Synthetic Methods and Reactions. 54.[1] Deoxygenation of Sulfoxides and Azoxides with Tris(dimethylamino)phosphine/Iodine/Sodium Iodide Reagent

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Sulfoxides and azoxyarenes are deoxygenated in excellent yield under mild conditions with tris(dimethylamino)phosphine activated by iodine. The reactions show marked catalysis by sodium iodide. Tris(dimethylamino)phosphine is superior to triphenylphosphine for deoxygenations.

We have previously reported the use of iodotrimethylsilane[2] for deoxygenation of sulfoxides. There is current interest in developing new methods of deoxygenation and their application in organic synthesis.[3-5] Some of the criteria of usefulness of a reagent are those of the mildness of reaction conditions, absence of side reactions, and ease of workup. Some phosphorus compounds, including phosphorus trichloride,[6] benzodioxachlorophosphole,[7] phosphorus pentasulfide,[8] and triphenylphosphine/carbon tetrachloride[9] have been used for deoxygenation of sulfoxides. All these reagents exploit the strong affinity between phosphorus and oxygen. These reagents are either expensive or provide undesirable side products via Pummerer and the like rearrangements.[6] Also, in some cases prolonged reaction times are needed.

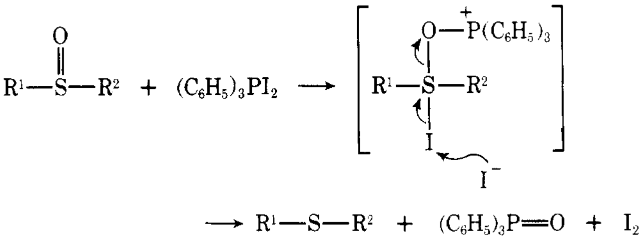
Recently, we reported a mild method for deoxygenation of sulfoxides with triphenylphosphine activated by iodine.[4] We report now on the use of a new, even more convenient, method using tris(dimethylamino)phosphine/iodine/sodium iodide reagent.

Results and Discussion

Triphenylphosphine in carbon tetrachloride has been used to cleave aryl sulfoxides. The deoxygenation proceeds via initial reaction of the phosphine with carbon tetrachloride. The mechanism of this reaction is not clear, but it was proposed that the deoxygenating agent is probably $Ph_3P{=}CCl_2$ or Ph_3PCl_2. However, work by Appel et al.[10] shows that the triphenylphosphine/carbon tetrachloride system is more complicated than originally proposed and that the intermediates in this system are $[Ph_3P\doteq C(Cl)\doteq PPh_3]^+Cl^-$ and Ph_3PCl_2. In addition, the existence of two other ionic intermediates $[Ph_3PCl]^+\ {}^-CCl_3$ and $[Ph_3PCCl_3]^+Cl^-$ has been proposed. All these intermediates seem to be well suited to act as deoxygenating agents.

When we attempted to deoxygenate alkyl sulfoxides with triphenylphosphine/carbon tetrachloride, chlorination was a major side reaction. Addition of iodine, instead of carbon tetrachloride, yielded a better reagent. As our previous results show,[4] sulfoxides were clearly cleaved to the corresponding sulfoxides in 70–90% yield in 10–60 min with triphenylphosphine/iodine/sodium iodide reagent in refluxing acetonitrile. Addition of sodium iodide reduced the reaction time considerably. On the basis of these observations, the mechanism in Scheme I was proposed.

Scheme I



The major drawback of the described method of deoxygenation is firstly the formation of an equivalent amount of triphenylphosphine oxide, which has to be separated from the product sulfide by column chromatography, and secondly, the need for higher temperatures. To avoid these problems, we now report that tris(dimethylamino)phosphine can be advantageously used instead of triphenylphosphine because the resultant byproduct, hexamethylphosphoric triamide, is completely miscible with water. Therefore, there is no need of column chromatographic separation of the product mixture. Product sulfides are isolated by extracting them with ether and washing the ethereal extract with aqueous sodium thiosulfate and water.

The data in Table I show that the tris(dimethylamino)phosphine/iodine/sodium iodide reagent deoxygenates sulfoxides and azoxybenzenes in excellent yield in homogeneous reactions.

This reagent is more effective than the corresponding triphenylphosphine reagent. Thus, for example, phenyl sulfoxide is completely reduced in 20 min instead of the 1-h reaction time required with the former reagent. In the case of aliphatic sulfoxides, no catalysis by sodium iodide is necessary, and the reaction is again completed in 20 min at ambient temperature. In contrast, with triphenylphosphine/iodine/sodium iodide reagent, aliphatic sulfoxides also require heating under reflux.

