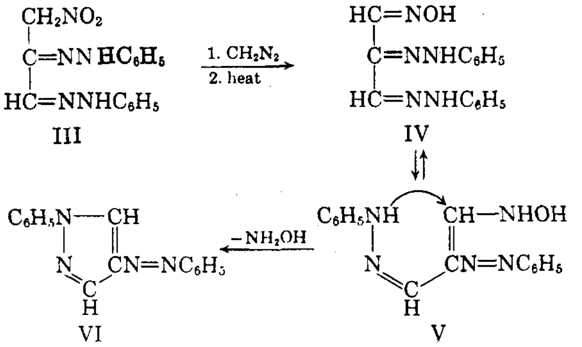
oxime (IV). Formation of VI may be rationalized as occurring *via* cyclization of the hydroxylamine compound V (a tautomer of IV), with elimination of a molecule of hydroxylamine. This reaction is exactly analogous to the reported formation of VI by the acid-catalyzed elimination of phenylhydrazine from mesoxaldehyde trisphenylhydrazone.[5]



EXPERIMENTAL

Quinoxaline-2-aldoxime. 2-Nitromethylquinoxaline[3] was added in portions to an ether solution containing a threefold excess of diazomethane and a little ethanol. After several hours the solution was filtered and the excess diazomethane and solvent were removed from the filtrate by distillation. The residue was sublimed at 120–140°/0.5 mm., giving a pale yellow solid, m.p. 189–199°. Recrystallization of the crude material from chloroform gave quinoxaline-2-aldoxime, white solid, m.p. 202° (lit.,[4] m.p. 197–198°).

1-Phenyl-4-benzeneazopyrazole. Nitropyruvaldehyde phenylosazone[3] (2.96 g., 9 mmoles) was added in portions to 50 ml. of an ether solution containing 22 mmoles of diazomethane. Ethanol (75 ml.) was added until the osazone was almost completely dissolved. The reaction mixture was stirred for 1.5 hr., filtered, and the filtrate was distilled first at atmospheric pressure and then at reduced pressure to remove solvent. The residue was sublimed at 120–130°/0.1 mm. for 18 hr., giving a yellow-orange sublimate. Recrystallization of the crude material from ethanol gave 0.31 g. of yellow needles, m.p. 124.6–126.2°, $\lambda_{max}^{ethanol}$ 332 mμ (broad), log ε 4.18 (lit.,[5] m.p. 124–125°, $\lambda_{max}^{ethanol}$ 335 mμ (broad), log ε 4.4).

Anal. Calcd. for $C_{15}H_{12}N_4$: C, 72.56; H, 4.87; N, 22.57. Found: C, 72.21; H, 5.09; N, 22.56.

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(4) Von W. Borsche and W. Doeller [*Ann.*, **537**, 39 (1939)] prepared IIc by treatment of the corresponding aldehyde with hydroxylamine.

(5) C. F. Huebner and K. P. Link, *J. Am. Chem. Soc.*, **72**, 4812 (1950).

Partial Side Chain Degradation in Alkali Fusion[1]

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Among the side reactions that can occur in the alkali fusion of alkylbenzenesulfonic acids, replacement of the sulfo group by hydrogen[3] oxidation of side chains,[4] and decarboxylation[5] are well known. Usually, alkyl groups—if attacked at all—are oxidized completely to carboxyl groups.[6] We have observed the conversion of an ethyl group into a methyl group in the alkali fusion of 4-ethyl-3,5-disulfobenzoic acid (I). This compound was prepared by the sulfonation of *p*-ethylbenzoic acid using a modification of the method of Asahina and Asano,[7] and characterized through its *p*-toluidine salt, it sulfonyl chloride, and its sulfonamide. The presence of the two sulfonic acid groups in the benzene ring was confirmed by sealed-tube oxidation with fuming nitric acid to 3,5-disulfoterephthalic acid.

