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TRIS(TRIMETHYLSILYL)ARSINE AND LITHIUM BIS(TRIMETHYLSILYL)ARSENIDE

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Checked by A. H. Cowley† and S. Kamepalli†

Tris(trimethylsilyl)arsine and lithium bis(trimethylsilyl)arsenide are valuable reagents for dehalosilylation and salt elimination reactions, respectively. Each reacts with a wide variety of metal halides to form metal-arsenic bonds.[1,2] The syntheses reported herein are a modification of the published procedures of Becker *et al.*,[3] designed to minimize Schlenk techniques and allow researchers to prepare two very useful compounds with a minimum of danger. However, since these *compounds do burn spontaneously in air and are very toxic, great care must be taken in their synthesis and subsequent manipulations. Adequate knowledge of both Schlenk and vacuum techniques is required.*[4]

The following procedure can be readily adapted for the preparation of $(Me_3Si)_3P$ and ether free $LiP(SiMe_3)_2$.[5,6]

A. TRIS(TRIMETHYLSILYL)ARSINE

$$3\ Na/K + As \xrightarrow{DME‡} "(Na/K)_3As" \xrightarrow[-3\ (Na/K)Cl]{3\ Me_3SiCl} (Me_3Si)_3As$$

• **Caution.** *Sodium-potassium alloy reacts violently with water and may ignite upon exposure to air. Tris(trimethylsilyl)arsine is a toxic, highly pyrophoric liquid which may form highly toxic arsine gas (AsH_3) upon reaction with air or water. This procedure and the following clean up must be performed in a well ventilated fume hood. Class D metal fire extinguisher should be on hand throughout the synthesis since an excess of sodium-potassium alloy is employed. The flammable solvent, DME, must be dried and deoxygenated by distillation from sodium benzophenone under nitrogen. Although this synthesis utilizes a minimum of Schlenk techniques, one must still be familiar with handling air sensitive/pyrophoric compounds.*

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‡DME = 1,2-dimethoxyethane.

The reaction vessel consists of a 1 L flask with 200 mL and 250 mL round bottom flask blanks attached *via* Teflon® valves* and a gas inlet (see Fig. 1). The neck of this apparatus consists of an inner 34.5 RODAVISS® joint† with a drip tip (the RODAVISS® joints are threaded and allow the components of the apparatus to be securely attached). A fritted filter is constructed with a 34.5 outer RODAVISS® joint inlet and a 24.4 inner RODAVISS® joint outlet with a drip tip. The receiving flask is a 2 L round-bottom flask which had been formed into a "mushroom" shape by heating the upper half and allowing it to partially collapse (see Fig. 2). A Teflon® valve is attached at the upper curve of the "mushroom". Each time this reaction is performed it is imperative that the o-rings on both the Teflon® valves and the RODAVISS® joints be replaced because they deteriorate, and also that the glassware be annealed by a qualified glassblower to ensure integrity of the components.

Procedure

All glassware and reagents must be scrupulously dried and deoxygenated prior to use. All ground glass connections should be lubricated with an inert and highly heat-stable grease such as Apiezon T-grease‡. A continuous and vigorous flow of argon must be maintained when the stirring rod is removed, the filtration glassware is assembled to the reaction flask, and when the filtration glassware is removed from the receiving flask.

In an inert-atmosphere glove box under an argon atmosphere, the 200 mL upper bulb is charged with 20 g of sodium-potassium alloy (44%:56%)§ using a disposable Pasteur pipette. The liquid alloy should be added quickly and in small amounts to the bulb to ensure that it does not back up into the valve stem. To the 250 mL bulb is added 77 g of chlorotrimethylsilane¶. After closing the valves to the upper bulbs, finely powdered arsenic (99.9995% pure)@ (14 g) is placed in the 1 L flask and covered with 800 mL DME. A TRUBORE®# stirrer equipped with a glass blade (a glass blade must be employed as Teflon will decompose in the reaction mixture) is fitted to the flask and lubricated with Stir-lube®#. To minimize vibration and alignment problems, the stirrer shaft is connected to the motor unit *via* a FLEXIBLE SHAFT®#.