Deoxygenation of sulfoxides can also be carried out with tris(dimethylamino)phosphine and carbon tetrachloride. The reaction requires, however, a longer time to go to completion. Also, although the yields are good, the reaction is not as clean, as some chlorinated byproducts are formed. No reaction was observed with chloroform.

If milder conditions are required, aromatic sulfoxides can also be deoxygenated at room temperature by stirring with the reagent overnight, but a molar excess of the reagent is required (Table I).

When we attempted to deoxygenate azoxybenzene with triphenylphosphine/iodine/sodium iodide, no reaction was observed. Azoxybenzene has been previously deoxygenated with phosphorous trichloride[11] and with triethyl phosphite.[12] Using tris(dimethylamino)phosphine/iodine/sodium iodide, azobenzene and bis(4-methoxy)azobenzene were obtained in excellent yield from their corresponding azoxides.

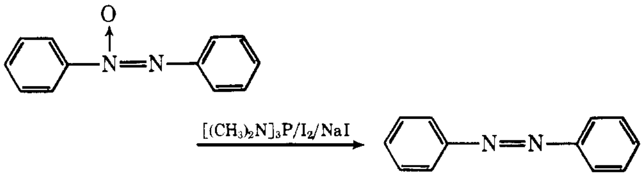


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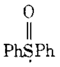
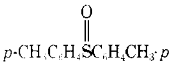
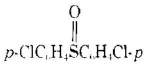
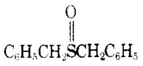
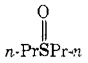
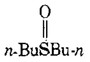
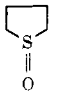
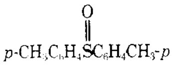
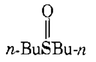
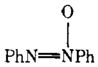
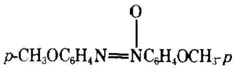
Table I. Deoxygenation of Sulfoxides and Azoxybenzenes with Tris(dimethylamino)phosphine

substrate	registry no.	solvent	reagent ratio (mmol) substrate $(Me_2N)_3P/I_2/NaI$	reaction conditions	deoxygenated product isolated crude yield, %[a]
 $\text{Ph}\overset{O}{\overset{\|}{S}}\text{Ph}$	945-51-7	CH_3CN	1:1:1:1	20 min; reflux	95[d]
 $\text{Ph}\overset{O}{\overset{\|}{S}}\text{Ph}$		CH_3CN	1:2:1:4	overnight, room temp	95[d]
 $p\text{-}CH_3C_6H_4\overset{O}{\overset{\|}{S}}C_6H_4CH_3\text{-}p$	1774-35-2	CH_3CN	1:1:1:1	20 min; reflux	96[e]
 $p\text{-}ClC_6H_4\overset{O}{\overset{\|}{S}}C_6H_4Cl\text{-}p$	3085-42-5	CH_3CN	1:1:1:1	20 min; reflux	94[f]
 $C_6H_5CH_2\overset{O}{\overset{\|}{S}}CH_2C_6H_5$	.21-08-9	CH_3CN	1:1:1:1	20 min; reflux	96[g]
 $n\text{-}Pr\overset{O}{\overset{\|}{S}}Pr\text{-}n$	4253-91-2	CH_3CN	1:1:1:0	20 min; room temp	70[h]
 $n\text{-}Bu\overset{O}{\overset{\|}{S}}Bu\text{-}n$	2168-93-6	CH_3CN	1:1:1:0	20 min; room temp	82[i]
	1600-44-8	CH_3CN	1:1:1:0	20 min; room temp	68[j]
 $\text{Ph}\overset{O}{\overset{\|}{S}}\text{Ph}$		CCl_4–CH_3CN	1:1:0:0	30–45 min; reflux[b]	92[d]
 $p\text{-}CH_3C_6H_4\overset{O}{\overset{\|}{S}}C_6H_4CH_3\text{-}p$		CCl_4–CH_3CN	1:1:0:0	30–45 min; reflux[b]	92[e]
 $n\text{-}Bu\overset{O}{\overset{\|}{S}}Bu\text{-}n$		CCl_4–CH_3CN	1:1:0:0	10–15 min; 60 °C[b]	mixture of products
 $n\text{-}Bu\overset{O}{\overset{\|}{S}}Bu\text{-}n$		$CHCl_3$	1:1:0:0	5–6 h; reflux[c]	in complete deoxygenation
 $n\text{-}Bu\overset{O}{\overset{\|}{S}}Bu\text{-}n$		CH_3CN	1:1:0:0	5–6 h; reflux	in complete deoxygenation
 $PhN{=}\overset{O}{\overset{\mid}{N}}Ph$	495-48-7	CH_3CN	1:1:1:1	5–6 h; reflux	93[k]
 $p\text{-}CH_3OC_6H_4N{=}\overset{O}{\overset{\mid}{N}}C_6H_4OCH_3\text{-}p$	1562-94-3	CH_3CN	1:1:1:1	2–3 h; reflux	91[l]

