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. 28–38°) 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*-hydroxyphenylpropiolic 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.).[2]

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

BY EUGENE HORT AND PAUL E. SPOERRI

Although recent electron diffraction studies have shown that benzene and pyrazine have very similar structures,[1] 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.[2] Even under such severe conditions as those used in the cleavage of lumazine,[3] *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,[4] this method was adopted for the preparation.

Chloropyrazine was obtained by the following sequence of operations. Lumazine prepared according to Cain, Mallette and Taylor,[5] was cleaved to 2-hydroxy-3-pyrazinoic acid and then to hydroxypyrazine according to Weijlard, Tishler and Erickson.[3] Chloropyrazine was then prepared by the method of Erickson and Spoerri[4] with the notable exception that phosphorus oxychloride (in a ratio of five moles to one of hydroxypyrazine) was used as sole chlorinating agent.[6]

### Experimental[7]

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 nitrtae 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 hydrion 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 $(C_4H_3N_2)SO_3Na\cdot H_2O$: 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.

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(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).

(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

BY DAVID C. O'DONNELL, JOHN K. KELLEY, JR.,[1] ROBERT F. O'MALLEY[1] AND ROY H. UPHAM[1]

The use of 3,4,5-triiodobenzoyl chloride for the identification of cellosolves and carbitols has been reported previously.[2] 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.[3]

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(1) Taken from theses submitted in partial fulfilment 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).

TABLE I

ESTERS OF 3,4,5-TRIIODOBENZOIC ACID

| Alcohol used | M. p., °C. | Yield, % | Formula | Iodine, % Calcd. | Iodine, % Found |
|---|---|---|---|---|---|
| Methyl | 168.2–168.8[a] | 36 | $C_8H_5O_2I_3$ | 74.11 | 73.50 |
| Ethyl | 160.8–161.6 | 59 | $C_9H_7O_2I_3$ | 72.12 | 72.40 |
| *n*-Propyl | 124.8–125.2[a] | 63 | $C_{18}H_9O_2I_3$ | 70.26 | 70.17 |
| Isopropyl | 133.7–134.2[a] | 59 | $C_{10}H_9O_2I_3$ | 70.26 | 70.71 |
| *n*-Butyl | 103.0–103.7 | 42 | $C_{11}H_{11}O_2I_3$ | 68.48 | 68.84 |
| Isobutyl | 107.6–108.1 | 56 | $C_{11}H_{11}O_2I_3$ | 68.48 | 69.05 |
| *s*-Butyl | 95.4–95.8 | 37 | $C_{11}H_{11}O_2I_3$ | 68.48 | 68.18 |
| *n*-Amyl | 88.0–88.6 | 50 | $C_{12}H_{13}O_2I_3$ | 66.80 | 66.73 |
| Isoamyl | 72.3–72.9 | 14 | $C_{12}H_{13}O_2I_3$ | 66.80 | 65.93 |
| 2-Methyl-1-butanol | 63.0–63.4 | 36 | $C_{12}H_{13}O_2I_3$ | 66.80 | 67.11 |
| 2-Pentanol | 72.6–73.4[a] | 23 | $C_{12}H_{13}O_2I_3$ | 66.80 | 67.11 |
| 3-Pentanol | 74.4–75.6 | 27 | $C_{12}H_{13}O_2I_3$ | 66.80 | 67.22 |
| *n*-Hexyl | 98.6–99.0 | 61 | $C_{13}H_{15}O_2I_3$ | 65.21 | 65.42 |
| 2-Hexanol | 99.1–99.9[b] | 50 | $C_{13}H_{15}O_2I_3$ | 65.21 | 65.21 |
| *n*-Heptyl | 58.5–58.9 | 30 | $C_{14}H_{17}O_2I_3$ | 63.67 | 64.28 |
| 2-Heptanol | 55.0–55.6[b] | 23 | $C_{14}H_{17}O_2I_3$ | 63.67 | 63.19 |
| *n*-Octyl | 71.2–71.8 | 51 | $C_{15}H_{19}O_2I_3$ | 62.20 | 61.60 |
| *n*-Nonyl | 71.5–72.3 | 37 | $C_{16}H_{21}O_2I_3$ | 60.81 | 61.11 |
| *n*-Decyl | 72.5–73.2[b] | 50 | $C_{17}H_{23}O_2I_3$ | 60.83 | 60.69 |
| *n*-Dodecyl | 76.9–77.3[b] | 49 | $C_{19}H_{27}O_2I_3$ | 56.99 | 57.07 |
| Myristyl | 80.2–81.2[a,b] | 71 | $C_{21}H_{31}O_2I_3$ | 54.69 | 54.58 |
| Cetyl | 79.9–80.8[a,b] | 67 | $C_{23}H_{35}O_2I_3$ | 52.57 | 52.58 |
| Octadecyl | 84.5–85.5[a,b] | 74 | $C_{25}H_{39}O_2I_3$ | 51.29 | 51.30 |
| Cyclohexanol | 151.1–151.9[a] | 36 | $C_{13}H_{13}O_2I_3$ | 65.42 | 65.29 |
| Allyl | 126.0–126.5[b] | 58 | $C_{10}H_7O_2I_3$ | 70.53 | 70.75 |
| Benzyl | 128.0–128.6[b] | 44 | $C_{14}H_9O_2I_3$ | 64.54 | 64.46 |
| *β*-Phenylethyl | 117.2–117.8 | 68 | $C_{15}H_{11}O_2I_3$ | 63.05 | 63.36 |
| *γ*-Phenyl-*n*-propyl | 78.0–78.8[c] | 52 | $C_{16}H_{13}O_2I_3$ | 61.59 | 62.26 |