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§Strem Chemicals, Inc., 7 Mulliken Way, Newburyport, MA 01950.

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@Atomergic Chemmetals Corp., 222 Sherwood Avenue, Farmingdale, NY 11735.

#Ace Glass, Inc., P.O. Box 688, 1430 Northwest Boulevard, Vineland, NJ 08360.

• **Caution.** *The reaction must be continually monitored while it is stirred, as the stir rod must be periodically lubricated to prevent it from freezing up.*

The apparatus is placed in an oil bath in a fume hood and a condenser, flushed with argon, attached to the gas inlet (see Fig. 3). Under a slight flow of argon, the solvent is stirred vigorously and heated to 76 °C at which point the sodium-potassium alloy is added over a 1.5 h period. The addition is controlled by carefully heating the gas above the alloy with a "heat gun" and allowing the increased pressure to force down the alloy. The solution becomes black before addition of the alloy is complete. The solution is heated at reflux and stirred for 24 h.

The solution is allowed to cool to room temperature, then the flask is placed in an ice water bath. The stir rate is increased and chlorotrimethylsilane* added over a 1.5 h period while adding ice to the water bath to maintain a temperature of 22 °C. Upon nearing complete addition of the chlorotrimethylsilane, the solution becomes extremely viscous and the color changes from black to pale gray. The mixture is heated at reflux and stirred vigorously for 24 h.

Upon cooling the reaction mixture to room temperature, the gas inlet on the vessel is closed and the condenser removed. Under a steady flow of argon, the TRUBORE® stir rod is removed and an inner RODAVISS® 34.5 cap is placed over the mouth of the flask. After the assembled frit and receiving flask have been evacuated and back-filled with argon five times, under a vigorous flow of argon, both the stopper in the RODAVISS® 34.5 joint of the frit and the cap on the matching joint of the reaction flask are removed and the frit assembled to the flask. The entire filtration apparatus is then inverted. After the first filtration is complete, the entire assembly is evacuated and the reaction flask partially placed in a liquid nitrogen bath. The "mushroom" shaped receiving flask allows the filtration apparatus to be laid horizontally without allowing the pale yellow filtrate to flow back into the neck of the frit. The DME which condenses in the reaction flask is thawed and used to wash this flask and the salt cake on the frit. This is repeated three additional times with approximately 150 mL portions of DME until the salt cake is clean. Under a blanket of argon, the fritted filter is removed from the receiving flask and the vessel capped. The solvent is removed at room temperature *in vacuo* (2.5×10^{-3} torr) and trapped at -196 °C to leave a pale yellow liquid, impure tris(trimethylsilyl)arsine. Under a constant flow of argon, a Teflon® stirring bar is placed in the vessel and a 20 cm Vigereux fractional distillation column equipped with a water cooled condenser and thermometer, and an attached 200 mL one bulbed receiving flask equipped with a Teflon® joint side arm is connected to the reaction vessel *via* the RODAVISS® 34.5 joint. The side arm of the receiving flask is attached to the

vacuum line. The entire assembly is evacuated and the contents of the reaction vessel are carried through three freeze (liquid nitrogen)-pump-thaw cycles to insure that there are no dissolved gases (*Note. The presence of dissolved gases causes the tris(trimethylsilyl)arsine to seriously "bump" during the distillation*). The reaction vessel is placed in an oil bath atop a stirring hot plate and with adequate stirring, the tris(trimethylsilyl)arsine is purified by fractional distillation . Bp 65-71 °C/2.5 x 10^{-3} torr. Yield: 34 g (62%).*

