Organic Syntheses

A Publication
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for the Preparation
of Organic Compounds

# Working with Hazardous Chemicals

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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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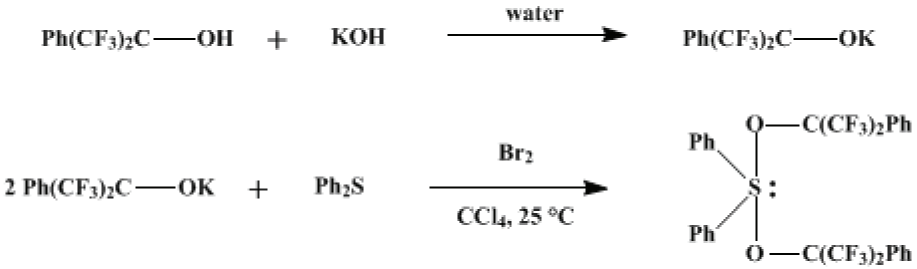
# BIS[2,2,2-TRIFLUORO-1-PHENYL-1-(TRIFLUOROMETHYL) ETHOXY] DIPHENYL SULFURANE

## [Sulfur, bis[α,α-bis(trifluoromethyl)benzenemethanolato]diphenyl-]



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Checked by H. G. Corkins, C. J. Stark, and C. R. Johnson.

## 1. Procedure

A. *Potassium 1,1,1,3,3,3-hexafluoro-2-phenyl-2-propanolate*. A 500-ml., round-bottomed flask equipped for simple vacuum distillation is charged with a solution of 25.4 g. (0.390 mole) of 86% potassium hydroxide (Note 1) and (Note 2) in 50 ml. of water, to which is added 100.0 g. (0.4098 mole) of 1,1,1,3,3,3-hexafluoro-2-phenyl-2-propanol (Note 3). The colorless solution obtained is concentrated to a syrup by vacuum distillation at aspirator pressure. Further evacuation with a vacuum pump with heating to 140° results in a white solid; under the greater vacuum volatile substances can be collected in a trap immersed in an acetone-dry ice bath. The trap must be cleaned or be replaced several times during the first hour. After drying the white solid at 140° for 12 hours, the flask is transferred to a glove bag (Note 4) equipped with a mortar and pestle, a vacuum adapter, a powder funnel, a spatula, and a tared, 500-ml., round-bottomed flask. Under a dry nitrogen atmosphere the white solid is ground to a fine powder, transferred to the 500-ml. flask, and dried on a vacuum pump ($10^{-2}$ mm.) to constant weight, yielding 107–109 g. (97–99%) of potassium 1,1,1,3,3,3-hexafluoro-2-phenyl-2-propanolate as a white powder.

B. *Bis*[2,2,2-*trifluoro*-1-*phenyl*-1-(*trifluoromethyl*)*ethoxy*] *diphenyl sulfurane*. Carbon tetrachloride is distilled directly from phosphorous pentoxide into a dry, 2-l., three-necked flask, fitted with stoppers, until 700 ml. is collected. The flask is quickly fitted with an adapter for use as a nitrogen-inlet, a mechanical stirrer, and an adapter for solid addition (Note 5) which is attached to the 500-ml. flask containing the potassium alkoxide from Part A. A positive pressure of dry nitrogen is used to maintain inert atmosphere conditions. A white slurry is obtained when the powdered alkoxide is added at room temperature to the stirred carbon tetrachloride. Since all of the alkoxide does not transfer, the tared, 500-ml. flask is reweighed, and the amount added to the reaction vessel is determined by difference (Note 6). The adaptor used for solid addition is quickly exchanged for a septum.

To a stirred suspension of 105 g. (0.372 mole) of the alkoxide, 34.7 g. (31.0 ml., 0.186 mole) of diphenyl sulfide is added by syringe. Bromine, 29.9 g. (9.6 ml., 0.186 mole), is then added by syringe over a 5-minute period, giving a red-brown mixture which gradually fades to a pale yellow within 30 minutes. Stirring is continued at room temperature for 2.5 hours, leaving a pale-yellow solution and a copious precipitate of potassium bromide containing some potassium alkoxide.

