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°, $n^{14}D$ 1.3832 (reported[3] 1.382 at 23°).

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

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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waste liquor has been reported by the authors,[1] but the experimental details, which are presented herewith, could not be published at that time for reasons of patent protection.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).

ucts was scrubbed with sufficient 10% caustic solution to remove the bulk of the dissolved solids. The caustic extract (vanillin content as determined by precipitation with *m*-nitrobenzoylhydrazine, 320 g.) was acidified with an excess of SO_2 and allowed to stand for several hours. A brown flocculent precipitate containing vanillil and some unidentified ligneous residues gradually precipitated out. After standing several hours the precipitate was filtered from the sodium bisulfite mother liquor, washed and dried; yield 16.6 g. This residue was then extracted with sodium bicarbonate solution and the crude vanillil precipitated from the extract as a pale pink floc by acidification with H_2SO_4. After several crystallizations from absolute alcohol, minute pale yellow prismatic crystals were obtained, m.p. 227–228°,[7] yield 10.2 g. (3.2% of the vanillin formed during the reaction). The pure material was fairly soluble in acetone, alcohol and butyl acetate, slightly soluble in ether and almost insoluble in water, benzene and toluene.

Anal. Calcd. for $C_{16}H_{14}O_6$: C, 63.57; H, 4.63; OCH_3, 20.53; mol. wt., 302. Found: C, 63.53; H, 4.61; OCH_3, 20.4; mol. wt.,[8] 288 and 312.

Vanillil (Mono) 2,4-Dinitrophenylhydrazone.—Attempts to form a semicarbazone were unsuccessful. The 2,4-dinitrophenylhydrazone, crystallized from alcohol, m.p. 247.5–248.5°, gave the correct analysis for the mono derivative.

Anal. Calcd. for $C_{22}H_{18}O_9N_4$: N, 11.62. Found: N, 11.5.

Vanillil Acetate.—1.0 g. of vanillil was refluxed for 1 hour with 5 ml. of acetic anhydride and then allowed to stand overnight. The resulting pale yellow needle-shaped crystals were filtered, washed free of acetic acid and dried; yield 1.15 g. (90%). After 3 crystallizations from absolute alcohol the m.p. was constant at 139.5–140.5°.

Anal. Calcd. for $C_{20}H_{18}O_8$: $OCOCH_3$, 30.57; OCH_3, 16.06. Found: $OCOCH_3$, 30.6; OCH_3, 16.0.

Quinoxaline Derivative of Vanillil (2,3-Di-(3-methoxy-4-hydroxyphenyl)-quinoxaline).—1.0 g. of vanillil was refluxed for 6 hours with 0.35 g. of *o*-phenylenediamine in 25 ml. of glacial acetic acid according to the method of Vanzetti.[9] The reaction product was placed in the refrigerator overnight and the resulting pale yellow crystals, yield 1.14 g. (92%), after being recrystallized twice from absolute alcohol, melted at 228.2–229.5°.

Anal. Calcd. for $C_{22}H_{18}O_4N_2$: OCH_3, 16.57. Found: OCH_3, 16.6.

Fully Methylated Vanillil.—One and one-half g. of vanillil was methylated repeatedly with NaOH and dimethyl sulfate. After each methylation the product was recovered by extraction with chloroform and its methoxyl content determined. The latter was constant after 4 methylations, yield 1.36 g. (83%). The fully methylated derivative crystallized from absolute alcohol as light yellow felted crystals with a m.p. of 219–221°. The m.p. was unchanged on further crystallization from glacial acetic acid. When mixed with an authentic sample of veratril, the m.p. was not depressed (mixed m.p. 218.5–220°)

Anal. Calcd. for $C_{18}H_{18}O_6$: OCH_3, 37.6. Found: OCH_3, 36.9.

Quinoxaline Derivative of Methylated Vanillil.—The procedure used was identical to that described above for the preparation of the quinoxaline derivative of vanillil. A yield of 0.82 g. (61.7%) was obtained (m.p. after two recrystallizations from absolute alcohol, 194–196°). A mixed m.p. with the quinoxaline derivative of an authentic sample of veratril was not depressed (mixed m.p. 194–195°.)

Anal. Calcd. for $C_{24}H_{22}O_4N_2$: OCH_3, 30.9. Found: OCH_3, 30.3.

