



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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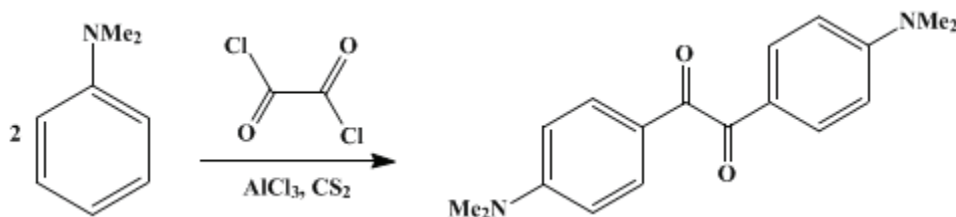
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 5, p.111 (1973); Vol. 41, p.1 (1961).

4,4'-BIS(DIMETHYLAMINO)BENZIL

[Benzil, 4,4'-bis(dimethylamino)-]



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1. Procedure

In a 3-l. three-necked flask equipped with an efficient mechanical stirrer of high torque (Note 1), a reflux condenser with a calcium chloride drying tube, a thermometer, and a dropping funnel are placed 133 g. (1.00 mole) of anhydrous aluminum chloride and 200 ml. of dry carbon disulfide. The mixture is cooled in an ice bath and stirred while 182 g. (1.50 moles) of *N,N*-dimethylaniline (Note 2) is added through the dropping funnel during a period of 15 minutes. The dropping funnel is rinsed with 20 ml. of carbon disulfide which is then run into the flask. Any aluminum chloride sticking to the walls of the flask is now scraped into the mixture, which is an easily stirred slurry of a white solid in a light-green liquid.

The reaction mixture is cooled to 5–10° in an ice-salt bath (Note 3), and, with continued stirring, a solution of 31.7 g. (21.3 ml., 0.250 mole) of oxalyl chloride in 200 ml. of dry carbon disulfide is added through the dropping funnel in the course of 20 minutes. After the addition is complete, the thick black reaction mixture is allowed to warm to room temperature, refluxed for 1 hour, and then cooled to 0–5° in an ice bath. The mixture is stirred throughout these steps. One hundred grams of chipped ice is added with stirring, followed by 400 ml. of cold water. Steam is then passed into the flask until the carbon disulfide and unreacted dimethylaniline are removed, and the green-black aluminum complex is decomposed to a mixture of a green solid and a blue solid; this requires 1–2 hours (Note 4). The mixture is cooled to 50°, and the solid, which is principally 4,4'-bis(dimethylamino)benzil, is collected on a Büchner funnel. In order to remove the major part of the impurity, which is somewhat soluble in water, the solid is slurried in 200 ml. of water at 50°, and the slurry is filtered. This process is repeated twice, and the crude benzil, now a green solid, is washed successively on the funnel with 200 ml. of water at 50° and with 100 ml. of cold methanol. After being dried in air, it weighs 44–55 g. and melts at 191–196°.

The crude benzil is dissolved in 500 ml. of chloroform. To remove the impurity that remains (Note 5), the solution is shaken with three 400-ml. portions of 6% aqueous hydrogen peroxide solution containing 1.0 g. of sodium hydroxide in each portion, and finally with 500 ml. of water. The aqueous layers are combined, warmed to drive off dissolved chloroform, and filtered to separate about 1.5 g. of a yellow-green solid, which is dissolved in the chloroform solution.

The chloroform layer is distilled to dryness and the residue is dissolved in 1.5 l. of acetone under reflux. The hot acetone solution is filtered and then allowed to cool in a refrigerator. Yellow 4,4'-bis(dimethylamino)benzil crystallizes from the acetone solution. It is separated by filtration and washed with 100 ml. of cold methanol. After being dried in air, it weighs 28–31 g. (38–42%); m.p. 200–202°; $\lambda_{\text{max}}^{\text{CH}_3\text{OH}}$ 371 m μ (ϵ 44,700) (Note 6).

The acetone filtrate is concentrated to 700 ml. and cooled to 0–5°. An additional 4–8 g. (6–11%) of slightly less pure benzil, m.p. 198–201°, crystallizes from solution (Note 7).

2. Notes

1. A magnetic stirrer is unsatisfactory. The submitters used a glass-blade stirrer at 300 r.p.m. The stirrer shaft must be rigidly attached to the motor because the reaction mixture becomes very thick during the addition of [oxalyl chloride](#).

2. Eastman Kodak white label compounds used without further purification are satisfactory starting materials.

3. Cooling below -10° should be avoided because the reaction stops at that temperature and large amounts of [oxalyl chloride](#) accumulate in the flask. If this mixture is then allowed to come to room temperature, a vigorous reaction that may get out of control will take place. It is probable that, at reaction temperatures about 10° , the yield of [4,4'-bis\(dimethylamino\)benzil](#) is less and some Crystal Violet is formed as an impurity, for it has been reported that [aluminum chloride](#) effects the conversion of [N,N-dimethylaniline](#) and [oxalyl chloride](#) to Crystal Violet in 92–95% yield when the reaction is allowed to proceed without cooling.²

4. The submitters recommend that the following purification procedure be used from this point for the preparation of [4,4'-bis\(diethylamino\)benzil](#) (72% yield) and [4,4'-bis\(di-*n*-propylamino\)benzil](#) (58% yield). The procedure has also been used as an alternative to the one given for [4,4'-bis\(dimethylamino\)benzil](#).