A glove bag is equipped with a spatula, a tared, 1-l., single-necked round-bottomed flask, a 350-ml. Buchner funnel with filter paper, a 1-l. flask, a vacuum adapter, an aspirator hose (Note 7), and a flask containing 100 ml. of dry carbon tetrachloride. Filtration of the reaction mixture under a nitrogen atmosphere can be achieved by pouring the solution into the filter funnel *via* one neck of the three-necked flask, which is inserted through a hole in the glove bag. The potassium bromide is removed and washed with two 50-ml. portions of dry carbon tetrachloride. The filtrate is then transferred to the 1-l.

flask, fitted with the vacuum adapter. After removal of the sulfurane solution from the glove bag (Note 8), the flask is quickly placed on a rotary evaporator (Note 9) and concentrated to a semisolid. Drying under reduced pressure ($10^{-2}$ mm.) for 24 hours results in crude sulfurane (115–119 g., 93–96%) as slightly yellow crystals.

The flask containing the crude sulfurane is transferred to the nitrogen atmosphere of the glove bag which contains a powder funnel, a fluted filter paper, a 1-l., single-necked, round-bottomed flask, a 250-ml. graduated cylinder, a 1-l. flask containing 700 ml. of dry pentane (Note 10), and a 500-ml. flask containing 250 ml. of dry diethyl ether (Note 10). After dissolving the sulfurane in 150 ml. of ether, 500 ml. of pentane is added, giving a cloudy solution that clarifies when filtered directly into the 1-l. flask. The flask, is stoppered with the vacuum adapter and removed from the bag. At this time everything but the pentane is removed from the glove bag and the following items are added: a 600-ml., medium-frit sintered-glass funnel, a 1-l., single-necked, round-bottomed flask, a tared, 500-ml., single-necked round-bottomed flask, a vacuum adaptor, two spatulas, and a powder funnel. The sulfurane solution is concentrated to *ca.* 350 ml. at reduced pressure and a temperature not exceeding 40° (Note 9), using a magnetic stirrer to prevent bumping as the solvent is evaporated through the vacuum adapter. After a drying tube is connected to the adapter, the flask is cooled in an acetone–dry ice bath to induce crystallization; swirling the flask during the crystallization prevents crystals from adhering to the sides. When crystallization is complete, the flask is exchanged for the three-necked flask inserted into the side of the glove bag. Cooling in the acetone–dry ice bath is continued while the neck of the flask penetrates the glove bag. The crystals, collected in the sintered-glass funnel by vacuum filtration, are washed with one 50-ml. portion of cold (−78°) pentane and transferred to the 500-ml. flask. After fitting with the vacuum adapter, the flask is removed from the bag and the crystals dried under reduced pressure ($10^{-2}$ mm.) until the powdered, white sulfurane is at constant weight (76–79 g., 61–64%, m.p. 103–108°). Further crystallization from the mother liquors, after concentration by rotary evaporation to one-half the original volume, gives up to 7 g. of crude sulfurane (m.p. < 95°) for a total yield of 79–83 g. (63–67%) (Note 11). Recrystallization by the same method as above gives analytically pure material, m.p. 109.5–110.5°.

