

the only acid isolated was 2-benzofurancarboxylic acid in the following crude yields: 13, 10, 23.5, 13 and 16%. From an experiment carried out in petroleum ether (b. p. 23–38°) with 3 g. (0.025 mole) of 3-bromobenzofuran and a slight excess of *n*-butyllithium, there was obtained, after carbonation and hydrolysis, 0.15 g. of crude *o*-hydroxyphenylacetylene and a trace of unidentified acid melting at 127–129° (possibly *o*-hydroxyphenylpropionic acid).

***o*-Hydroxyphenylacetylene from 3-Bromobenzofuran.**—A solution of 10 g. (0.051 mole) of 3-bromobenzofuran in 30 cc. of ether was added during five minutes to a solution of 0.154 mole of *n*-butyllithium in 220 cc. of ether at room temperature. The solution was stirred for one hour and then hydrolyzed by pouring on iced dilute hydrochloric acid. The yield of *o*-hydroxyphenylacetylene, distilling at 95–98° under 10 mm., was 4 g. (67%). A part of the phenol was converted to the *p*-nitrobenzoate by treatment with *p*-nitrobenzoyl chloride in pyridine. The melting point was 108–109°, and the reported melting point is 107–108° (cor.).<sup>2</sup>

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## Syntheses in the Pyrazine Series: The Preparation and Properties of Pyrazine Sulfonic Acid

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Although recent electron diffraction studies have shown that benzene and pyrazine have very similar structures,<sup>1</sup> direct substitution with the usual electrophilic reagents, which proceeds so well with benzene operates only with great difficulty or not at all with pyrazine. This deactivation seems to be due to the electron-withdrawing inductive and resonance effects of the nitrogen atoms.<sup>2</sup> Even under such severe conditions as those used in the cleavage of lumazine,<sup>3</sup> *i. e.*, treatment with 100% sulfuric acid at 240°, sulfonation has not been observed. In fact, no direct sulfonation of the pyrazine nucleus has ever been reported. It seemed, therefore, of interest to attempt the synthesis of pyrazine sulfonic acid by means of indirect methods.

Methods based on the oxidation of pyrazine thiol were considered impractical because of the susceptibility of pyrazine to strong oxidizing agents. The reaction of chloropyrazine with sodium sulfite solutions was therefore investigated. Since chloropyrazine had previously been found to possess a chlorine atom intermediate in activity between an alkyl and aryl halide,<sup>4</sup> this method was adopted for the preparation.

Chloropyrazine was obtained by the following sequence of operations. Lumazine prepared according to Cain, Mallette and Taylor,<sup>5</sup> was cleaved to 2-hydroxy-3-pyrazinoic acid and then to hydroxypyrazine according to Weijlard, Tishler and Erickson.<sup>3</sup> Chloropyrazine was then prepared by

the method of Erickson and Spoerri<sup>4</sup> with the notable exception that phosphorus oxychloride (in a ratio of five moles to one of hydroxypyrazine) was used as sole chlorinating agent.<sup>6</sup>

### Experimental<sup>7</sup>

Chloropyrazine was heated in a sealed tube for twelve hours at 150° with a solution of sodium sulfite. The resulting solution was evaporated and the product crystallized from alcohol as bundles of white needles. Analysis after drying at room temperature *in vacuo* showed that the product was sodium pyrazine sulfonate monohydrate. It was extremely soluble in water, slightly soluble in alcohol, insoluble in ether and petroleum ether, and melted at 295°. Neither silver nitrate nor barium chloride precipitated an insoluble salt.

The free pyrazine sulfonic acid was prepared by treatment of the sodium salt suspended in dry ether with dry hydrogen chloride gas followed by filtration and evaporation of the ether. It was found to be extremely hygroscopic and unsuitable for an analysis even after extensive drying at 50° *in vacuo*. Its aqueous solution gave a strong acid reaction with hydron paper.

Three grams (0.026 mole) of 2-chloropyrazine, 4.0 g. (0.032 mole) of anhydrous sodium sulfite, and 25 ml. of water were sealed in a Carius tube and thoroughly mixed. The 2-chloropyrazine remained as a separate layer and some of the sodium sulfite remained undissolved. After keeping the tube at 150° for twelve hours and then allowing to cool, it was opened and the homogeneous yellow solution was evaporated to dryness *in vacuo*. The yellow solid residue was extracted with three 50-ml. portions of boiling 95% ethanol. On cooling the solution, masses of white needle clusters separated and were filtered. The filtrate was evaporated to dryness and extracted with two 8-ml. portions of boiling 95% ethanol. The combined extracts were allowed to stand (crystallization is slow), filtered, and the crystals added to the previously obtained portion; yield, 0.75 g. (15%) of colorless needles, m. p. 295°.

The analytical sample was recrystallized twice from 95% ethanol and dried at room temperature for sixty hours *in vacuo* over phosphorus pentoxide. *Anal.* Calcd. for (C<sub>4</sub>H<sub>3</sub>N<sub>2</sub>)SO<sub>3</sub>Na·H<sub>2</sub>O: C, 24.00; H, 2.52; S, 16.02; Na, 11.49. Found: C, 24.08; H, 2.79; S, 16.02; Na, 11.50.

(6) Suggested in a personal communication from B. Klein of G. D. Research Inst., Inc.

(7) Microanalyses performed by Dr. Otto Schwarzkopf, 62-12 79th Street, Elmhurst, Long Island, New York.

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## 3,4,5-Triiodobenzoyl Chloride as a Reagent for Alcohols

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The use of 3,4,5-triiodobenzoyl chloride for the identification of cellosolves and carbitols has been reported previously.<sup>2</sup> Since the compound is relatively stable to water, it was applied to the monohydric alcohols. The alcohols were used as obtained from the manufacturer without further purification. The acid chloride of the 3,4,5-triiodobenzoic acid was prepared by the method of Klemme and Hunter.<sup>3</sup>

(1) Taken from theses submitted in partial fulfillment for the M.S. degree.

(2) O'Donnell and Carey, *THIS JOURNAL*, **68**, 1865 (1946).

(3) Klemme and Hunter, *J. Org. Chem.*, **5**, 508–511 (1940).

(1) Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., Schomaker and Pauling, *THIS JOURNAL*, **61**, 1776 (1939).

(2) Krems and Spoerri, *Chem. Rev.*, **40**, 328 (1947).

(3) Weijlard, Tishler and Erickson, *THIS JOURNAL*, **67**, 802 (1945).

(4) Erickson and Spoerri, *ibid.*, **68**, 401 (1946).

(5) Cain, Mallette and Taylor, *ibid.*, **68**, 1996 (1946).