• **Caution.** *The residues on the glassware and the frit may contain sodium-potassium alloy and/or tris(trimethylsilyl)arsine and should not be exposed to air until disposal. tert-Butyl alcohol and iso-propyl alcohol can be used to destroy these pyrophoric compounds, however, this should be performed in a fume hood, as arsine gas may be generated. The solid on the frit can be mixed with class D metal fire extinguisher and subsequently treated with either of the aforementioned alcohols.*

Properties

Tris(trimethylsilyl)arsine is a colorless liquid which melts slightly below room temperature, and is stable at room temperature under an inert atmosphere or in a degassed, flame-sealed ampoule. The ^{1}H NMR spectrum in C_7D_8 (reference δ 2.09) consists of a single resonance at δ 0.30 and the ^{13}C NMR spectrum shows a single peak at δ 4.31. Solubility: very soluble in benzene, toluene, pentane, THF†, and diethyl ether.

B. LITHIUM BIS(TRIMETHYLSILYL)ARSENIDE

$$(Me_3Si)_3As \xrightarrow[-Me_4Si]{MeLi\ /\ THF} LiAs(SiMe_3)_2$$

• **Caution.** *Lithium bis(trimethylsilyl)arsenide is very sensitive to moisture and can react explosively upon exposure to air. Methyllithium is corrosive and reacts violently with water. Both compounds should be manipulated in a dry argon or nitrogen atmosphere. Lithium bis(trimethylsilyl)arsenide should not be heated above 80 °C, as it begins to decompose.*

The reaction flask consists of a 100 mL round-bottomed flask blank attached to a 250 mL round-bottomed flask through a Teflon® valve. The 250 mL flask has a 24/40 ground glass joint and a gas inlet equipped with a Teflon® valve.

*The checkers obtained %.

†THF = tetrahydrofuran.

Procedure

The upper 100 mL bulb is charged with 4.85 mL of 1.4 M methyllithium in diethyl ether. This is best accomplished in an inert-atmosphere glove box , but can also be done in a fume hood using Schlenk transfer techniques. Approximately 10 mL of THF, freshly distilled from sodium benzophenone, is added to this solution to ensure a quantitative transfer. After closing the valve to the upper bulb, 2 g of tris(trimethylsilyl)arsine in 40 mL of THF is added to the main bulb and a stir bar is added. A greased 24/40 male stopper is used to seal the vessel and it is then attached to a vacuum line. The solution is cooled in an ice water bath to 0 °C with stirring. The methyllithium solution is added drop wise over a 15 min. period, producing a bright yellow solution. After stirring for 2 h, the solution is allowed to warm to room temperature and stirred for an additional 2 h. The volatiles are then removed *in vacuo*, leaving a yellow, solid residue. The flask is placed in an oil bath and heated to 70 °C under dynamic vacuum (2.5×10^{-3} torr). The solid slowly becomes bright white and after 48 h, THF free lithium bis(trimethylsilyl)arsenide is recovered in nearly quantitative yield. Yield: 1.45 g (94%).*

Properties

Lithium bis(trimethylsilyl)arsenide is a white powder which is stable at room temperature under an inert atmosphere. It is important for stoichiometric reasons to ascertain whether there is any residual THF. This can be readily determined by ^{1}H NMR. The ^{1}H NMR spectrum in C_6D_6 (reference δ 7.15) consists of a single resonance at δ 0.62. Solubility: very soluble in THF and diethyl ether, and minimally soluble in non-ethereal solvents.

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4. D. F. Shriver, *The Manipulation of Air-Sensitive compounds*, McGraw-Hill, New York, 1969.
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6. G. Becker, H. Schmidt, G. Uhl, and W. Uhl, *Inorg. Syn.*, **27**, 243 (1990).

