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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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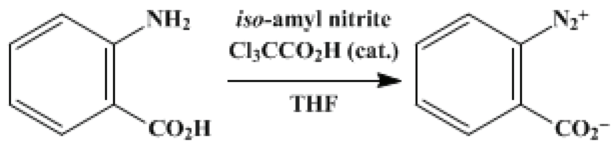
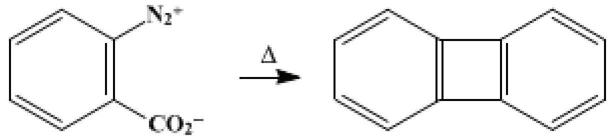
BENZENEDIAZONIUM-2-CARBOXYLATE AND BIPHENYLENE

[Benzenediazonium, *o*-carboxy-, hydroxide, inner salt]





Submitted by Francis M. Logullo, Arnold H. Seitz, and Lester Friedman[1].
Checked by G. D. Abrams, Hermann Ertl, and Peter Yates.

1. Procedure

Caution! Benzenediazonium-2-carboxylate when dry detonates violently on being scraped or heated, and it is strongly recommended that it be kept wet with solvent at all times. It should be prepared and used in a hood behind a safety screen. A wet towel or sponge should be kept within easy reach with which to deactivate any spilled material, which should then be disposed of by flooding with water.

A. *Benzenediazonium-2-carboxylate*. A solution of 34.2 g. (0.25 mole) of anthranilic acid (Note 1) and 0.3 g. of trichloroacetic acid (Note 2) in 250 ml. of tetrahydrofuran (Note 3) is prepared in a 600-ml. beaker equipped with a thermometer and cooled in an ice-water bath. The solution is stirred magnetically, and 55 ml. (48 g., 0.41 mole) of isoamyl nitrite (Note 4) is added over a period of 1–2 minutes. A mildly exothermic reaction occurs, and the reaction mixture is maintained at 18–25° and stirred for a further 1–1.5 hours. A transient orange to brick-red precipitate may appear (Note 5) which is slowly converted to the tan product. When the reaction is completed, the mixture is cooled to 10°, and the product is collected by suction filtration on a plastic Buchner funnel and washed on the funnel with cold tetrahydrofuran until the washings are colorless. *(Caution! The filter cake should not be allowed to become dry.)* The benzene-diazonium-2-carboxylate is then washed with two 50-ml. portions of 1,2-dichloroethane to displace the tetrahydrofuran, and the solvent-wet material is used in the next step (Note 6), (Note 7), and (Note 8).

B. *Biphenylene*. The solvent-wet benzenediazonium-2-carboxylate is washed from the funnel into a 400-ml. beaker with *ca.* 150 ml. of 1,2-dichloroethane, dispensed from a plastic wash bottle, with the aid of a plastic spatula (Note 9). The resultant slurry is added during 3–5 minutes to 1250 ml. of gently boiling, stirred 1,2-dichloroethane in a 2-l. beaker on a magnetic stirrer-hot plate in the hood (Note 10). Frothing ceases a few minutes after completion of the addition, and the mixture assumes a clear red-brown color, signaling the end of the reaction.

A 1-l., two-necked, round-bottomed flask is equipped with a 1-l. addition funnel and a Claisen distillation head and water-cooled condenser. The cooled reaction mixture is transferred to the funnel, and enough of it is admitted to the flask to half-fill the latter. The 1,2-dichloroethane, b.p. 83–84°, is distilled with the use of magnetic stirring to maintain even ebullition; the remainder of the reaction mixture is added from the funnel at a rate such that the flask remains about half-full. When *ca.* 75 ml. of dark residue remains in the flask, 300 ml. of ethylene glycol is added. An air condenser is substituted for the water-cooled condenser, and distillation is recommenced. A forerun, b.p. <150°, is discarded, and the fraction, b.p. 150–197°, is collected (Note 11). The distillate is cooled to 10°, and the product is collected by suction filtration, washed with 10–15 ml. of cold ethylene glycol and several times with water, and dried at atmospheric, pressure over phosphorus pentoxide. The yield of biphenylene, m.p. 109–112°, is 4.0–5.6 g. (21–30%, based on anthranilic acid). Additional biphenylene (0.2–0.5 g.) can be obtained from the mother liquor and ethylene glycol washings by redistillation or dilution with water (Note 12).

