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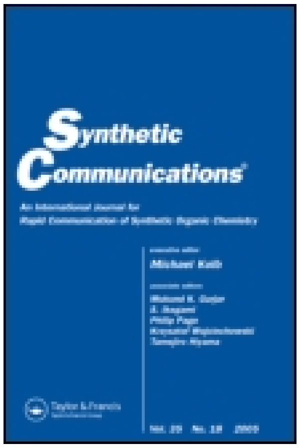

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CONVERSION OF ALCOHOLS INTO ALKYL CHLORIDES USING TRICHLOROISOCYANURIC ACID WITH TRIPHENYLPHOSPHINE

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CONVERSION OF ALCOHOLS INTO ALKYL CHLORIDES USING TRICHLOROISOCYANURIC ACID WITH TRIPHENYLPHOSPHINE

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ABSTRACT

Trichloroisocyanuric acid with triphenylphosphine in anhydrous acetonitrile will convert alcohols into alkyl halides.

Key Words: Alkyl chlorides; Alcohols; Trichloroisocyanuric acid; Triphenylphosphine; Synthesis; Preparation

A variety of reagents can be used to convert alcohols into alkyl chlorides.[1] Many of these reagents are water reactive and do not store well. Recently we reported that a freshly prepared mixture of trichloroisocyanuric acid (**1**) [1,3,5-trichloro-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione; TCICA] (CAS Reg. No. [87-90-1]) and triphenylphosphine (Ph_3P) in anhydrous acetonitrile is an effective reagent for carrying out a variety of substitution reactions for which PCl_5 and similar reagent are often used.[2] It is reasonable to assume that **1** transfers a chlorine to the phosphorus to

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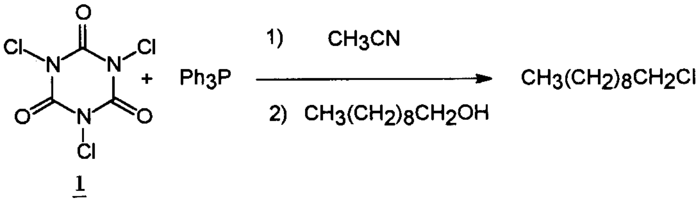
form a reactive complex of the type $Ph_3P^+Cl\ Z^-$, where Z^- is the remaining portion of **1**. The overall reaction is shown in the equation.



The triphenylphosphine oxide produced in these reaction can be difficult to separate from the products, however. In order to accomplish this separation, all of the reaction reported in our previous paper were carried out on a small scale with purification by means of flash chromatography. Now we report the results of reactions carried out on an 8 g scale with isolation by means of extraction with pentane, which effectively separated the triphenylphosphine oxide, and purification by distillation.

After an initial examination of the reaction between **1** and Ph_3P, it was determined that with a 1.05 : 1 equivalent ratio of **1** : Ph_3P neither reagent would be present in excess. Since there are three equivalents per mole of **1**, the corresponding mole ratio is 0.35 : 1.

In the general reaction procedure 1.50 equivalents of Ph_3P was dissolved in anhydrous acetonitrile, and 1.58 equivalents of **1** was added slowly because the reaction is highly exothermic. The yellow mixture was then heated in a 60°C oil bath, 1.0 equivalent of the alcohol was added, and the mixture stirred for 2 h. Two different work-up procedures were used. For compounds which did not contain an aromatic ring, a large amount of water was added to the reaction mixture, the solid (cyanuric acid) was removed by filtration, the filtrate was then extracted with pentane, the pentane solution dried, and the product distilled. This procedure was not satisfactory for compounds with an aromatic ring. In those cases, the reaction was quenched with a small amount of water, and after filtration, most of the solvent was removed with a rotary evaporator. The residue was extracted with pentane, the pentane solution dried, and the product distilled.

Primary alcohols gave the best yields and secondary and benzyl alcohols gave lower yields of chlorides. Cyclohexanol gave a low yield of cyclohexene. The results are summarized in Table 1.

Both **1** and Ph_3P are stable and inexpensive, but when combined, they form a reactive complex capable of converting alcohols to the corresponding alkyl chlorides.

Table 1. Conversion of Alcohols into Alkyl Chlorides Using Trichloroisocyanuric Acid with Triphenylphosphine

Alcohol	Chloride	Boiling Point, °C (pres.)	Dist. Yield, %	GC Purity, %
1-Hexanol	1-Chlorohexane	133.4–134.3	62	97.8
1-Octanol	1-Chlorooctane	180.7–181.4	65	99.1
1-Decanol	1-Chlorodecane	92.0–93.4 (10 torr)	74	99.4
2-Octanol	2-Chlorooctane	168.2–171.8	52	96.7[a]
Cyclopentanol	Chlorocyclopentane	110.8–112.0	29	93.5[b]
Cyclohexanol	[Cyclohexene]	81.1–81.3	19	92.3[c]
Cycloheptanol	Chlorocycloheptane	171.5–172.0	47	88.1[d]
Benzyl alcohol	Benzyl chloride	72.8–73.2 (23 torr)	55	99.3
3-Phenyl-1-propanol	1-Chloro-3-phenylpropane	85.8–88.1 (10 torr)	70	99.7
Cinnamyl alcohol	Cinnamyl chloride	107.3–109.0 (10 torr)	27	94.3[e]
4-Methoxybenzyl alcohol	4-Methoxybenzylchloride	100.8–103.0 (10 torr)	17	dec.[f]

[a] Contains 1.5% 2-octene by GC; [b] Contains 4.1% pentane by GC; [c] Contains 6.9% pentane by GC; [d] Contains 10.6% of an unidentified compound; [e] Contains 2.6% of an unidentified compound; [f] Sample appeared to decompose on GC.

EXPERIMENTAL

All alcohols were of 97% or greater purity and were used as received except for benzyl alcohol and cyclohexanol which were distilled before use. Alkyl chloride and alkene standards were commercially available except for 2-chlorooctane which was prepared from 2-octanol using thionyl chloride. Anhydrous acetonitrile was used for all reactions and was obtained from Aldrich. Trichloroisocyanuric acid (**1**) (99% pure) was obtained from Chem Lab Products. Pentane was distilled prior to use. IR spectra were recorded using a Perkin Elmer 1650 FT-IR spectrometer. NMR were recorded using a Bruker AC-200 spectrometer. GC analyses were performed with a Hewlett Packard 5890 Series II instrument with a 6 ft. by 1/8 in. 10% Carbowax 20 M column. All reaction products were compared with standards by means of IR, NMR, and GC.

Preparation of 1-Chlorodecane

To a 300-mL three-neck round-bottom flask were added a magnetic stir bar, a reflux condenser, and 100 mL acetonitrile by syringe. Ph_3P, 19.88 g (75.79 mmol), was added through a funnel, and 10 mL of acetonitrile was used to rinse the funnel. While stirring, 6.17 g (26.55 mmol) of **1** was added over about a 10 min period through a funnel and then 10 mL of acetonitrile was used to rinse the funnel. The flask was placed in a 60°C oil bath, 7.98 g (50.41 mole) of 1-decanol was added to the mixture by syringe, and the reaction was stirred for 2 h. Then 30 mL water was added, the mixture filtered, and the solid washed with pentane. The filtrate was transferred to a separatory funnel and extracted with pentane (60 mL and 3 × 40 mL). The combined pentane solution was washed with sat. NaCl solution (50 mL) and dried over $MgSO_4$. After filtration and removal of the pentane, the residue was distilled to give 6.61 g (74%, 99.4% pure) of 1-chlorodecane. The GC retention time and the IR and NMR spectra were identical to those of the standard.

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