



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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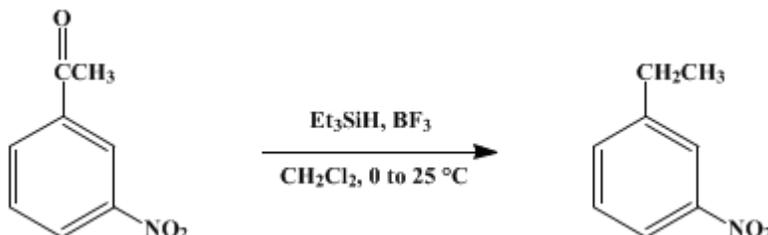
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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REDUCTION OF KETONES TO HYDROCARBONS WITH TRIETHYLSILANE: *m*-NITROETHYLBENZENE

[Benzene, 1-ethyl-3-nitro-]



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Checked by Jack W. Muskopf and Robert M. Coates.

1. Procedure

Caution! Boron trifluoride gas is highly corrosive; this preparation should be conducted in a well-ventilated hood.

A dry, 250-mL, three-necked, round-bottomed flask is equipped with a magnetic stirring bar, a gas-inlet tube (Note 1), a pressure-equalizing dropping funnel, and a Dewar condenser cooled with ice-water and fitted with a drying tube containing anhydrous calcium sulfate (Drierite). A solution of 20.9 g (0.180 mol) of triethylsilane (Note 2) in 80 mL of dichloromethane (Note 3) is placed in the flask. The solution is stirred rapidly and cooled in an ice bath while boron trifluoride gas (Note 4) is introduced below the surface of the liquid at a moderate rate. The first appearance of white fumes at the exit of the drying tube (Note 5) indicates that the solution is saturated and the apparatus is filled with boron trifluoride. The flow of boron trifluoride is adjusted to a level sufficient to maintain a slight emission of white fumes from the drying tube, and a solution of 10.0 g (0.0606 mol) of *m*-nitroacetophenone (Note 6) in 30 mL of dichloromethane is added dropwise during 10 min. Stirring and cooling are continued for 30 min, after which the flow of boron trifluoride gas is stopped and the cooling bath is removed. The mixture is stirred at room temperature for 20 min, cooled again with the ice bath, and hydrolyzed by adding 20 mL of aqueous saturated sodium chloride. The upper organic layer is decanted from the salts, which are then dissolved in 50 mL of water. The aqueous solution is extracted with two 25-mL portions of pentane, which are combined with the original organic layer. The organic solution is washed with two 25-mL portions of saturated sodium chloride and dried with anhydrous sodium sulfate. Distillation at atmospheric pressure through a 10-cm Vigreux column serves to separate solvent and ca. 15 g of a mixture of primarily triethylsilane and triethylfluorosilane, bp 106–109°C (Note 7). The remaining liquid is distilled in a short-path distillation apparatus under reduced pressure, affording 8.33–8.38 g (91–92%) of pale yellow *m*-nitroethylbenzene, bp 120–121°C (15 mm), 134–135°C (22 mm), n_D^{25} 1.5330 (Note 8).

2. Notes

1. A Pasteur pipet clamped in an O-ring thermometer adapter served as a convenient, adjustable gas-inlet tube. The large end of the pipet was fitted with a small rubber septum, through which a syringe needle was passed for introducing the boron trifluoride gas.
2. Triethylsilane was purchased from either Petrarch Systems, Inc., or PCR Research Chemicals, Inc. The reagent was dried with anhydrous sodium sulfate and distilled before use, bp 107–108°C.
3. Reagent-grade dichloromethane was extracted repeatedly with concentrated sulfuric acid, washed twice with water, dried with anhydrous calcium chloride, and distilled from phosphorus pentoxide before use.²
4. A cylinder of boron trifluoride gas was purchased from Linde Division, Union Carbide Chemical

Corporation. The gas was passed through Teflon tubing to a 250-mL gas-washing bottle equipped with a fritted-glass inlet and containing a saturated solution of boric anhydride (ca. 16 g) in 150 mL of concentrated sulfuric acid. Another section of Teflon tubing was connected to the exit port of the gas-washing bottle and to the barrel of a 2-mL, gastight syringe that fitted into the syringe needle in the septum. Boric anhydride (boron oxide) is available from Fisher Scientific Company. The purpose of the boric anhydride-sulfuric acid scrubber is to remove hydrogen fluoride.³ All ground-glass joints in the system were lined with Nalgene or Teflon standard-taper sleeves to prevent them from sticking together. Nalgene standard-taper sleeves are supplied by Nalge Sylron Corporation. Any stopcocks used should be Teflon. The checkers placed one empty 250-mL trap in the gas line before the gas-washing bottle and another after it.