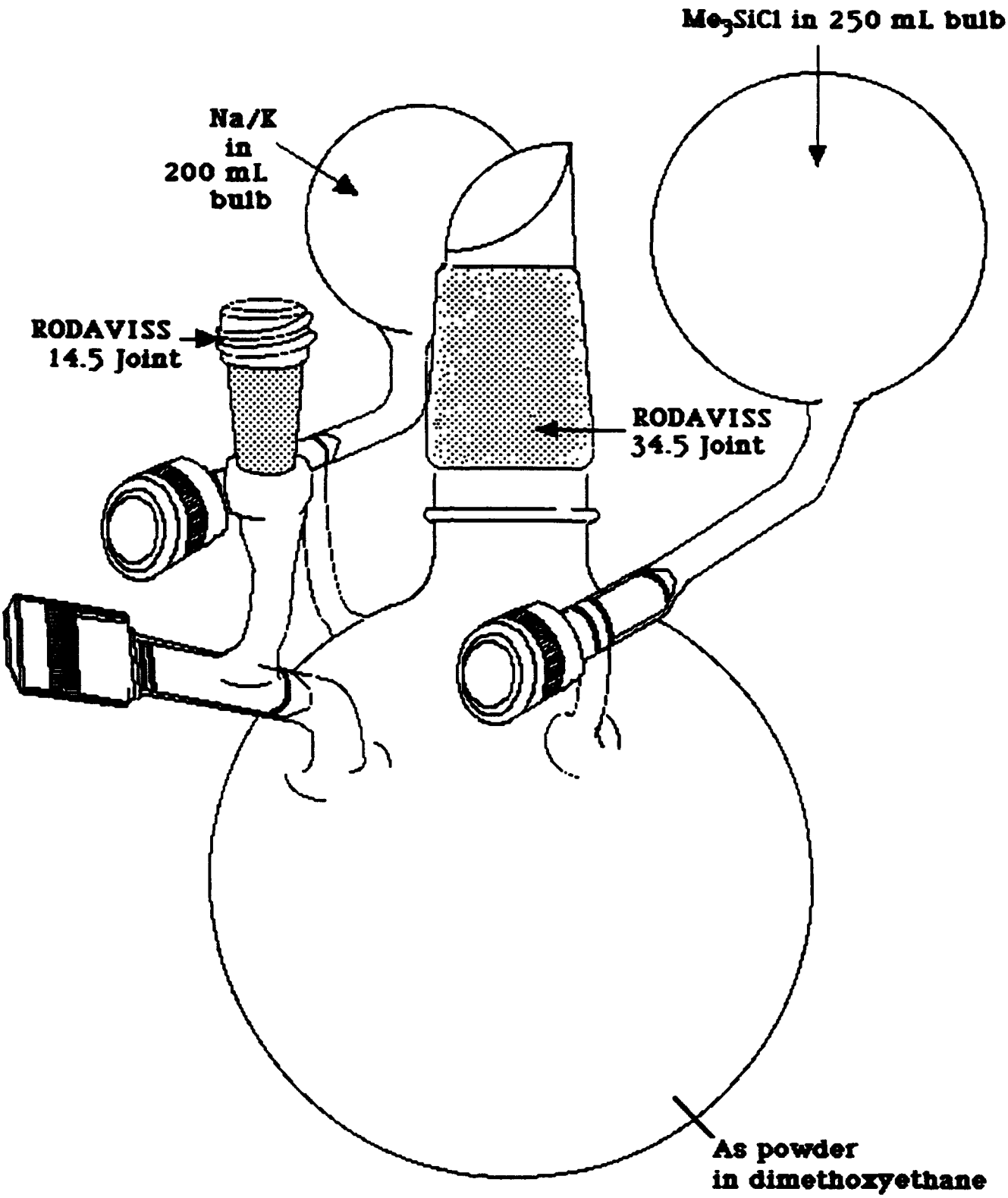
*The checkers obtained %.

Captions to figures.

Fig. 1. Three-bulbed reaction vessel.

Fig. 2. "Mushroom" flask with attached filtration apparatus .

