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Working with Hazardous Chemicals

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September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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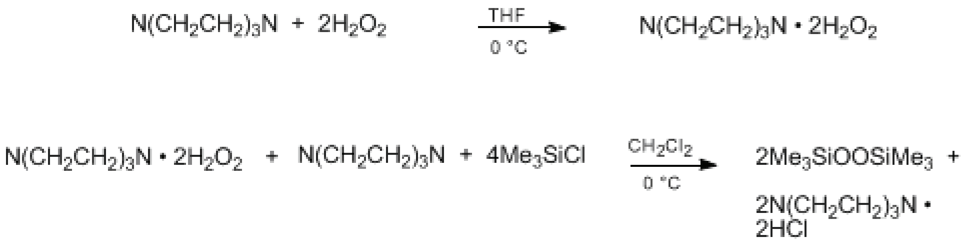
BIS(TRIMETHYLSILYL) PEROXIDE (BTMSPO)

[Silane, dioxybis[trimethyl-]



$$N(CH_2CH_2)_3N + 2H_2O_2 \xrightarrow[0\ ^\circ C]{THF} N(CH_2CH_2)_3N \cdot 2H_2O_2$$

$$N(CH_2CH_2)_3N \cdot 2H_2O_2 + N(CH_2CH_2)_3N + 4Me_3SiCl \xrightarrow[0\ ^\circ C]{CH_2Cl_2} 2Me_3SiOOSiMe_3 + 2N(CH_2CH_2)_3N \cdot 2HCl$$

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Checked by Christopher S. Brook, Mark Guzman, and Amos B. Smith, III.

1. Procedure

Caution! The possibility of explosions when handling bis(trimethylsilyl) peroxide (BTMSPO) has been reported,[2] especially in the presence of metal needles, cannulas, etc., although the product was prepared using a different procedure that included the use of 85% H_2O_2 and pyridine. Our method never gave rise to explosions in the general practice of an organic chemistry laboratory. Nevertheless all the reactions were carried out in safety cupboards and behind blast shields(Note 1).

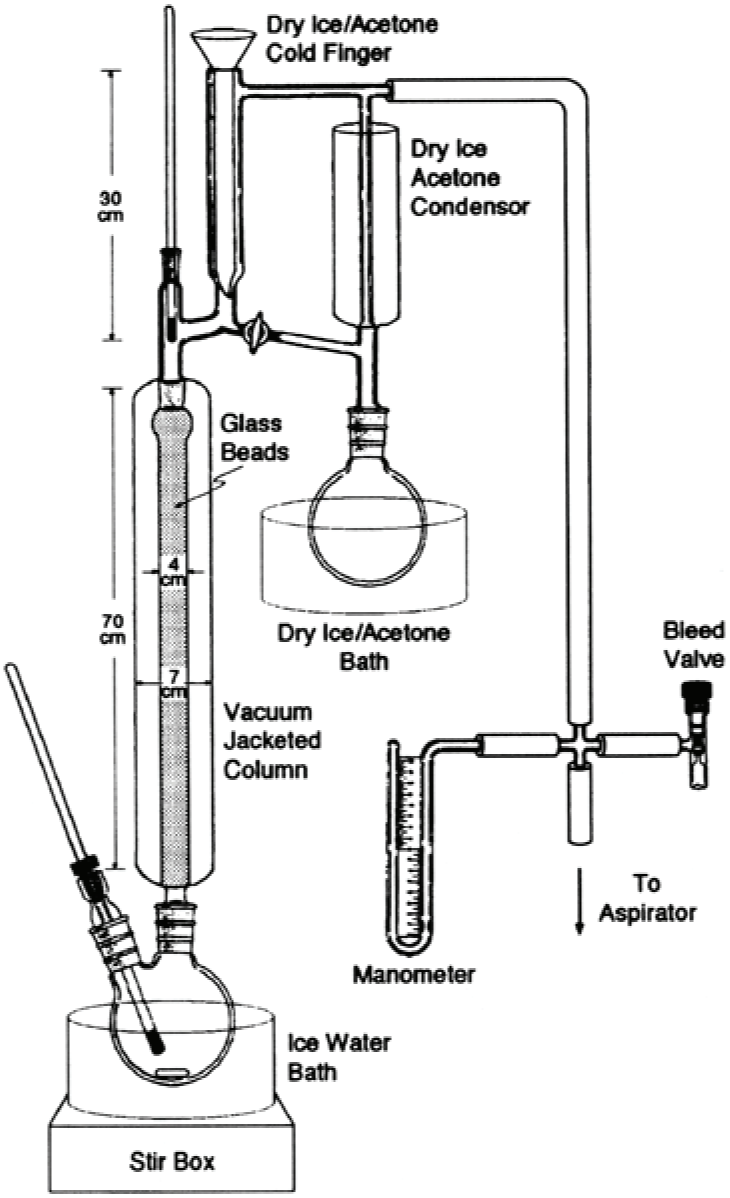
A. *Diazabicyclooctane-hydrogen peroxide (DABCO · $2H_2O_2$) complex*. A 1-L, two-necked flask, fitted with a dropping funnel, 3-cm stirring bar, and a thermometer, is charged with diazabicyclooctane (DABCO) (28.05 g, 0.25 mol) (Note 2) dissolved in commercial grade tetrahydrofuran (THF) (375 mL) (Note 3). The flask is cooled to 0°C (internal temperature, ice-salt bath), and hydrogen peroxide (49 mL of a 35% solution, 0.5 mol) (Note 4) is slowly added at such a rate that the temperature remains constant, under vigorous stirring. A precipitate appears immediately and, after completing the addition of hydrogen peroxide, stirring is continued at 0°C for 1 hr. The mixture is then filtered through a Büchner funnel and the collected precipitate washed with cold THF (3 × 50 mL) and dried under reduced pressure (2 mm, 35–40°C) in a flask for 2 hr. The yield of DABCO · $2H_2O_2$ obtained is 28.3 g (63%), m.p. 102–105°C (sealed tube) with decomposition, softness at 80°C (lit.[3] m.p. 112°C) (Note 5).