5. The submitters recommend that the effluent gases be directed toward a water trap to reduce the amount of boron trifluoride and hydrogen fluoride released into the atmosphere.

6. *m*-Nitroacetophenone was supplied by Aldrich Chemical Company, Inc. and recrystallized from ethanol, mp 76–78°C. The compound may also be prepared by the method of Corson and Hazen.⁴

7. If desired, the mixture of triethylsilane and triethylfluorosilane can be reconverted into triethylsilane by reduction with lithium aluminum hydride.⁵

8. The product was analyzed by the checkers. Anal. calcd. for C₈H₉NO₂: C, 63.56; H, 6.00; N, 9.27. Found: C, 63.51; H, 6.17; N, 9.04. The spectral properties of the product are as follows: IR (CCl₄) cm⁻¹: 3100, 3075, 2975, 2940, 2880, 1532, 1348, 1095, 895; ¹H NMR (CDCl₃) δ: 1.27 (triplet, 3, *J* = 7.5, CH₃), 2.74 (quartet, 2, *J* = 7.5, CH₂), 7.3–8.1 (multiplet, 4, aromatic *H*); ¹³C NMR (CDCl₃) δ: 14.7, 28.2, 120.4, 122.2, 128.8, 133.9, 145.9, 148.2.

3. Discussion

This procedure illustrates a method for the selective reduction of a carbonyl group to a methylene group in compounds having other potentially reducible functional groups. The method is applicable to the reduction of aryl aldehydes without electron-withdrawing ring substituents, aryl alkyl ketones, diaryl ketones, and dialkyl ketones.⁶ Under the above conditions, aryl aldehydes having strongly electron-withdrawing ring substituents (*viz.*, NO₂, CN) and alkyl aldehydes yield alcohols. Benzylic alcohols and secondary or tertiary aliphatic alcohols are also reduced to hydrocarbons under these reaction conditions,⁷ as are some epoxides.⁸ Functional groups that are not affected during ketone reductions include nitro, cyano, ether, ester, carboxylate, and ring halogens.

The effectiveness of this reduction procedure is related to the ability of free boron trifluoride to coordinate strongly to the carbonyl oxygen and to the strong driving force provided by the formation of the silicon-fluorine bond.⁶ Similar carbonyl reductions using organosilicon hydrides in conjunction with Brønsted acids^{9,10} or boron trifluoride etherate¹¹ are generally only successful with aryl ketones and aldehydes bearing electron-donating ring substituents; with other carbonyl substrates by-products other than hydrocarbons become the predominant products.

Other carbonyl reduction methods include the familiar Clemmensen¹² and Wolff-Kishner¹³ reactions. These are usually conducted for extended periods of time at elevated temperatures under strongly acidic or basic conditions, respectively. Mixed metal hydride-Lewis acid reagents constitute strong reducing systems that are often effective in the deoxygenation of diaryl ketones and some aryl alkyl ketones. However, even the mixed lithium aluminum hydride-aluminum chloride¹⁴ and sodium borohydride-boron trifluoride¹⁵ reagents reduce dialkyl ketones only to the corresponding alcohols, often with the formation of significant amounts of olefinic by-products. *m*-Nitroethylbenzene has been prepared by reductive deamination of 4-amino-3-nitroethylbenzene¹⁶ and by nitration of ethylbenzene and subsequent fractional distillation to separate the isomers.¹⁷

References and Notes

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 17. For example, see Brown, H. C.; Bonner, W. H. *J. Am. Chem. Soc.* **1974**, *76*, 605–606.
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

lithium aluminum hydride-aluminum chloride

ethanol (64-17-5)

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

sodium chloride (7647-14-5)

sodium sulfate (7757-82-6)

hydrogen fluoride (7664-39-3)

calcium sulfate (7778-18-9)

ethylbenzene (100-41-4)

Pentane (109-66-0)

dichloromethane (75-09-2)

boric anhydride

boron trifluoride (7637-07-2)
lithium aluminum hydride (16853-85-3)
boron trifluoride etherate (109-63-7)
sodium borohydride (16940-66-2)
phosphorus pentoxide (1314-56-3)
TRIETHYLSILANE (617-86-7)
Benzene, 1-ethyl-3-nitro- (7369-50-8)
triethylfluorosilane (358-43-0)
boron oxide
boric anhydride-sulfuric acid
4-amino-3-nitroethylbenzene
m-Nitroacetophenone (121-89-1)
m-Nitroethylbenzene (6125-24-2)