkaline solution to mesitamide and α-hydroxyisobutyric acid. That the intramolecular rearrangement proceeds faster than simple hydrolysis of the nitrile is not unexpected since it has been demonstrated by Fuson and his co-workers[2,3] that the hindrance offered to intramolecular processes by the *o*-methyl groups is considerably less than to intermolecular processes. For instance, Fuson and Hammann[3] have shown that highly hindered ketones undergo a series of intramolecular ring closures involving the hindered carbonyl function and neighboring groups.

This hydrolytic rearrangement appears to be specific for sterically hindered esters as α-cyanoisopropyl benzoate was hydrolyzed rapidly and quantitatively to benzoic acid. In this case attack by hydroxide ion at the ester carbonyl proceeded normally.

Experimental[4]

α-Cyanoisopropyl Mesitoate.—To 51.0 g. (0.52 mole) of acetone cyanohydrin contained in a 200-ml. flask was added 91.5 g. (0.5 mole) of mesitoyl chloride with stirring. After addition was complete, the mixture was refluxed for two hours and then poured into water. The resulting mixture was extracted with four 100-ml. portions of methylene chloride. The organic extracts were washed with 10% sodium hydroxide solution and water, then dried and concentrated to yield 90.7 g. (79%) of α-cyanoisopropyl mesitoate, m.p. 40–42°. An analytical sample was prepared by distillation, b.p. 135–136° (8 mm.).

Anal. Calcd. for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41; N, 6.06. Found: C, 73.11; H, 7.63; N, 5.56.

Reaction of α-Cyanoisopropyl Mesitoate with Sodium Hydroxide.—A solution of 4.6 g. (0.02 mole) of α-cyanoisopropyl mesitoate in 50 ml. of ethanol was added to a solution of 8.0 g. (0.2 mole) of sodium hydroxide in 50 ml. of ethanol. The resulting mixture was heated under reflux for six hours and then poured into water. The solid that separated was collected on a filter; yield 1.6 g. The filtrate was extracted with ether and upon concentration of these extracts an additional 0.5 g. of solid was obtained. Recrystallization from benzene gave white crystals of mesitamide, m.p. 187–189° (lit. m.p.[5] 189°); total yield 2.1 g. (71%).

The aqueous extracts were acidified and subjected to continuous ether extraction for 18 hours. Upon drying and concentrating the ether solution there was obtained 1.8 g. (86%) of α-hydroxyisobutyric acid, which was identified by comparison of its infrared spectrum with that of an authentic sample.

α-Cyanoisopropyl Benzoate.—To 109.2 g. (0.52 mole) of trifluoroacetic anhydride contained in a 500-ml. 3-neck flask was added 62.2 g. (0.51 mole) of benzoic acid at 0–10°. The resulting mixture was stirred under reflux for 30 minutes. It was then cooled to 10° and 42.5 g. (9.5 mole) of acetone cyanohydrin was added at such a rate that the temperature did not rise above 20°. After the addition was complete the mixture was stirred at room temperature for 30 minutes, and then poured into water and the product isolated by conventional methods. α-Cyanoisopropyl benzoate was isolated by distillation at 0.01 mm. as a white solid, m.p. 37–38°, yield 48.7 g. (52%).

Anal. Calcd. for $C_{11}H_{11}NO_2$: C, 69.82; H, 5.86. Found: C, 69.51; H, 5.16.

Reaction of α-Cyanoisopropyl Benzoate with Sodium Hydroxide.—When 3.8 g. (0.02 mole) of α-cyanoisopropyl benzoate was treated with 8.0 g. of sodium hydroxide in the manner described for the corresponding mesitoate, 2.3 g. (96%) of benzoic acid, m.p. 120–122°, was obtained.

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[1] This work was carried out under Army Ordnance Contract W-01-021-ORD-334.

[2] R. C. Fuson, W. D. Emmons and R. Tull, *J. Org. Chem.*, **16**, 648 (1951).