## 2. Notes

1. The submitters report no problems in running the entire procedure on four times the scale described here.
2. The use of potassium hydroxide rather than sodium hydroxide is dictated by solubility characteristics which make purification of the sodium alkoxide difficult.
3. The alcohol was obtained from PCR, Incorporated, or was prepared from hexafluoroacetone (E.I. du Pont de Nemours and Company), benzene, and aluminum chloride by the published[2] procedure.
4. Glove bags may be purchased from Instruments for Research and Industry, 108 Franklin Avenue, Cheltenham, Pennsylvania 19012. The 27 × 27 × 15 inch bag was found to be a convenient size for this procedure. The submitters performed all inert atmosphere operations in a dry box. All apparatus must be oven or flame dried prior to use.
5. This adapter consisted of two 24/40 joints connected with Gooch tubing.
6. The quantities of bromine and diphenyl sulfide must be adjusted according to the amount of alkoxide added.
7. A stopcock and a drying tube were inserted into the hose between the glove bag and the aspirator.
8. The other materials in the bag may be removed at this time, but the three-necked flask inserted through the side of the glove bag must not be removed.
9. During solvent removal or recrystallization, temperatures should be kept below 50° to avoid degradation of product quality.
10. Dry ether was obtained by distillation of reagent grade dry ether from sodium dispersion or by drying over three portions of sodium wire over a 48-hour period. Dry pentane was prepared by adding sodium wire directly to reagent grade solvent at least twice or by distilling it from a sodium dispersion.
11. Hexafluoro-2-phenyl-2-propanol may be recovered from mother liquors, recovered solvent, and the KBr salt cake by extracting the mixture with aqueous base. Neutralization of the aqueous phase gives the alcohol (13–23 g.), which is purified by distillation.

## 3. Discussion

This dialkoxy diphenyl sulfurane has been prepared by the reaction of diphenyl sulfide, 2,2,2-trifluoro-1-phenyl-1-(trifluoromethyl)ethyl hypochlorite, and potassium 1,1,1,3,3,3-hexafluoro-2-phenyl-2-propanolate[3] and by the reaction of diphenyl sulfide with 1 equivalent of chlorine and 2 equivalents of potassium 1,1,1,3,3,3-hexafluoro-2-phenyl-2-propanolate in ether.[4]

The present method offers several advantages over earlier methods. The use of carbon tetrachloride instead of ether as solvent avoids the intrusion of certain radical-chain reactions with the solvent which are observed with bromine and to a lesser degree with chlorine. In addition, the potassium bromide has a reduced solubility in carbon tetrachloride compared to ether, thus providing additional driving force for the reaction and ease of purification of product. The selection of bromine over chlorine as the oxidizing agent is made in consideration of the ease of handling the bromine by syringe compared to the greater number of operations and more complex apparatus required for chlorine.

Another dialkoxy diaryl sulfurane has been prepared[5] under conditions similar to those reported here, indicating that this reaction for sulfurane formation may have wide applicability.

The great reactivity of the sulfurane prepared by this procedure toward active hydrogen compounds, coupled with an indefinite shelf life in the absence of moisture, makes this compound a useful reagent for dehydrations,[6,7] amide cleavage reactions,[8] epoxide formation,[9] sulfilimine syntheses,[10] and certain oxidations and coupling reactions.

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## References and Notes

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

phosphorous pentoxide

Sulfur, bis[α,α-bis(trifluoromethyl)benzenemethanolato]diphenyl-

Benzene (71-43-2)

ether,
diethyl ether (60-29-7)

sodium hydroxide (1310-73-2)

bromine (7726-95-6)

carbon tetrachloride (56-23-5)

nitrogen (7727-37-9)

aluminum chloride (3495-54-3)

chlorine (7782-50-5)

potassium hydroxide (1310-58-3)

sodium (13966-32-0)

potassium bromide (7758-02-3)

Pentane (109-66-0)

Diphenyl sulfide (139-66-2)

BIS[2,2,2-TRIFLUORO-1-PHENYL-1-(TRIFLUOROMETHYL) ETHOXY] DIPHENYL SULFURANE,
Bis[2,2,2-trifluoro-1-phenyl-1-(trifluoromethyl)ethoxy] diphenyl sulfurane (32133-82-7)

1,1,1,3,3,3-hexafluoro-2-phenyl-2-propanol,
Hexafluoro-2-phenyl-2-propanol (718-64-9)

potassium 1,1,1,3,3,3-hexafluoro-2-phenyl-2-propanolate

Hexafluoroacetone (684-16-2)

sulfilimine

2,2,2-trifluoro-1-phenyl-1-(trifluoromethyl)ethyl hypochlorite