CHEMISTRY LETTERS, pp. 1173 - 1174, 1984.

A CONVENIENT METHOD FOR THE TRANSFORMATION OF ALCOHOLS TO ALKYL CHLORIDES USING N,N-DIPHENYLCHLOROPHENYLMETHYLENIMINIUM CHLORIDE

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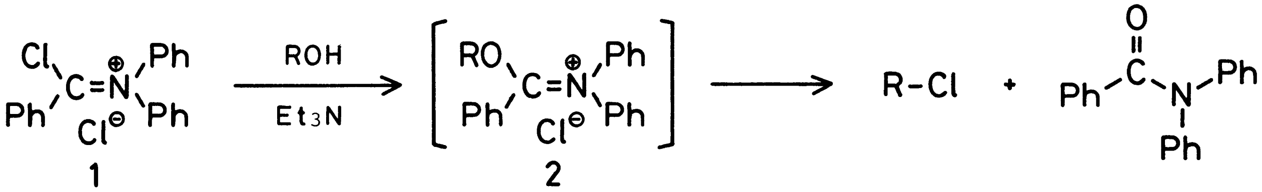
N,*N*-Diphenylchlorophenylmethyleniminium chloride reacts smoothly with a variety of alcohols in the presence of triethylamine to afford the corresponding alkyl chlorides in high yields. Replacement of a hydroxyl group at an asymmetric carbon atom with chlorine proceeds with complete inversion.

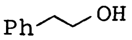
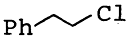
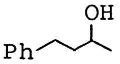
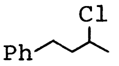
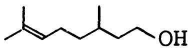
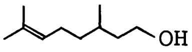
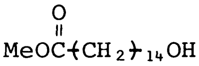
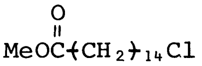
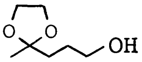
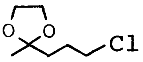
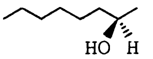
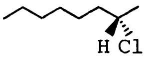
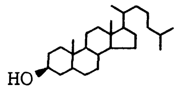
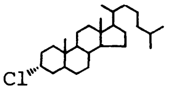
Conversion of alcohols into alkyl chlorides is one of the important processes in organic synthesis. Recently iminium salts have been shown to replace the hydroxyl groups of alcohols by chlorine.[1,2] These methods, however, suffer some disadvantages with respect to reaction conditions, yields or applicability. We wish to report here that *N*,*N*-diphenylchlorophenylmethyleniminium chloride (1), prepared easily from *N*,*N*-diphenylbenzamide and oxalyl chloride,[3] reacted smoothly with various kinds of alcohols in the presence of triethylamine under mild conditions to give the corresponding chlorides in high yields.



A typical procedure for the preparation of alkyl chlorides is as follows. To a stirred solution of *N*,*N*-diphenylchlorophenylmethyleniminium chloride (1) (1.2 mmol) in dichloromethane (5 ml) was added a mixture of 3β-cholestanol (1.0 mmol) and triethylamine (1.4 mmol) in dichloromethane (3 ml) at room temperature under an argon atomosphere and the resulting mixture was stirred at the same temperature for additional 3 h. The reaction mixture was then quenched with water, and the organic layer was extracted with dichloromethane and dried over anhydrous magnesium sulfate. After removal of the solvent, the residue was washed with hexane. *N*,*N*-Diphenylbenzamide was recovered quantitatively by washing the resulting white precipitate with water. The hexane solution was chromatographed on silica gel eluting with hexane to give 3α-chlorocholestane in 85% yield, mp 105-106 °C (lit.[4] mp 105 °C).

As shown in Table 1, acyclic primary and secondary alcohols were converted to the corresponding chlorides in high yields (entries 1,2, and 3). In contrast to the result using *N*,*N*-dimethylchloromethyleniminium salt,[1b] the present method could convert an alicyclic alcohol, 3β-cholestanol into the desired chloride in a high yield without accompanying a dehydration product. Moreover, the reaction of 3β-cholestanol or (*R*)-(-)-2-octanol proceeded with complete inversion of

Table 1. Synthesis of Alkyl Chlorides

Entry	Alcohol	Chloride[a]	Yield/%
1	n-$C_{11}H_{23}OH$	n-$C_{11}H_{23}Cl$	96
2			92
3			93
4			84
5	 $MeOC(=O)\text{-}(CH_2)_{14}OH$	 $MeOC(=O)\text{-}(CH_2)_{14}Cl$	88
6			78
7	 b)	 c)	77
8			85

a) These products were identified by NMR, IR, and in some cases, by physical constants (melting point or optical rotation). b) $[\alpha]_D^{23}$ -9.62° (lit,[5] $[\alpha]_D^{21}$ -10.1°). c) $[\alpha]_D^{23}$ +36.02° (lit,[6] $[\alpha]_D^{20}$ +36.2°).

configuration at the asymmetric carbon (entries 7 and 8). The reaction may be explained by assuming the initial formation of *N*,*N*-diphenylalkoxyphenylmethyleniminium salt (2), which in turn reacts with chloride ion through S_N2 type process to afford alkyl chloride and *N*,*N*-diphenylbenzamide.

The utility of the present method was further demonstrated in effective conversion of several alcohols possessing acid-labile functional groups into the corresponding chlorides. When citronellol, methyl 15-hydroxypentadecanoate and 4,4-ethylenedioxypentan-1-ol were treated with 1 in the presence of triethylamine, the desired chlorides were obtained in high yields without any damage of carbon-carbon double bond, ester, and acetal functions, respectively (entries 4,5, and 6).

Thus, the present method using *N*,*N*-diphenylchlorophenylmethyleniminium salt (1) possesses several advantages over conventional ones in respects of 1) high yield, 2) mild and slightly basic reaction conditions, and 3) high stereospecificity by S_N2 type reaction.[7]

References

1) H. Eilingsfeld, M. Seefelder, and H. Weidinger, *Angew. Chem.*, 72, 836 (1960); D. R. Hepburn and H. R. Hudson, *J. Chem. Soc., Perkin Trans. 1*, 1976, 754; M. Yoshihara, T. Eda, K. Sakaki, and T. Maeshima, *Synthesis*, 1980, 746.
2) For a related method using benzoxazolium salts, see T. Mukaiyama, *Angew. Chem., Int. Ed. Engl.*, 18, 707 (1979).
3) Iminium salt 1 was prepared by treatment of *N*,*N*-diphenylbenzamide with 4 equivalents of oxalyl chloride in dichloroethane at 60 °C for 12 h. Evaporation of the solvent and excess oxalyl chloride gave a yellow solid, which was used without purification.
4) C. W. Shoppee and J. C. Coll, *J. Chem. Soc., Chem. Commun.*, 1970, 1124.
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7) This work was partially assisted by the Asahi Glass Foundation.

(Received April 27, 1984)