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SEVERAL NEW 4′-SULFO-ORTHO-BENZOYLBENZOIC ACID DERIVATIVES AND THE CORRESPONDING ANTHRAQUINONE COMPOUNDS[1]

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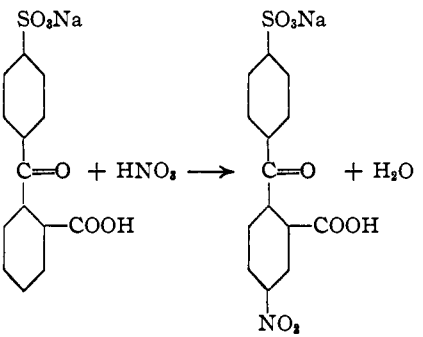
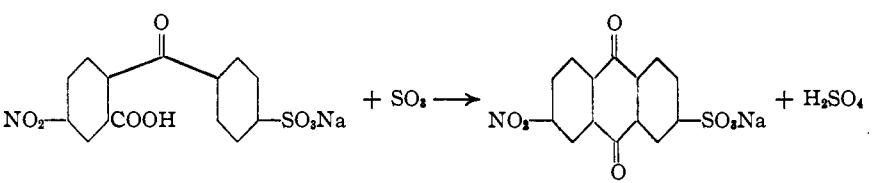
Several new 4′-sulfo-*o* benzoylbenzoic acid derivatives and the corresponding anthraquinone compounds are described. They are, 4′-sulfo-2-benzoyl-5-nitrobenzoic acid, 2-nitroanthraquinone-7-sulfonic acid, 2-nitro-7-chloroanthraquinone, 2-amino-7-chloroanthraquinone, 4′-sulfo-2-benzoyl-5-aminobenzoic acid, 2-aminoanthraquinone-7-sulfonic acid, 2,7-diaminoanthraquinone.

In the synthesis of anthraquinone derivatives from 4′-sulfo-*o*-benzoylbenzoic acid, a very interesting series of new compounds has been studied.

When 4′-sulfo-*o*-benzoylbenzoic acid is nitrated the nitro group enters the benzoic acid ring, not the sulfo benzene ring, as expected. The main product formed is 4′-sulfo-2-benzoyl-5-nitrobenzoic acid.

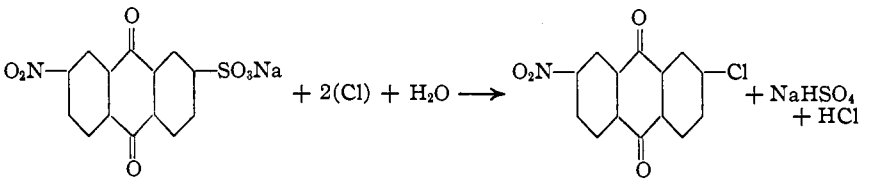


4′-Sulfo-2-benzoyl-5-nitrobenzoic acid is soluble in concentrated sulfuric acid and on heating the solution the ring closes to form 2-nitroanthraquinone-7-sulfonic acid.

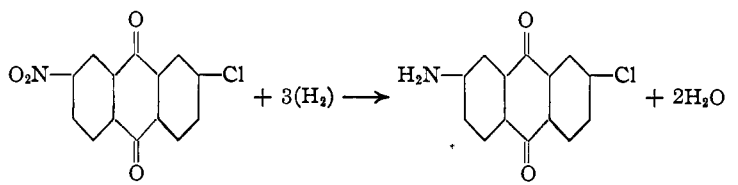


By treating 2-nitroanthraquinone-7-sulfonic acid with sodium chlorate in dilute acid solution, the sulfonic acid group is replaced by chlorine and 2-nitro-7-chloroanthraquinone is produced quantitatively.

[1] Presented before the Division of Dye Chemistry at the 80th Meeting of the American Chemical Society, Cincinnati, Ohio, September 8–12, 1930, by J. M. Tinker.

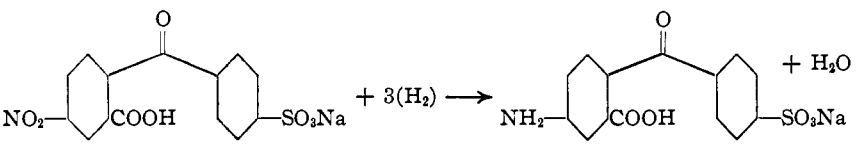


This nitrochloro compound crystallizes from chlorobenzene in light yellow crystals melting at 251 to 252° and has not been described. By reducing the 2-nitro-7-chloroanthraquinone with sodium sulfide, the 2-amino-7-chloroanthraquinone is formed.

