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Triphosgene/ Triphenylphosphine: A Mild Reagent for the Conversion of Alcohols to Chlorides

I. A. Rivero^a, R. Somanathan^a & L. H. Hellberg^a ^a Centro de Graduados e Investigacion del Instituto Tecnológico de Tijuana, Apdo. Postal 1166, 22000, Tijuana, B. C., Mexico Version of record first published: 27 Oct 2006.

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TRIPHOSGENE/TRIPHENYLPHOSPHINE: A MILD REAGENT FOR THE CONVERSION OF ALCOHOLS TO CHLORIDES.

I.A. Rivero, R. Somanathan* and L.H. Hellberg.

Centro de Graduados e investigacion del instituto Tecnológico de Tijuana, Apdo. Postal 1166, 22000 Tijuana, B.C. Mexico.

Abstract: A mixture of triphosgene/ triphenylphosphine in methylene chloride converts primary and secondary alcohols to chlorides at room temperature.

Numerous methods have been developed for the conversion of chlorides¹; Ph_P/CCl_2 alcohols to alkyl of these and Ph_P/hexachioroacetone³ have proven to be useful synthetic reagents due to the mild reaction conditions and for the regioselectivity in the conversion of allylic alcohols to chlorides. Recently we have shown that triphosgene, a solid phosgene equivalent (Aldrich Chemical Co.) plus DMSO can be used to oxidize primary and secondary alcohols to carbonyl compounds⁴. Here we wish to report another useful application of this reagent in converting primary and alcohols chlorides secondary to in the presence of triphenylphosphine (Table). Triphosgene (1 equivalent) was added to a solution of triphenylphosphine (3 equivalents) dissolved in methylene chloride at 0^{0} C.(at RT $Ph_{q}P$ reacts vigorously with triphosgene with the evolution of phosgene gas). To this stirred solution was added the alcohol, dissolved in methylene chloride. After stirring at ambient temperature for 20 min., flash

* To whom correspondence should be addressed.

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Alcohol Product		Yield(%)	
4-Methoxybenzyl alcohol	4-Methoxybenzyl chiloride	96	
Cinnamyi alcohol	Cinnamyi Chioride	98	
Sec-phenethy lalcohol	Sec-phenethyl Chloride	85	
Benzyl alcohol	Benzyl Chloride	95	
Allyl alcohol	Ally! Chloride	94	
2-Methy1-2-propen-1-01	3-Chloro-2-methylpropen	97	
Propargy1 alcoho1	Propargyl Chloride	96	
1-Pentanol	1-Chloropentane	98	
1-Octanol	1-Chlorooctane	98	
3-Pentanol	3-Chloropentane	91	
5-Nonano I	5-Chlorononane	92	
2-Methy I-2-propano I	2-Chloro-2-methylpropane	89	
2-Hethy 1-2-butanol	2-Choro-2-methy ibutane	90	

TABLE .	Chlor	inat ion	of	Alcohols
INDLL.	011101	IL ALCION I		A100 N 10

distillation of the reaction mixture gave the desired chloride in excellent yield.

In the case of low bolling chlorides, chlorobenzene was used as the solvent, thus eliminating any solvent contamination of the product as encountered in the case of CCl_4/Ph_3P reaction. It is reported that chloroformate esters react with Ph_3P to give the corresponding chloride⁵, at elevated temperatures (>100⁰C'). This intermediate in our reaction was ruled out based on the fact the reaction proceeds at RT and goes to completion in 20 min.. The reactive intermediates in this reaction are probably similar to those seen in the hexachloroacetone/Ph_3P reaction^{3,6} (Eqn.).



Experimental. Infrared spectra were recorded on a Perkin-Elmer FT-IR 1750 spectrophotometer. The proton nuclear magnetic resonance spectra were recorded on a Chemagnetic 200 MHz and Varian EM-390 90 MHz spectrometer. Mass spectra were obtained on a Finnigan 3000 GC-MS at 70 ev., using SPB-1 capillary column and data processed using the Teknivent system. Products were compared with authentic samples prepared from alcohols using SOCI₂.

GENERAL METHOD FOR CHLORINATION

To a stirred solution of triphenylphosphine (1.67g, 6.37 mmol)in dry methylene chloride (25 mL) at 0° C, triphosgene (0.686 g, 2.45 mmol) was added portion wise over a period of 5 min. After vigorous gas evolution had subsided the mixture was stirred for an additional 5 min. The solvent was removed under reduced pressure, and to the residue was added 4-methoxybenzyl alcohol (0.8 g, 5.79 mmol) in dry methylene chloride (10 mL) dropwise. The mixture was stirred for 20 min. at RT.

The solvent was removed under reduced pressure and the residue was extracted with pentane (2x25mL). The organic phase was dried over Na_2SO_4 and subjected to bulb to bulb distillation using a Buchi GKR-51 oven to give the chioride (0.868 g, 96%). IR (Liquid film): 1600, 1250, 1034, 832, 731, 666 cm⁻¹. ¹H-NMR (CDCl₃): δ 7.30 (d, J=8.6 Hz, 2H, Ar-H), 6.87 (d, J=8.6 Hz, 2H, Ar-H), 4.56 (s, 2H, CH₂), 3.79 (s, 3H, OCH₂). MS: m/e 156 (M⁺, 36%), 121 (100%).

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