Fusion of the barium salt of I with potassium hydroxide at 260–290° gave a mixture from which hydroxyterephthalic acid, 4-ethyl-3-hydroxybenzoic acid, *m*-hydroxybenzoic acid, and 3-hydroxy-4-methylbenzoic acid (II) were isolated together with several small, unidentified fractions. No 4-ethyl-3,5-dihydroxybenzoic acid was found. Compound II was obtained from a chromatographic separation of the mixture resulting from the alkali fusion, using moist silicic acid as the fixed phase and eluting with butanol-hexane mixtures. It was identified by its neutralization equivalent, carbon-hydrogen analysis, and by a mixed melting point determination.

The formation of II could be accounted for by assuming that the oxidation of the ethyl group occurred in steps, leading first to 2-hydroxyhomoterephthalic acid, which on side chain decarboxylation could yield II, which could then be oxidized further to hydroxyterephthalic acid. This is in agreement with the observation that 2,6-dimethoxyhomoterephthalic acid gives on decarboxylation 3,5-dimethoxy-4-methylbenzoic acid as one of the principal products.[8]

EXPERIMENTAL

4-Ethyl-3,5-disulfobenzoic acid (I). A mixture of 45 g. (0.3 mole) of twice recrystallized *p*-ethylbenzoic acid (m.p. 111–113°) and 180 g. of 65% oleum was refluxed for 8 hr. at

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(1) Abstracted from the dissertation submitted by Johann C. F. Schulz to the Graduate School of Syracuse University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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(3) O. Jacobsen and H. Meyer, *Ber.*, **16**, 190 (1883); O. Jacobsen, *Ann.*, **206**, 172 (1881); L. Barth and J. Herzig, *Monatsh.*, **1**, 808 (1880).

(4) C. M. Suter, *The Organic Chemistry of Sulfur*, John Wiley and Sons, Inc., New York (1944), p. 422.

(5) C. Fahlberg, *Am. Chem. J.*, **2**, 181 (1880); E. H. Charlesworth and R. Robinson, *J. Chem. Soc.*, 1531 (1934).

(6) O. Jacobsen, *Ann.*, **196**, 282 (1879); J. Stahl, *Ber.*, **23**, 990 (1890); C. W. Blomstrand and P. Hakansson, *Ber.*, **5**, 1084 (1872).

(7) Y. Asahina and J. Anano, *Ber.*, **66B**, 687 (1933).

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170–190° (bath temperature). The cooled mixture was poured on ice, diluted, and neutralized with excess barium carbonate. After digestion, filtration, and evaporation of the filtrate to dryness 144 g. (93%) of barium 4-ethyl-3,5-disulfobenzoate was obtained; *p-toluidine salt*[9]*:* m.p. 287–289° dec. (297–299° corr.).

Anal. Calcd. for $C_{23}H_{28}O_8N_2S_2$: C, 52.5; H, 5.34; N, 5.34; neut. equiv., 174.9. Found: C, 52.2; H, 5.48; N, 5.22; neut. equiv.,[10] 174.6.

The *sulfonyl chloride* was obtained as white rods (from ligroin), m.p. 82–83°.

Anal. Calcd. for $C_9H_7O_5S_2Cl_3$: S, 17.54. Found: S, 17.38.

The *sulfonamide* was obtained as white crystals (from water), m.p. 269° dec. (rate of heating 1°/min.).

Anal. Calcd. for $C_9H_{13}O_5S_2N_3$: S, 20.87. Found: S, 20.97.

3,5-Disulfoterephthalic acid. A mixture of 5.00 g. (0.00187 mole) of barium 4-ethyl-3,5-disulfobenzoate and 30 ml. of fuming nitric acid (*d*, 1.5 g./ml.) was heated in a sealed tube (enclosed in an iron pipe) for 6.5 hr. at 170–184° (183–196° bath temperature). After evaporating excess nitric acid, 100 ml. of water was added with stirring. Barium sulfate was filtered off and the filtrate was neutralized by the addition of 2.3 g. of barium carbonate. The white, flocculent precipitate which formed in the hot solution was removed (2.3 g.) and was recrystallized from dilute hydrochloric acid, yielding glistening, translucent needles.