2. Notes

1. The submitters used practical grade anthranilic acid from Mallinckrodt Chemical Works.
2. Perfluorobutyric or trifluoroacetic acid may be used in place of trichloroacetic acid. Strong mineral acids and acetic acid are wholly unsatisfactory. If a catalyst is not used, the product is of poor quality and the yield only 30%. Trichloroacetic acid is conveniently added as a solution in tetrahydrofuran (0.01 g./ml.).
3. The submitters used commercial tetrahydrofuran. The checkers found that the product yield was the same when either practical grade or Fisher Certified reagent grade tetrahydrofuran was used.
4. The submitters used "amyl nitrite" U.S.P. from Mallinckrodt Chemical Works; isoamyl nitrite supplied by Matheson, Coleman and Bell is apparently the same material. They found that other alkyl nitrites (ethyl, *n*-butyl, *t*-butyl, *n*-amyl) may be used with equal success. Subsequent to the checking of this procedure, they reported that the amount of nitrite can be reduced to a 20% molar excess.
5. This precipitate is apparently 2,2'-dicarboxydiazoaminobenzene.
6. The product should be used immediately because it deteriorates slowly at room temperature. It is freed of tetrahydrofuran by washing with the solvent to be used in subsequent reactions and transferred as a slurry in that solvent (cf. procedure B). Traces of water, if present, do not appear to interfere with subsequent reactions of diazonium carboxylates, as observed in the submitters' laboratory.
7. The submitters have found that this procedure works equally well with many substituted anthranilic acids; however, it does not work with 3-chloro-, 5-cholro, 4-nitro-, 5-nitro-, and 4,5-benzoanthranilic acids.
8. Although it strongly recommended that the product not be dried, particularly when prepared on the scale described here, the following slightly modified procedure can be used for the preparation of solvent-free benzenediazonium-2-carboxylate. A solution of 2.74 g. (0.020 mole) of anthranilic acid and 0.030 g. of trichloroacetic acid in 30 ml. of tetrahydrofuran is prepared in a 100-ml. beaker equipped with a thermometer and cooled in a bath of *ca.* 25 g. of crushed ice. The solution is stirred magnetically, and 5 ml. (4.4 g., 0.038 mole) of isoamyl nitrite (Note 4) is added during *ca.* 0.5 minute. The mixture is stirred and allowed to warm to room temperature over a period of 1 hour. It is cooled to 10°, and the product is collected by suction filtration with the use of a plastic Buchner funnel and plastic spatula and washed with ice-cold tetrahydrofuran until the washings are colorless. The yield of air-dried (30 minutes) benzenediazonium-2-carboxylate is 2.55–2.88 g. (86–97%). *(Caution! Danger of detonation! See above.)* (Note 13).
9. The checkers transferred the benzenediazonium-2-carboxylate to the beaker with the aid of gentle air pressure (Note 13) and then slurried it with *ca.* 150 ml. of 1,2-dichloroethane.
10. The checkers added the slurry via a large, medium-bore, glass funnel with fire-polished edges. In one of three runs a small, sharp report was heard, apparently from a source above the liquid in the beaker; the yield of biphenylene in this run did not differ significantly from that obtained in the other runs.
11. The checkers found it necessary to heat the condenser with a microburner from time to time to prevent clogging with biphenylene. The submitters have reported that this can be avoided by connecting the Claisen head via an adapter to a two-necked receiving flask fitted with an upright water-cooled condenser and cooled by immersion in ice-water.
12. For convenient preparation and workup of larger amounts of biphenylene, several runs can be combined after the decomposition of the benzenediazonium-2-carboxylate. Thus the submitters obtained 19.1 g. (25%) of air-dried biphenylene by combining four batches. They found that the use of larger amounts of 1,2-dichloroethane resulted in a moderate increase in yield; by combining four batches, each prepared in 2. 75 l. of 1,2-dichloroethane in a 4-l. beaker, they obtained 22.8 g. (30%) of product.
13. The checkers transferred the solvent-moist product to a tared Petri dish by means of gentle puff of compressed air through the stem of the funnel; solid adhering to the filter paper and funnel was transferred to the dish with the aid of a soft rubber policeman, which was also used to spread the

product over the surface of the dish. The product was then air-dried for 30 minutes in the hood.

3. Discussion

Benzenediazonium-2-carboxylate[2] and its substituted derivatives[3] have been prepared by diazotization of anthranilic acids in the presence of hydrochloric acid followed by dehydrochlorination of the resultant diazonium carboxylate hydrochlorides with silver oxide.

Biphenylene has been prepared in low yield by the reaction of 2,2'-dibromobiphenyl or 2,2'-biphenyliodonium iodide with cuprous oxide,[4] by the action of cupric chloride on 2,2'-biphenyl-dimagnesium dibromide,[5] from 2,2'-diiodobiphenyl via dibenzomercurole (*o,o*'-biphenylenemercury) (49%),[6] by pyrolysis or photolysis of phthaloyl peroxide (27%),[7] by reaction of *o*-fluoro-bromobenzene with lithium amalgam (24%),[8] by reaction of *o*-bromoiodobenzene with magnesium (12%),[9] and by the decomposition of diphenyliodonium-2-carboxylate,[10] 1,2,3-benzothia-diazole-1,1-dioxide,[11] benzenediazonium-2-carboxylate,[12,13] and by the oxidation of 1-aminobenzotriazole with lead tetraacetate (83%).[14]

4. Merits of the Preparation

These procedures illustrate facile methods for the preparation of benzenediazonium-2-carboxylate and its derivatives[15] and of biphenylene and certain biphenylene derivatives.[13] The latter preparation is far more convenient and proceeds in much better yield than do previous, syntheses, which involve more steps, less accessible intermediates, and more complicated techniques.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 5, 196

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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

Perfluorobutyric or trifluoroacetic acid

2,2'-biphenyliodonium iodide

o,o'-biphenylenemercury

hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

magnesium (7439-95-4)

silver oxide (20667-12-3)

1,2-dichloroethane (107-06-2)

cuprous oxide

ethylene glycol (107-21-1)

cupric chloride (7758-89-6)

amyl nitrite (463-04-7)

Anthranilic Acid (118-92-3)

lithium (7439-93-2)

Isoamyl nitrite (110-46-3)

trichloroacetic acid (76-03-9)

Tetrahydrofuran (109-99-9)

phthaloyl peroxide

Benzenediazonium-2-carboxylate,
benzene-diazonium-2-carboxylate (1608-42-0)

Biphenylene (259-79-0)

dibenzomercurole

diphenyliodonium-2-carboxylate (1488-42-2)

1,2,3-benzothia-diazole-1,1-dioxide (37150-27-9)

1-aminobenzotriazole (1614-12-6)

o-fluoro-bromobenzene (1072-85-1)

phosphorus pentoxide (1314-56-3)

Benzenediazonium, o-carboxy-, hydroxide

o-bromoiodobenzene (583-55-1)

lead tetraacetate (546-67-8)

2,2'-dicarboxydiazoaminobenzene

2,2'-dibromobiphenyl

2,2'-biphenyl-dimagnesium dibromide

2,2'-diiodobiphenyl