

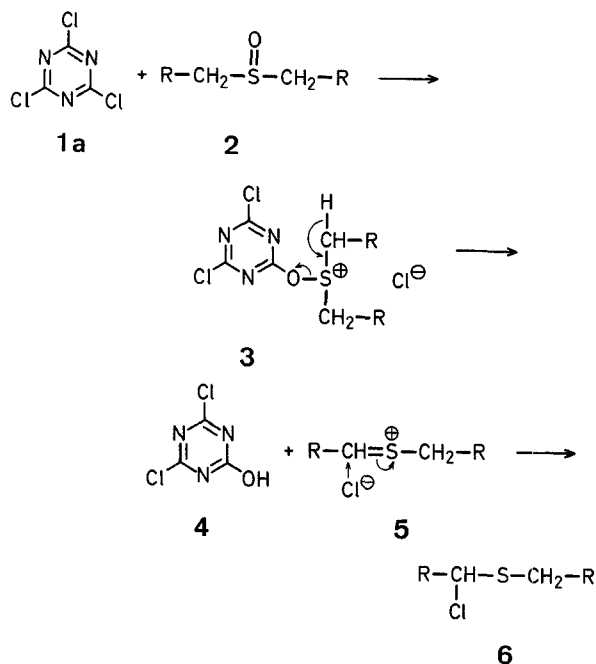
Synthetic Methods and Reactions; 80¹. Deoxygenation of Sulfoxides with Cyanuric Chloride and Fluoride

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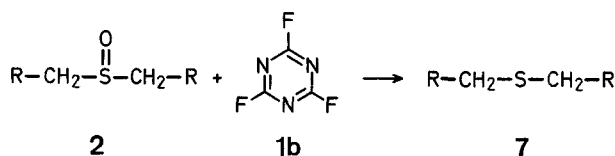
Cyanuric chloride^{2,3} (**1a**) is a readily available, useful reagent, but has found only limited application in organic synthesis. We have previously reported the preparation of cyanuric fluoride⁴ (**1b**) and its use in the synthesis of acid fluorides. The high reactivity of these reagents coupled with the ease of removal of the products should make them suitable for synthetic transformations. In continuation of our interest in these reagents, we now report their use in the deoxygenation of alkyl, aralkyl, and aryl sulfoxides **2**.

Aryl sulfoxides undergo facile cleavage to the corresponding sulfides when heated under reflux with **1a** in dioxan. Shorter reaction times were sufficient when carrying out the reactions in triethyl phosphate, allowing higher reaction temperatures. In contrast, aralkyl and alkyl sulfoxides reacted exothermically with **1a** yielding a complex mixture of chlorinated products. Complex product mixtures were



obtained even at lower temperatures or in the presence of sodium iodide. The chlorination probably occurs as shown below.

In order to avoid the formation of halogenated products, cyanuric chloride (**1a**) was replaced with cyanuric fluoride (**1b**) in order to take advantage of the relatively low nucleophilicity of the fluoride ion. Indeed, when aliphatic sulfoxides were reacted with **1b** in dioxan, the corresponding sulfides **7** were obtained in high yield with no concomitant formation of undesired halogenated sulfides. The higher reactivity of **1b** was also indicated by the shorter times required for completion of the reaction.



Deoxygenation of Sulfoxides **2**; General Procedures:

Method A: To a stirred solution of cyanuric chloride (**1a**; 1.84 g, 10 mmol) in dioxan (25 ml) is added a solution of the sulfoxide **2** (10 mmol) in dioxan (10 ml) under nitrogen. The mixture is heated under reflux and monitored by T.L.C. (silica gel plates with hexane as an eluent). On completion of the reaction, the reaction mixture is quenched with ice/water (100 ml), filtered, and the filtrate extracted with hexane (2 × 50 ml). The hexane extract is washed with water, dried with anhydrous sodium sulfate, and the solvent evaporated. The product is chromatographed on a silica gel column using hexane as an eluent to yield the pure sulfide **7**.

Method B: The reaction is carried out as described above except that dioxan is replaced with triethyl phosphate as the reaction medium.

Method C: To a stirred solution of cyanuric fluoride (**1b**; 1.6 ml) in dioxan (25 ml) is added a solution of the sulfoxide **2** (10 ml) in dioxan (10 ml) under nitrogen. The reaction is monitored by T.L.C. and worked up as described above.

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¹ For Part 79, see: G. A. Olah, M. Arvanaghi, G. K. S. Prakash, *Synthesis* **1980**, 220.

² E. M. Smolin, L. Rapoport, *The Chemistry of Heterocyclic Compounds. s-Triazines and Derivatives*, A. Weissberger, Ed., Interscience, New York, 1959.

³ K. Venkataraman, D. R. Wagle, *Tetrahedron Lett.* **1979**, 3037, and references therein.

⁴ G. A. Olah, M. Nojima, I. Kerekes, *Synthesis* **1973**, 487.

⁵ *Handbook of Tables for Organic Compound Identification*, 3rd Ed., Chemical Rubber Company, Cleveland, Ohio, 1978.

Table. Deoxygenation of Sulfoxides **2** with Cyanuric Chloride (**1a**) and Cyanuric Fluoride (**1b**)

R	R	Method	Yield ^a [%]	Reaction time [h]	m.p. or b. p./torr found	m.p. or b. p./torr reported ⁵
<i>n</i> -C ₃ H ₇	<i>n</i> -C ₃ H ₇	C	70	4	140–142 °C/760	142 °C/760
<i>n</i> -C ₄ H ₉	<i>n</i> -C ₄ H ₉	C	78	9	70–72 °C/7	185–185.5 °C/760
	(CH ₂) ₄	C	65	3	119–120 °C/760	121.1 °C/760
C ₆ H ₅ CH ₂	C ₆ H ₅ CH ₂	C	72	4	48–49 °C	49–50 °C
C ₆ H ₅	C ₆ H ₅	A	86	14	130–131 °C/2	296 °C/760
		B	82	1		
4-Cl-C ₆ H ₄	4-Cl-C ₆ H ₄	A	91	15	94–95 °C	95 °C
		B	93	1		
4-H ₃ C-C ₆ H ₄	4-H ₃ C-C ₆ H ₄	A	94	12	55 °C	57.3 °C
		B	91	1		

^a Yield of pure, isolated products; purity ≥ 98% as determined by T.L.C. (silica/hexane), I.R., and N.M.R. spectroscopy.