One liter of water is added, making the total volume about 2 l., and, after the solution has been cooled to room temperature, it is extracted with 1 l. of [chloroform](#) and then with 150 ml. of [chloroform](#). The combined dark-blue extracts are washed with 550 ml. of 8.5% [hydrochloric acid](#), then with 200 ml. of water and dried over anhydrous [sodium sulfate](#). The [chloroform](#) solution is distilled until the volume is 250 ml., and it is then passed through an 8.5×25 -cm. column (300 g.) of Alcoa F-20 alumina. The adsorbate is eluted with 1 l. of [chloroform](#). The eluate is evaporated to a volume of 250 ml., washed with 500 ml. of 10% [sodium hydroxide](#) solution then with 100 ml. of water, and distilled to essential dryness.

The residual crude, yellow, semi-solid product is stirred and brought to a boil with 250 ml. of [ethyl acetate](#) and then allowed to cool to room temperature while stirring. Filtration affords 39–41 g. (52–55%) [4,4'-bis\(dimethylamino\)benzil](#), m.p. $201-203^{\circ}$. Concentration of the mother liquor to 50 ml. gives, after cooling, an additional 3.5–4.5 g. of product, m.p. $175-180^{\circ}$. Recrystallization of 10 g. of the combined products from 120–150 ml. of [benzene](#) gives 9.1–9.3 g. of yellow crystals, m.p. $202-203^{\circ}$.

5. The checkers found that at least part of the colored impurity is Crystal Violet. Alkaline [hydrogen peroxide](#) is reported to cleave Crystal Violet to [N,N-dimethylaniline](#) and Michler's ketone.³

6. The product is sometimes pale green because of traces of impurities, but it is nevertheless very pure, for repeated recrystallization does not change ϵ_{\max} .

7. Addition of 1 l. of cold water to the [acetone](#) filtrate from which the second crop of [benzil](#) is separated causes about 5 g. of impure [benzil](#) to precipitate. This may be added to the crude [benzil](#) of a subsequent run prior to the treatment with [hydrogen peroxide](#) and alkali.

3. Discussion

[4,4'-Bis\(dimethylamino\)benzil](#) has been made previously by heating a mixture of [oxalyl chloride](#) and [N,N-dimethylaniline](#) under a pressure of 300 atmospheres of [carbon monoxide](#) in a steel pressure vessel at 100° .⁴ The present method is simpler and gives better yields. As [4-dimethylaminobenzaldehyde](#) cannot be converted to the corresponding [benzoin](#),⁵ this common route to benzils cannot be used to prepare [4,4'-bis\(dimethylamino\)benzil](#).

The present procedure is reported by the submitters to be a general way of making [4,4'-bis\(dialkylamino\)benzils](#) and, with a somewhat modified purification scheme ([Note 4](#)), has been used by them to prepare [4,4'-bis\(diethylamino\)benzil](#) from [N,N-diethylaniline](#) and [4,4'-bis\(dipropylamino\)benzil](#) from [N,N-dipropylaniline](#).

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 5, 1114](#)
- [Org. Syn. Coll. Vol. 5, 1135](#)

References and Notes

1. Polytechnic Institute of Brooklyn, Brooklyn 1, N. Y.
 2. G. v. Georgievies, *Ber.*, **38**, 884 (1905).
 3. I. N. Postovskii, *J. Chem. Ind. (U.S.S.R.)*, **4**, 552 (1927) [*C.A.*, **22**, 957 (1928)].
 4. H. Staudinger and H. Stockmann, *Ber.*, **42**, 3485 (1909).
 5. S. M. McElvain, "The Acyloins," *Org. Reactions*, **4**, 273 (1948).
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Appendix

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

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

ethyl acetate (141-78-6)

methanol (67-56-1)

sodium hydroxide (1310-73-2)

carbon monoxide (630-08-0)

chloroform (67-66-3)

sodium sulfate (7757-82-6)

aluminum (7429-90-5)

acetone (67-64-1)

aluminum chloride (3495-54-3)

Benzil (134-81-6)

Benzoin (119-53-9)

carbon disulfide (75-15-0)

hydrogen peroxide (7722-84-1)

dimethylaniline,
N,N-dimethylaniline (121-69-7)

N,N-diethylaniline (91-66-7)

oxalyl chloride (79-37-8)

4-dimethylaminobenzaldehyde (100-10-7)

N,N-dipropylaniline (2217-07-4)

4,4'-Bis(dimethylamino)benzil,
Benzil, 4,4'-bis(dimethylamino)- (17078-27-2)

4,4'-bis(diethylamino)benzil

4,4'-bis(di-n-propylamino)benzil,
4,4'-bis(dipropylamino)benzil