Anal. Calcd. for $C_{16}H_6O_{20}S_4Ba_3$: Ba, 38.9. Found: Ba, 38.4.

p-Toluidine barium salt[9]*:*

Anal. Calcd. for $C_{30}H_{24}O_{20}S_4N_2Ba_3$: S, 10.1; neut. equiv., 636. Found: S, 10.2; neut. equiv.,[10] 641.

Alkali fusion. Barium 4-ethyl-3,5-disulfobenzoate (167 g.) was stirred into 516 g. of molten potassium hydroxide in a large copper beaker, and the mixture was kept at 260–290° for 2 hr. The melt was then poured into water, barium sulfite was filtered, and the filtrate was acidified with excess concentrated hydrochloric acid. The resulting brown precipitate (10 g., mainly hydroxyterephthalic acid and 4-ethyl-3-hydroxybenzoic acid) was filtered and the filtrate was extracted with ether, yielding 36.7 g. of a tan solid.

Hydroxyterephthalic acid. The brown solid (10 g.) obtained on acidification of the melt was boiled with 100 ml. of water. The mixture was filtered, and the residue was recrystallized twice from aqueous methanol, yielding a white substance melting between 312° and 327° (with sublimation) depending on the rate of heating (reported[11] m.p. 327°).

Anal. Calcd. for $C_8H_6O_5$: Neut. equiv., 91.1. Found: Neut. equiv., 91.7.

Dinitroderivative: m.p. 177–178° (reported[12] 178°).

Chromatography. The tan solid (36.7 g.) obtained from the ether extraction of the acidified melt was stirred with 367 ml. of water at 55° for 5 min., and the mixture was filtered. The filtrate was treated with 106 g. of salt, the resulting precipitate was filtered, and the filtrate was extracted with ether. A 6.5-g. portion of the material obtained by evaporation of the ether was dissolved in 30 ml. of hot water, mixed thoroughly with 75 g. of silicic acid, and covered with hexane. This mixture was ladled into a 92 cm. high (8 cm. I.D.) column packed with 1.6 kg. of silicic acid (100 mesh, containing 28.6% water) to a height of 65 cm., and covered with hexane. Elution was effected with mixtures of butanol in hexane, the percent of butanol (by volume) rising gradually from 1% to 4.5%. Fifteen-milliliter samples were collected at an average flow rate of 1.5 ml./min. One-milliliter aliquots were titrated against 0.0025*N* alcoholic potassium hydroxide.

4-Ethyl-3-hydroxybenzoic acid. The first fraction obtained from the chromatography contained 0.46 g. of a substance, which after recrystallization from water melted at 169° and did not depress the melting point of an authentic specimen of 4-ethyl-3-hydroxybenzoic acid.[13]

3-Hydroxy-4-methylbenzoic acid (II). The second fraction obtained from the chromatography followed immediately after the separation of the first one, and contained 0.90 g. of a substance which crystallized from water in needles, m.p. 206–207° (reported[14] 206–207°), and which did not depress the melting point of an authentic specimen.

Anal. Calcd. for $C_8H_8O_3$: C, 63.15; H, 5.30; neut. equiv., 152. Found: C, 63.00; H, 5.30[15]; neut. equiv., 155.

m-Hydroxybenzoic acid. The third fraction obtained from the chromatography did not appear until long (137 fractions) after the second one had separated, and contained 2.24 g. of a substance which melted at 199–200°, and did not lower the melting point of an authentic specimen of *m*-hydroxybenzoic acid.

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Derivatives of Fluorene. XIII. Formation of 9-Arylimino Compounds in the Presence of Boron Trifluoride

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In previous papers[3] we reported use of several catalysts in the formation of 9-aryliminofluorenes. In a search for catalysts which, while highly effective, can be used under milder conditions, we have found that boron trifluoride, used as the diethyl etherate, effects condensation at lower temperatures than are necessary with zinc chloride and others.

Twenty-four azomethine derivatives of fluorene, mostly new, have been prepared in excellent yield, either in a suitable solvent or by fusion. The latter was resorted to when the substituted fluorenone was relatively insoluble. In Table I a few boron trifluoride catalyzed condensations are compared with fusions of the same starting materials in the presence of zinc chloride.

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