B. *Bis(trimethylsilyl) peroxide (BTMSPO)*. A 2-L, three-necked flask, containing a 3-cm stirring bar, and a thermometer, dropping funnel, and an argon inlet adapter, is maintained under a slight pressure of argon. The flask is charged with the DABCO · $2H_2O_2$ complex (28.3 g, 0.157 mol) and DABCO (28 g, 0.25 mol). Dry dichloromethane (700 mL) (Note 6) is added and the mixture is cooled to 0°C. Chlorotrimethylsilane (80 mL, 0.628 mol) (Note 7) is added dropwise, maintaining the temperature at 0°C, and the resulting mixture is stirred for 5 hr at room temperature. The mixture is filtered through a sintered Büchner funnel and the precipitate is washed with pentane (2 × 25 mL). The solution, transferred to a 2-L flask fitted with a vacuum-jacketed, packed column (70 cm long, 4-cm i.d.) and a distillation head equipped with a dry ice/acetone cold finger (Note 8), is concentrated to ca. 80 mL under reduced pressure (Note 9). Pentane (25 mL) is added to the mixture, the additional precipitate is filtered off, and the solution is transferred to a smaller flask, (500 mL). It is concentrated under reduced pressure with the distillation apparatus previously employed to give a residue of 40.1 g (71% yield) of BTMSPO as a clear colorless liquid. It is shown (Note 10) from multinuclear NMR to be contaminated by ca. 8% of hexamethylsiloxane (Note 11).

For synthetic purposes the BTMSPO obtained can be used without further purification; on the other hand, distillation (40°C/30 mm) or column chromatography (Florisil–eluent pentane) does not seem to improve the grade of purity (Note 12). The compound can be stored under nitrogen in a refrigerator for months without any appreciable decomposition.