[3] R. C. Fuson and W. C. Hammann, THIS JOURNAL, **74**, 1626 (1952).

[4] We are indebted to Dr. Keith S. McCallum for infrared interpretations and to Miss Annie Smelley for the micro-combustion data.

[5] I. Heilbron, "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1953, Vol. III, p. 84.

ROHM AND HAAS COMPANY
REDSTONE ARSENAL RESEARCH DIVISION
HUNTSVILLE, ALABAMA

Perfluorinated Butadiene

BY A. L. HENNE AND WM. POSTELNECK

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To allow a new, three-step synthesis of perfluorobutadiene,[1] we have treated 1,2,2-trifluoro-1,2-dichloroiodomethane[2,3] with zinc in acetic anhydride

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[1] W. T. Miller, *et al.*, *Ind. Eng. Chem.*, **39**, 401 (1947).

[2] J. T. Barr, *et al.*, THIS JOURNAL, **73**, 1352 (1951).

[3] R. N. Haszeldine, *J. Chem. Soc.*, 4423 (1952).

to obtain 1,1,2,3,4,4-hexafluoro-1,2,3,4-tetrachlorobutane by chain length doubling,[4] in preference to olefin formation. The starting compound was obtained from iodine chloride and chlorotrifluoroethylene.[2,3] The reaction product was dechlorinated with zinc in alcohol[3] to the desired perfluorobutadiene.

Experimental

1,1,2,3,4,4-Hexafluoro-1,2,3,4-tetrachlorobutane.—Acetic anhydride (80 ml.), methylene chloride (80 ml.), granular zinc (32.7 g.) and 1,2,2-trifluoro-1,2-dichloroiodoethane[2,3] (140 g. or 0.5 mole) were placed in a round-bottom flask equipped with a mercury-sealed stirrer, a thermometer dipping in the liquid, and a reflux condenser backed by a Dry-Ice cooled trap. The reaction started spontaneously and was kept under control by intermittent cooling with an ice-bath. After three hours, the unreacted zinc (13.5 g.) was removed, the flask was immersed in ice-water, and 150 ml. of dilute sulfuric acid was added dropwise, with constant stirring, to hydrolyze the acetic anhydride. The lower layer was decanted, neutralized, rinsed and dried; it must be free of acetic acid to avoid later difficulties during fractional distillation. After removal of most of the methylene chloride, fractionation gave 38.1 g. (51%) of 1,1,2,3,4,4-hexafluoro-1,2,3,4-tetrachlorobutane, b.p. 133–135°, $n^{14}\text{D}$ 1.3832 (reported[3] 1.382 at 23°).

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[4] A. L. Henne, THIS JOURNAL, **75**, 5750 (1953).

DEPARTMENT OF CHEMISTRY
THE OHIO STATE UNIVERSITY
COLUMBUS 10, OHIO

The Isolation and Identification of Vanillil in the Oxidation Products of Sulfite Waste Liquor

BY A. MARGARET JOHNSON AND H. BORDEN MARSHALL

RECEIVED OCTOBER 8, 1954

The presence of vanillil in the alkaline oxidation products of sulfite waste liquor is of theoretical interest from the point of view of lignin chemistry. The isolation and identification of this compound in the products obtained on oxidation of fermented sulfite waste liquor has been reported by the authors,[1] but the experimental details, which are presented herewith, could not be published at that time for reasons of patent protection. Subsequently, Pearl and Dickey[2] isolated vanillil in a yield of 0.1% (based on the lignin present) from sulfite waste liquor which had been oxidized with copper hydroxide and sodium hydroxide. These authors based their identification on a comparison of their compound with synthetic vanillil, which they prepared by the oxidation, with copper oxide in acetic acid solution, of hydrovanilloin, which in turn was obtained by the electrolytic reduction of vanillin.