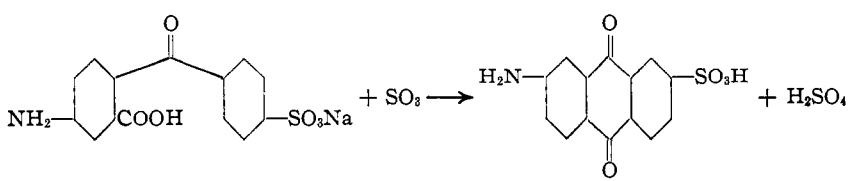


When pure it crystallizes in light orange needles melting at 302 to 303°.

Instead of ring closing 4′-sulfo-5-nitro-2-benzoylbenzoic acid, the nitro group may be first reduced to the 4′-sulfo-2-benzoyl-5-aminobenzoic acid.



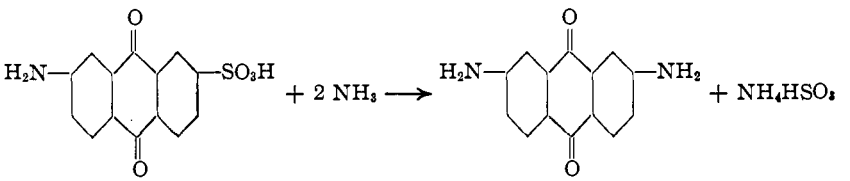
This amino compound analyzes 99.8% by nitrite titration based on a molecular weight corresponding to the formula above and on ring closing this amino compound with sulfuric acid, the 2-amino-anthraquinone-7-sulfonic acid is formed.



This product corresponds to the 2-aminoanthraquinone-7-sulfonic acid described by F. Kaufler,[2] obtained from the 2,7-anthraquinone-disulfo acid by amination.

By treating this aminoanthraquinone-sulfo acid with ammonia and arsenic acid, the well-known 2,7-diaminoanthraquinone is produced.

[2] F. Kaufler, *Ann.*, **351**, 158 (1907).



This diaminoanthraquinone is easily recrystallized from nitrobenzene, giving dark violet crystals melting at 330 to 332°. On conversion to the dioxy derivative by the Sandmeyer method, a dioxy body is formed melting above 340°. On acetylation a diacetyldioxyanthraquinone is formed which melts at 190 to 191°.

E. Noelting and W. Wortmann[3] describe a diaminoanthraquinone obtained from 2,7-dinitroanthraquinone, which is the same in properties as the one obtained by this synthesis.

Compound	M. p., °C.	Compound M. p., °C.
2,7-Dioxy-anthraquinone	Over 330	Diacetyl 190 to 191
2,6-Dioxy-anthraquinone	Over 330	Diacetyl 228 to 229
2,3-Dioxy-anthraquinone	Over 260	Diacetyl 203 to 205
1,7-Dioxy-anthraquinone	Over 292 to 293	Diacetyl 198 to 199
1,8-Dioxy-anthraquinone	Over 191	Diacetyl 227 to 232
1,6-Dioxy-anthraquinone	Over 276	Diacetyl 204 to 205
1,5-Dioxy-anthraquinone	Over 280	Diacetyl 244 to 245
1,4-Dioxy-anthraquinone	Over 194 to 195	Diacetyl 200
1,3-Dioxy-anthraquinone	Over 270	Diacetyl 183 to 184
1,2-Dioxy-anthraquinone	Over 289 to 290	Diacetyl 184
Unknown dioxy-anthraquinone	Over 330	Diacetyl 190 to 191

Experimental Part

(1) **Preparation of 4′-Sulfo-2-benzoyl-5′-nitrobenzoic acid, Monosodium Salt.**—Dissolve 328 g. of 4′-sulfo-*o*-benzoylbenzoic acid monosodium salt in 650 parts of 100% sulfuric acid at 15 to 20°. While agitating, add over a period of six to eight hours, 580 g. of mixed acid (made by mixing 100 g. of mixed acid containing 70% nitric acid, 22% sulfuric acid and 8% water with 480 parts of 25% oleum). Hold the temperature at 15 to 20° during the addition, then raise to 35° and hold for three hours.

Dilute the finished nitration by pouring onto 2500 g. of ice and 1500 g. of water, then salt out the 4′-sulfo-2-benzoyl-5-nitrobenzoic acid monosodium salt with 1000 g. of salt. Filter after a few hours, wash with cold water and dry (weight 350 g.). It is a white crystalline powder easily soluble in water to a pale yellow solution. With alkalies it forms the diacid salts, which are very soluble in water. It is difficultly soluble in cold alcohol and is best purified by crystallizing from a hot dilute sulfuric acid solution.