Fig. 3. Fully assembled apparatus for the synthesis of the organoarsine.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RODAVISS
34.5 Joint
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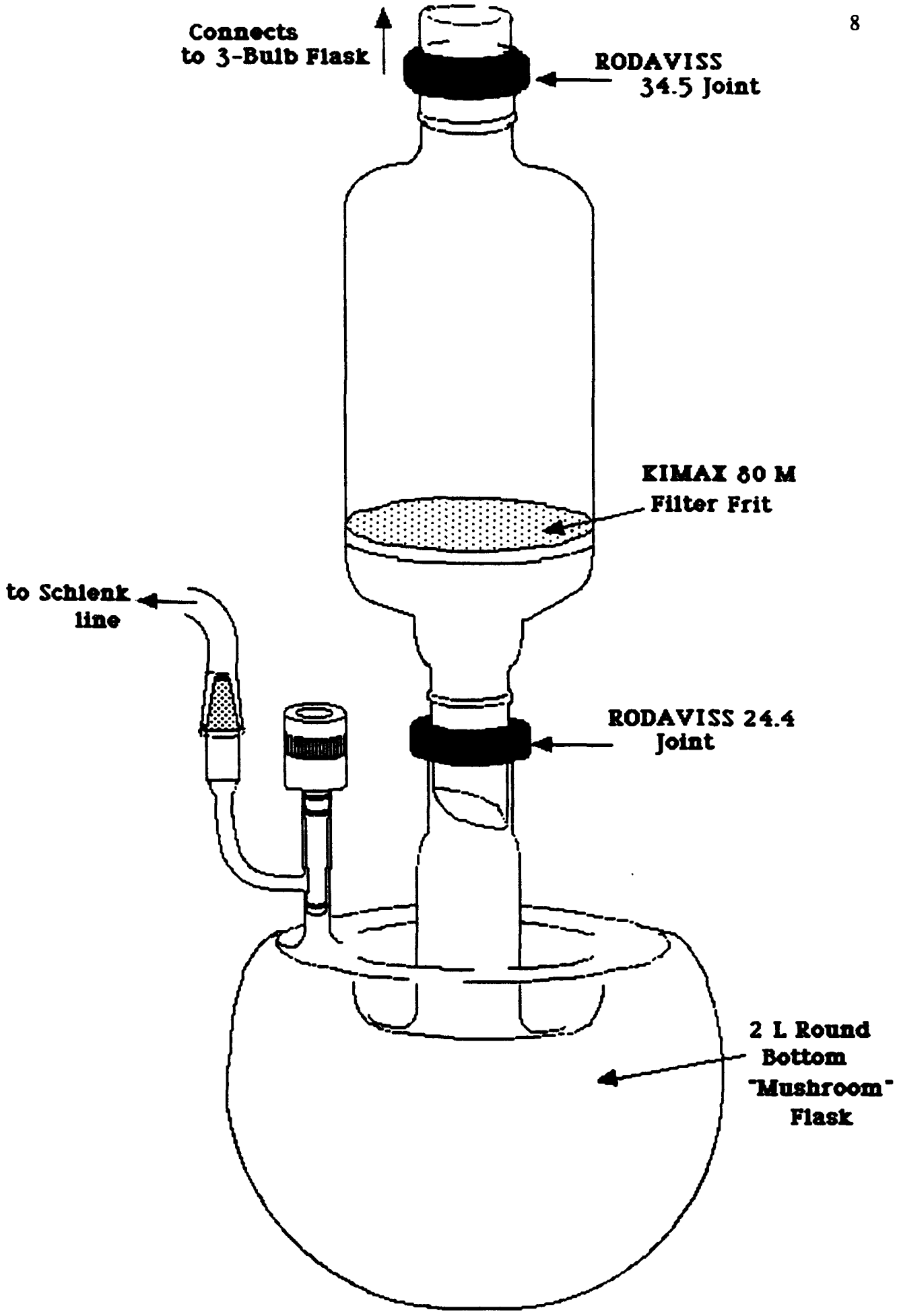
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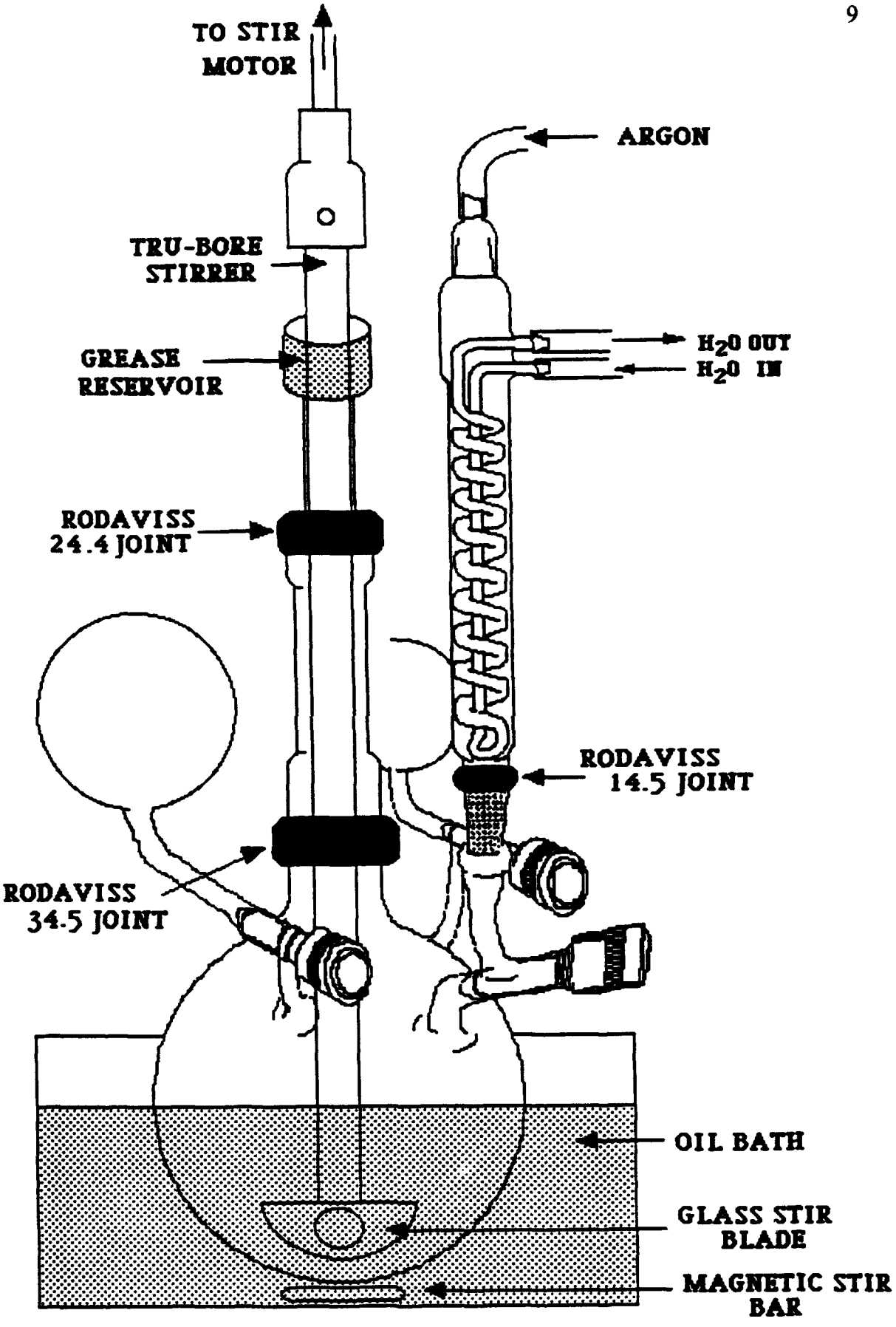
TO STIR MOTOR
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