[a] Ethyl alcohol as solvent. [b] Granules. [c] Plates.

### Experimental

To 1 g. of the acid chloride in a 10-cm. test-tube was added 0.5 cc. of the liquid alcohol or 0.5 g. of the solid alcohol and the mixture gently heated over a micro burner until the evolution of hydrogen chloride ceased. This usually required about ten minutes. The molten mass was then poured into 20 cc. of an ice and water mixture. Most of the esters solidified instantly. Those that came down as oils usually changed to solids in a few minutes, but in a few instances it was necessary to wash the oil with a 20% solution of alcohol to obtain a solid. One recrystallization will usually give a pure compound, but the results in Table I are from compounds which were recrystallized twice, with the exception of the ethyl and the 3-pentanol esters which were recrystallized three times. Either methyl or 95% ethyl alcohol can be used as a recrystallizing solvent. Methyl alcohol was used for the compounds in the table unless otherwise indicated. They crystallized in needles, unless otherwise noted. The isoamyl ester when crystallized from 95% ethyl alcohol sometimes came down as needles with the melting point shown and sometimes as plates with a melting point of 40.4–40.8°. The plates after melting, solidification and remelting had a melting point of 72.3–72.9°. When recrystallized from methyl alcohol, it always had the melting point of 72.3–72.9°. The melting points were all taken by Anschütz thermometers, which were checked against a thermometer with a Bureau of Standards certificate.

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## The Potassium Permanganate Test for Detection of Unsaturation[1]

BY V. N. IPATIEFF, W. W. THOMPSON[2] AND HERMAN PINES

Many books suggest for the detection of unsaturation (particularly in compounds insoluble in water) a procedure comprising treatment of an acetone solution of the compound dropwise with a 2% potassium permanganate solution, until the purple color of the permanganate persists.

It was found that such procedure gave a negative test for unsaturation with several olefinic compounds. The results with the various hydrocarbons tested were not consistent. For example, *β*-pinene showed a negative test for unsaturation, while *α*-pinene showed a positive test. It was found, however, that when the olefins showing a positive test were redistilled, the unsaturation test for olefins was negative. These results indicate that the olefins on standing might have undergone some changes, which caused the discoloration of the permanganate solution.

Absolute or 96% ethanol is a more suitable solvent for the unsaturation test; in the presence of olefins the color of the permanganate solution is

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(2) American Chemical Society Predoctoral Fellow (1947–1948).