[a] The identification of these compounds was by physical and spectral data, which were consistent with those of authentic samples, as given in footnotes *d*–*l*. [b] CCl_4 was added at −20–30 °C (CCl_4–dry ice bath) and the reaction mixture was then brought slowly to reflux.[4] [c] No appreciable reaction was observed with $CHCl_3$ and $(Me_2N)_3P$. [d] The Aldrich Library of IR, 1970, p 527C. [e] Sadtler infrared spectra, midget ed, 1959, no. 9235. [f] Sadtler infrared spectra, 1976, no. 50793. [g] mp 48–49 °C (lit. 49 °C), "Dictionary of Organic Compounds", 4th ed., Oxford University Press, New York, N.Y., 1965. [h] The Aldrich Library of IR, 1970, p 121H. [i] The Aldrich Library of IR, 1970, p 122C. [j] NMR Spectra Catalog, Varian Associates, 1962, no. 80. [k] Sadtler ultraviolet spectra, 1966, no. 136 U.V. [l] mp 164–166 °C [lit. 160.5–162.5 °C (165 °C)], "Dictionary of Organic Compounds", 4th ed, Oxford University Press, New York, N.Y., 1965.

Tris(dimethylamino)phosphine is clearly more effective than triphenylphosphine as a deoxygenating agent in terms of mildness of reaction conditions, ease of workup, and formation of deoxygenated product in high yield.

Experimental Section

Starting Materials. All the sulfoxides and azoxy compounds used in this work were commercially available (Aldrich Chemical Co.) generally 97% or higher purity and used without further purification, as was tris(dimethylamino)phosphine (Aldrich). Acetonitrile was purified by the usual method.

Melting points were determined on Fisher–Johns apparatus and are not corrected. NMR and IR spectra were obtained on Varian EM-360 and Perkin-Elmer 297 spectrometers, respectively.

Typical Procedure for Deoxygenation of Butyl Sulfoxide Using Tris(dimethylamino)phosphine/Iodine Reagent. In a 50-mL flask equipped with a magnetic stirring bar and flushed continuously with dry nitrogen, iodine (2.54 g, 10 mmol) was suspended in acetonitrile (10 mL). To this suspension, 10 mmol (1.65 g) of tris(dimethylamino)phosphine was slowly added at room temperature with continuous stirring. Soon iodine dissolved, with slight warming of the solution, giving a clear solution of the reagent. It was cooled to 0 °C in an ice bath and with good stirring, a solution of butyl sulfoxide (1.62 g, 10 mmol) in acetonitrile (5 mL) was slowly added. Immediately, an exothermic reaction took place with liberation of iodine. The reaction mixture was maintained at 0 °C throughout the addition. After the addition of sulfoxide (10 min) was completed, progress of the reaction was monitored by TLC (benzene as eluent). Complete conversion took place in 20 min. The reaction mixture was then taken up in ether (2 × 50 mL) and washed successively with aqueous sodium thiosulfate (10% solution), water, and brine. The ethereal extract was dried over anhydrous sodium sulfate and gave upon evaporation of the ether 1.21 g of butyl sulfide, 82% yield.

The same procedure was used for other aliphatic sulfoxides, tetramethylene sulfoxide and benzyl sulfoxide, results of which are summarized in Table I.

Typical Procedure for Deoxygenation of Phenyl Sulfoxide with Tris(dimethylamino)phosphine/Iodine/Sodium Iodide Reagent. Tris(dimethylamino)phosphine/iodine reagent (10 mmol) was prepared as described above in a 50-mL flask equipped with a magnetic stirring bar and reflux condenser, purged with dry nitrogen. To this reagent was slowly added with continuous stirring a solution of phenyl sulfoxide (2.02 g, 10 mmol) in acetonitrile (5 mL). No reaction took place during the addition, and the reaction mixture remained colorless. Powdered sodium iodide (1.5 g, 10 mmol) was then added, which dissolved completely giving a homogeneous solution. Refluxing of the reaction mixture soon resulted in the liberation of iodine, and the reaction was complete in 20 min, as monitored by TLC (benzene as eluent). Workup of the reaction mixture was as described above, giving phenyl sulfide (1.77 g) in 95% yield.