Later Pearl and Beyer[3] oxidized a series of vanillin derivatives under conditions of lignosulfonate oxidations and obtained only monoguaiacyl compounds in the oxidation mixture. Under the same conditions, bis-vanillyl compounds yielded vanillil, vanillovanillone, vanillin, vanillic acid and dehydrodivanillin. Hence it was concluded that vanillil did not originate in the oxidation products of sulfite waste liquor through secondary condensation of the vanillin present, but rather from the oxidation of bis-vanillyl structures present in at least a portion of the lignin molecule.

Sulfite waste liquor was oxidized with lime and air to form vanillin in a yield of 5.3% of the lignin. The oxidation products were extracted from the acidified oxidation mixture with toluene, from which they were subsequently extracted with 10% caustic solution. On acidification of the caustic extract with an excess of SO_2, vanillil slowly crystallized out along with other unidentified ligneous residues. The crude material was purified by precipitation from a sodium bicarbonate solution with sulfuric acid and by recrystallization from absolute alcohol. The yield was 0.17% based on the lignin content of the sulfite waste liquor.

The identity of the pure material was established by analysis and by the preparation and analysis of several derivatives. Acetylation, and methylation with dimethyl sulfate, indicated the presence of one free hydroxyl group for each methoxyl present. The α-diketone structure was proven by reaction with *o*-phenylenediamine to form 2,3-di-(3-methoxy-4-hydroxyphenyl)-quinoxaline and by reaction with 2,4-dinitrophenylhydrazine to form a monohydrazone. The introduction of only one hydrazine residue into substituted benzils has been noted previously by Raiford[4] who suggested steric hindrance as the explanation.

Molecular weight determinations by the Rast method were not satisfactory because of the limited solubility of vanillil in camphor, but gave values of 288 and 312. (mol. wt. vanillil = 302).

Veratril, the methylated derivative of vanillil, is well known. Therefore, as a final proof of the identity of our material as vanillil, the methylated derivative was shown to be identical to veratril, prepared by the benzoin condensation of veratric aldehyde. The quinoxaline derivative of veratril also is known and its identity with the quinoxaline derivative of the product obtained on methylation was established. Vanillil was found to be quite stable when refluxed in concentrated caustic solution.

Experimental

Oxidation of Sulfite Waste Liquor.—The oxidation of sulfite waste liquor[5,6] was carried out in a special reactor equipped with a turbomixer, a steam inlet for heating purposes, a gas inlet for introducing air directly below the blades of the turbomixer and an exhaust outlet fitted with a back pressure valve. Twenty-five gallons of fermented sulfite waste liquor (lignin content 53.1 g./l. based on a methoxyl content of 15.5%) was mixed with 25 pounds of slaked lime and the mixture heated for 80 minutes at 170°. Air was introduced into the reactor at the rate of 32 lb./hour and the turbomixer was operated throughout the entire reaction period. The exhaust gases were relieved through the back pressure valve, set at 10 atm. pressure, so that the total pressure throughout the reaction was maintained automatically at this pressure. The reaction mixture was discharged through a cooler and allowed to settle. The clear supernatant liquor was drawn off, acidified first with CO_2 then with H_2SO_4 to a *p*H of approximately 6.2, and extracted with toluene.

Isolation of Vanillil.—The toluene extract containing vanillin, acetovanillone, vanillil and other oxidation prod-

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[1] A. M. Johnson and H. B. Marshall, paper presented before the Division of Cellulose Chemistry at the 118th Meeting of the American Chemical Society, Chicago, Ill., September 3–8, 1950.

[2] I. A. Pearl and E. E. Dickey, THIS JOURNAL, **74**, 614 (1952).

[3] I. A. Pearl and D. L. Beyer, *ibid.*, **76**, 2224 (1954).

[4] L. C. Raiford and W. F. Talbot, *ibid.*, **54**, 1092 (1932).

[5] The sulfite waste liquor was from a relatively short cook using a high SO_2 content on a mixture of spruce and balsam and was supplied by the Ontario Paper Company.

[6] J. H. Fisher and H. B. Marshall, Canadian Patent 467,552 (August 22, 1950); U. S. Patent 2,576,752 (November 27, 1951).