



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at http://www.nap.edu/catalog.php?record_id=12654). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 of Prudent Practices.

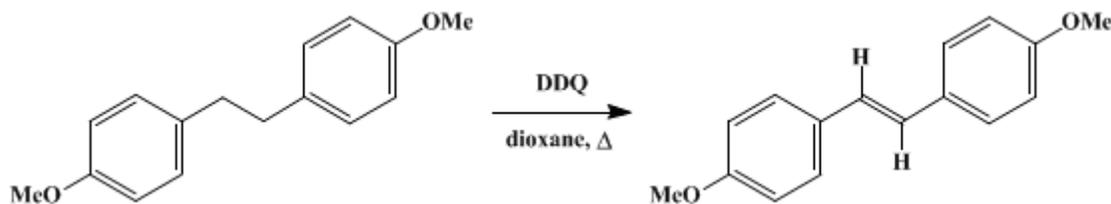
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 5, p.428 (1973); Vol. 49, p.53 (1969).

***trans*-4,4'-DIMETHOXYSTILBENE**

[*trans*-Stilbene, 4,4'-dimethoxy-]



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Checked by R. E. Ireland and G. Brown.

1. Procedure

A solution of 100 mg. (0.41 mmole) of 4,4'-dimethoxybibenzyl (Note 1) in 1.5 ml. of anhydrous dioxane (Note 2) was placed in a 10-ml. round-bottomed flask. To this was added 103 mg. (0.45 mmole) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ; (Note 3)) dissolved in 1.5 ml. of anhydrous dioxane. The flask was fitted with a reflux condenser and heated in an oil bath at 105° for 18 hours. The solution, which was initially deep green, became pale yellow as the hydroquinone crystallized out. The mixture was cooled, and the solid was filtered off. It was washed with 1 ml. of warm benzene followed by 6 ml. of warm chloroform (Note 4), and dried at 100° to give 95 mg. (91%) of pure 2,3-dichloro-5,6-dicyanohydroquinone (Note 5). The filtrate and washings were combined and evaporated under reduced pressure. The semisolid residue was dissolved in 5 ml. of ethyl acetate and passed through a short column of neutral alumina (2.0 g.; (Note 6)). The column was eluted with 100 ml. of ethyl acetate (Note 7). Evaporation of the solvent under reduced pressure left the crude product, which was recrystallized from 35 ml. of ethanol to give 82–84 mg. (83–85%) of *trans*-4,4'-dimethoxystilbene as colorless plates, m.p. 212–213.5°.

2. Notes

1. The starting bibenzyl was prepared from *p*-methoxybenzyl chloride by a modified Wurtz reaction.² The checkers found the procedure described by Buu-Hoï and Lavit² inadequate and used the copper(I) chloride-catalyzed coupling of *p*-methoxybenzylmagnesium chloride in its place.
2. Dioxane was purified by the method of Vogel³ and stored over molecular sieves.
3. DDQ was obtained from Koch-Light Laboratories, Ltd. It can be recrystallized from benzene if required.
4. Washing with chloroform is necessary to dissolve some of the stilbene which crystallizes out with hydroquinone. In many reactions, washing the hydroquinone with hot benzene is sufficient, as the dehydrogenation products crystallize to a limited extent from dioxane.
5. The amount of precipitated hydroquinone is a convenient measure of the extent of hydrogen transfer. DDQ is readily regenerated in good yield from the hydroquinone by oxidation with nitric acid.⁴
6. Woelm neutral alumina, activity grade 1.
7. The volume of ethyl acetate required to elute the product can be reduced considerably for more soluble products.

3. Discussion

DDQ was first introduced for the dehydrogenation of hydroaromatic compounds, such as tetralin and bibenzyl, which yield naphthalene and stilbene, respectively.⁵ A benzene ring or an olefinic bond provides sufficient activation, although it is sometimes difficult to force the reaction to completion. This highpotential quinone has since found wide application,⁶ particularly in the steroid field, and its scope has been extended by the dehydrogenation of carbonyl compounds (ketones and lactones) and alcohols. DDQ is also useful for preparing stable cations and radicals. These reactions are commonly carried out

in refluxing [benzene](#) or [dioxane](#), and the procedure described here is a general one. An alternative workup procedure involves washing with alkali.

A number of compounds react rapidly with DDQ at room temperature. They include allylic and benzylic alcohols, which can thus be selectively oxidized, and enols and phenols,⁷ which undergo coupling reactions or dehydrogenation, depending on their structure. Rapid reaction with DDQ is also often observed in compounds containing activated tertiary hydrogen atoms.⁸ The workup described here can be used in all these cases.

A number of side products can arise with this quinone. They include Diels-Alder adducts (DDQ is a powerful dienophile) and Michael adducts derived from the hydroquinone.

General methods for the preparation of *trans*-stilbenes have been covered previously.⁹ [4,4'-Dimethoxystilbene](#) has been prepared from deoxyanisoin and *n*-propylmagnesium iodide,¹⁰ by treatment of [thiophenol](#) with [2-bromo-1, 1-di-*p*-methoxyphenylethane](#),¹¹ and by the action of [nitrous acid](#) on the corresponding amine.¹²

References and Notes

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Appendix

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

Deoxyanisoin

DDQ

[ethanol](#) (64-17-5)

[Benzene](#) (71-43-2)

[ethyl acetate](#) (141-78-6)

[hydrogen](#) (1333-74-0)

[chloroform](#) (67-66-3)

hydroquinone (123-31-9)
nitric acid (7697-37-2)
nitrous acid (7782-77-6)
Naphthalene (91-20-3)
copper(I) chloride (7758-89-6)
Thiophenol (108-98-5)
Tetralin (119-64-2)
dioxane (123-91-1)
stilbene
bibenzyl (103-29-7)
2,3-dichloro-5,6-dicyano-1,4-benzoquinone
2,3-dichloro-5,6-dicyanohydroquinone
p-methoxybenzyl chloride (824-94-2)
p-methoxybenzylmagnesium chloride
n-propylmagnesium iodide
2-bromo-1, 1-di-p-methoxyphenylethane
trans-4,4'-Dimethoxystilbene,
trans-Stilbene, 4,4'-dimethoxy- (15638-14-9)
4,4'-dimethoxybibenzyl
4,4'-Dimethoxystilbene