Anal. Calcd.: S, 8.58; N, 3.75. Found: S, 8.49; N, 3.70.

(2) **Preparation of 2-Nitroanthraquinone-7-sulfonic Acid.**—Dissolve 100 g. of 4′-sulfo-2-benzoyl-5-nitrobenzoic acid in 400 g. of 25% oleum and heat to 150°. Cool quickly and pour onto 2500 g. of ice. Filter the precipitated 2-nitroanthraquinone-7-sulfonic acid and wash well with cold water. This yield is 80 g.

[3] Noelting and Wortmann, *Ber.*, **39**, 641 (1906).

(3) **Preparation of 2-Nitro-7-chloroanthraquinone.**—Suspend 35.5 g. of 2-nitroanthraquinone-7-sulfo acid (sodium salt) in 1750 cc. of water and 90 g. 20° Bé. hydrochloric acid in a five-liter flask with a glass agitator. Heat to boiling and add a solution of 35.5 g. of sodium chlorate dissolved in 500 cc. of water over a period of twenty to twenty-four hours. The volume is kept constant at 2 liters. When finished, filter, wash well with hot water and dry at 100° in vacuum. The yield is quantitative.

The 2-nitro-7-chloroanthraquinone is easily purified by crystallizing from chlorobenzene or glacial acetic acid as light yellow crystals melting at 251 to 252°.

(4) **Preparation of 2-Amino-7-chloroanthraquinone.**—287 g. of 2-nitro-7-chloroanthraquinone is suspended in 5 liters of water containing 40 g. of sodium hydroxide and 625 g. of sodium sulfide crystals. Heat to boiling in two to three hours and hold at the boiling point for two hours. The 2-amino-7-chloroanthraquinone is then filtered off and washed well with hot water. The yield is almost quantitative. This body crystallizes easily from chlorobenzene in light orange needles melting at 302 to 303°.

Anal. Calcd. for $C_{14}H_8SO_2NCl$: N, 5.44; Cl, 13.8. Found: N, 5.34; Cl, 14.3.

(5) **Preparation of 4'-Sulfo-2-benzoyl-5-aminobenzoic Acid.**—373 g. of 4'-sulfo-2-benzoyl-5-nitrobenzoic acid monosodium salt is suspended in about 300 g. of hot water. Add this mixture in about three to four hours to an agitated mixture of water, 750 g. of powdered iron and 75 g. of glacial acetic acid held at 93 to 97°. Hold for another hour at 95 to 97°, then neutralize with about 175 g. of sodium carbonate. Filter off the iron sludge and wash well with about 1 liter of boiling water. Acidify the mother liquor and wash water with hydrochloric acid, when the 4'-sulfo-2-benzoyl-5-aminobenzoic acid monosodium salt will precipitate and is filtered and washed with cold water. The yield is 300 g. This is a white crystalline product, easily purified by crystallizing from hot water. It is easily soluble in alkalies but sparingly soluble in cold water and dilute mineral acid, 95% alcohol, glacial acetic acid or other organic solvents.

(6) **Preparation of 2-Amino-anthraquinone-7-sulfo Acid.**—Dissolve 40 g. of 4'-sulfo-2-benzoyl-5-aminobenzoic acid monosodium salt in 240 g. of a mixture of 87 g. of 66° Bé. acid and 113 g. of 25% oleum, heat to 180° and hold at this temperature for one hour. Pour onto ice, then filter, wash and dry.

(7) **Preparation of 2,7-Diaminoanthraquinone.**—Charge a high-pressure steel autoclave with 318 g. of ammonium salt of 2-aminoanthraquinone-7-sulfo acid, 156 g. of arsenic acid and 1860 g. of 27% ammonia and heat for twenty-four hours at 180°.

After cooling, the reaction mass is filtered and washed well. The dried product is red needles melting at 330 to 332°. Further crystallization from nitrobenzene does not change this melting point.

Conclusion

When 4'-sulfo-2-benzoylbenzoic acid is nitrated, the nitro group enters the benzoic acid ring. Proof of structure is based on the melting point of the 2,7-diaminoanthraquinone, as well as the melting point of the 2,7-dioxyanthraquinone and 2,7-diacetyl-dioxyanthraquinone, which are prepared from the sulfo-benzoyl-*o*-benzoic acid. The several intermediate products are described.

MILWAUKEE, WISCONSIN