2. Notes

1. Because of the reported[4] instability of the DABCO · $2H_2O_2$ complex, the checkers found it prudent to use new glassware for each run.
2. Diazabicyclooctane (DABCO) was used as purchased from Aldrich Chemical Company, Inc.
3. In the preparation of the complex the use of THF, miscible with water, produced a fine precipitate.
4. Hydrogen peroxide, 35% m/v, 120 volumes, from Aldrich Chemical Company, Inc., was used without titration.
5. The submitters ran this procedure on twice the scale (i.e., 0.5 mol of DABCO) in 59% yield. The complex is hygroscopic and can be stored in a desiccator overnight, but decomposes over long storage.
6. DABCO is previously dried at 20–27°C (room temperature) under reduced pressure (2 mm) Dichloromethane was used as purchased from Aldrich Chemical Company, Inc., (99.9%).
7. Trimethylchlorosilane was used as purchased from Aldrich Chemical Company, Inc.
8. If the solvent is removed with a rotary evaporator, considerable loss of product results from codistillation with dichloromethane. The checkers found that if this exact distillation set-up was not used the yield of BTMSPO decreased substantially (30–40%) because of the codistillation of CH_2Cl_2 and BTMSPO (observed in distillate by ^1H NMR). The distillation set-up requires use of a "walk-in" hood (see diagram).



9. Important points of this procedure are the temperature of the pot, which never must exceed 0°C, the temperature of the cooled head of the column, which should vary in the range of −5–0°C, and the vacuum, which throughout the distillation has been kept in the range of 90–100 mm (90–100 drops/min). These conditions apply to CH_2Cl_2 removal, whereas for pentane distillation a pressure of about 200 mm is recommended. To remove the last traces of solvent at the very end of the fractionation, the pot temperature was raised to 15–20°C and the pressure decreased to 40 mm.

10. The submitters ran this procedure on twice the scale (i.e., 0.28 mol of DABCO · $2H_2O_2$) and report a yield of 94%. The checkers found that the final stillpot residue still contained some DABCO · HCl salt that had to be filtered to obtain pure BTMSPO. Filtration was done via a fluted filter paper.

11. A typical NMR spectroscopic analysis was as follows: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.187 ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: −1.40

12. Recently another procedure has appeared,[4] dealing with the large scale preparation of BTMSPO. The costs and the yield of the two procedures are comparable, calculated on the amount of H_2O_2-base complex used, but the present procedure avoids the *potential* danger of violent decomposition[2] of the silylated peroxide during its distillation.

Waste Disposal Information

All toxic materials were disposed of in accordance with "Prudent Practices in the Laboratory"; National Academy Press; Washington, DC, 1995.

3. Discussion

The procedure described here, based on a modification of that of A. G. Davies,[5] provides the first large scale preparation of BTMSPO, a reagent widely used for synthetic purposes over the last few years. The present method is characterized by high reliability; the low concentration of H_2O_2, high yields, and the safe procedure are further major advantages.

BTMSPO has been mainly employed as a reagent for the transformation of carbanions into the corresponding trimethylsiloxy or hydroxy derivatives,[6] [7] and in the hydroxylation of neutral aromatic systems[8] (in the presence of TfOH).

It has, for example, been used in the preparation of 3-trimethylsiloxyfuran,[9] and to prepare stereochemically pure E- or Z-silyl enol ethers starting from the corresponding E- or Z-vinyl bromides[10] or vinylstannanes.[6,7]

It can also be used as a mild aprotic oxidizing agent (soluble in all common organic solvents), for the transformation of sulfides into the corresponding sulfoxides,[11] [12] phosphines into phosphine oxides,[13]. [14] in the oxidation of alcohols to aldehydes[15] (as cooxidant of $CrO_3 \cdot Py$), in the Baeyer-Villiger reaction[16] (in the presence of $TfOSiMe_3$). It has also been employed in the transformation of acetylenes to the corresponding iodoacetylenes.[17]

References and Notes

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

Florisil

BIS(TRIMETHYLSILYL) PEROXIDE (BTMSPO)

Diazabicyclooctane-hydrogen peroxide (DABCO · $2H_2O_2$) complex

DABCO · $2H_2O_2$

DABCO · $2H_2O_2$ complex

DABCO

BTMSPO

DABCO · HCl

TfOH

nitrogen (7727-37-9)

pyridine (110-86-1)

hydrogen peroxide (7722-84-1)

Pentane (109-66-0)

dichloromethane (75-09-2)

Tetrahydrofuran,
THF (109-99-9)

argon (7440-37-1)

CHLOROTRIMETHYLSILANE,
trimethylchlorosilane (75-77-4)

hexamethylsiloxane (107-46-0)

Silane, dioxybis[trimethyl- (5796-98-5)

diazabicyclooctane

3-trimethylsiloxyfuran