Stability of Vanillil toward Alkali.—0.6444 g. of vanillil was dissolved in 18 ml. of water containing 2 g. of NaOH and the solution refluxed for 1 hour. It was then diluted to 100 ml. with water and extracted with three 100-ml. portions of butanol to remove any cleavage products present. An ultraviolet absorption curve on 0.5 ml. of the butanol extract indicated the presence of only vanillil. The remainder of the butanol extract was evaporated to dryness, the residue taken up in a minimum of water and acidified with sulfuric acid. A white flocculent precipitate was obtained (0.04 g.) which had a m.p. of 220° and hence was considered to be vanillil.

Acknowledgments.—The work described herein was carried out under a Fellowship of The Ontario Paper Company Limited and as part of its investigation, under the direction of Dr. Charles A. Sankey, of means to utilize sulfite waste liquor. The authors acknowledge with thanks permission of the Ontario Paper Company Limited to publish this paper. Grateful acknowledgment is also made to Miss Mary Krizsan for assistance in carrying out these experiments.

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The Reaction of Styrene Oxide with Sulfonamides

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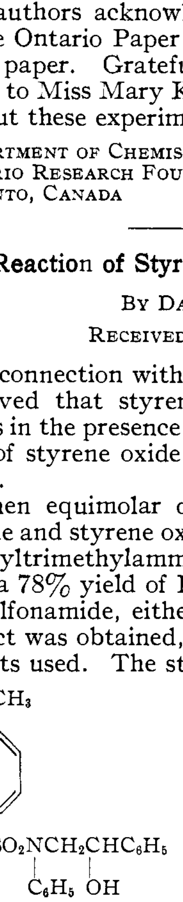
RECEIVED DECEMBER 2, 1954

In connection with another problem, it has been observed that styrene oxide reacts with sulfonamides in the presence of a basic catalyst. This reaction of styrene oxide has not been reported previously.

When equimolar quantities of *p*-toluenesulfonanilide and styrene oxide were heated with Triton B (benzyltrimethylammonium hydroxide) as catalyst, a 78% yield of I was obtained. With *p*-toluenesulfonamide, either the mono II or the bis III adduct was obtained, depending on the ratio of reactants used. The structures were assigned on the assumption that nucleophilic attack occurred preferentially at the primary carbon atom of styrene oxide. No further work was conducted to examine the scope of the reaction, but it appears to be general for primary and secondary sulfonamides.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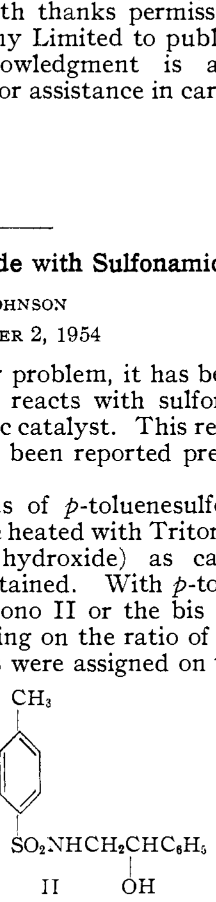
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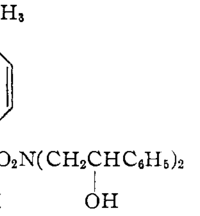
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Experimental[1,2]

N-(β-Hydroxy-β-phenethyl)-N-phenyl-*p*-toluenesulfonamide (I).—A mixture of styrene oxide (6.0 g., 0.050 mole), *p*-toluenesulfonanilide (12.4 g., 0.050 mole) and Triton B (0.5 ml.) was heated on a steam-cone for 2 hours. The resulting glass was dissolved in 25 ml. of hot toluene and stored at 5° whereupon 12.3 g. of hard prisms separated, m.p. 116.5–121°. Dilution of the filtrate with Skellysolve A (b.p. 28–38°) yielded a second crop of 2.0 g., m.p. 98–115°, bringing the total yield of crude I to 78%. Recrystalliza-

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[7] All melting points reported in this investigation are uncorrected.

[8] Rast camphor method.

[9] B. L. Vanzetti, *Gazz. chim. ital.*, **57**, 162 (1927).

[1] The microanalyses were performed by Mr. Richard M. Downing.

[2] All melting points are corrected.