By increasing the molar ratio of tris(dimethylamino)phosphine and sodium iodide as shown in Table I, it was possible to perform the reaction at room temperature.

A similar procedure was used for the deoxygenation of other aromatic sulfoxides, as well as azoxy compounds.

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Registry No.—$[(CH_3)_2N]_3P$, 1608-26-0; I_2, 7553-56-2; NaI, 7681-82-5.

References and Notes

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Synthesis of the Perfluoropoly(ethylene glycol) Ethers by Direct Fluorination

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A new general technique has been developed for the synthesis of perfluorocarbon polyethers by the reaction of elemental fluorine with high molecular weight polyether under conditions selected to promote fragmentation of the ether chain during complete fluorination. A number of new perfluorocarbon ethers of the type $R_fO(CF_2CF_2O)_nR_f$ ($R_f = CF_3, C_2F_5$) have been prepared.

Saturated perfluoro polyethers are of current interest for new material applications due to their unusual properties. Lack of chemical reactivity and thermal stability (>300 °C) is their outstanding feature. They have been described as equally stable in perfluoroalkanes and unaffected by concentrated acids and bases at elevated temperatures over extended periods of time.[1] The only reported reaction of saturated perfluoropolyethers is chain cleavage at the ether linkage by aluminum chloride (at elevated temperatures and autogenous pressure) to produce acyl chloride and trichloromethyl end groups.[2] These remarkable stabilities along with their interesting surface properties, viscosities, and the broad liquid ranges of the low molecular weight compounds make saturated perfluoro polyethers attractive for numerous applications[3] as solvents, hydraulic fluids, heat-transfer agents, lubricants, greases, sealants, elastomers, and plastics.

Synthetic methods have limited the preparation of saturated perfluoro polyethers. The most successful perfluoro polyether synthetic chemistry has been DuPont's anionic polymerization of perfluoro epoxides, particularly hexafluoropropylene oxide and tetrafluoroethylene oxide.[4] Their synthetic procedure is a three-step scheme for saturated perfluoro polyether production involving oxidation of perfluoroolefins to perfluoro epoxides, anionic polymerization to acyl fluoride terminated perfluoro polyethers, and conversion of acyl fluoride end groups to unreactive end groups by decarboxylation reactions or chain coupling photolytic decarboxylative reactions. Other general synthetic methods for perfluoro ether and perfluoro polyether production are the addition reactions of perfluoro hypofluorite, R_fOF, with perfluoroolefins,[5] and the perfluoro peroxide, R_fOOR_f, addition reaction with perfluoroolefins[6] and electrolytic fluorination in anhydrous HF of the corresponding hydrocarbon ethers.[7]

We have developed a useful new synthetic method for the production of saturated perfluoropoly(ethylene glycol) ethers. A one-step reaction, the direct fluorination of poly(ethylene oxide) polymer with reaction conditions chosen to promote fragmentation of the polymer during the fluorination process, has resulted in the synthesis of saturated perfluoro polyethers over a broad range of molecular weights.

$$(CH_2CH_2O)_n \xrightarrow{F_2/He} R_f(OCF_2CF_2)_nOR_f$$
$$R_f = CF_3, C_2F_5$$

The low molecular weight compounds (n = 1–6) which have been isolated are volatile liquids; medium molecular weight compounds are novolatile oils; and the high molecular weight compounds are gellike and powdery solids. Previously we have found that milder fluorination conditions designed to prevent fragmentation lead to an extremely stable high molecular weight perfluoro polyether.[8] Of the perfluoro polyethers reported here, only three have been reported previously by methods other than direct fluorination. Perfluoromonoglyme,[9,10] perfluoroethylene glycol methyl ethyl ether,[9] perfluoroethylene glycol diethyl ether,[11] and perfluorodiethylene glycol diethyl ether[10] have all been prepared by electrolytic fluorination in anhydrous HF in low yield. Direct fluorination has been used previously for the synthesis of specific perfluoro ethers. We have previously reported the successful direct fluorination of monoglyme and diglyme at low temperatures

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