

A Simple, Mild Elimination of Hydrogen Halide from Primary Alkyl Bromides and Iodides

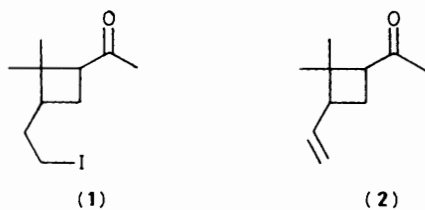
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Addition of a solution of a primary alkyl bromide or iodide and 1,8-diazabicyclo[5.4.0]undec-7-ene in tetrahydrofuran (THF) to a solution prepared from dichlorobis(triphenylphosphine)nickel, triphenylphosphine, and *n*-butyl-lithium in THF results in an elimination at room temperature to give, in most cases, the terminal alkene.

The base-mediated elimination of hydrogen halide from a primary alkyl halide to give the terminal alkene is reported to be a difficult and inefficient reaction.¹ A common side reaction at the temperatures usually used in this procedure (80–100 °C) is the formation of a quaternary ammonium salt by nucleophilic attack of the nitrogenous base on the unhindered halide.² The room temperature decomposition of aryl selenoxides is also unsatisfactory for the synthesis of terminal alkenes unless the *o*-nitro or *p*-chloro derivatives are used.³ In this report we describe a method for carrying out this elimination which compares favourably in its mildness with the selenoxide method but which has the advantages of using readily available, cheap materials, is compatible with a range of common functional groups, and gives clean products.

If a suspension of dichlorobis(triphenylphosphine)nickel (1 equiv.) and triphenylphosphine (2 equiv.) in dry, degassed tetrahydrofuran (THF) is treated with a solution of *n*-butyl-lithium (2 equiv.) in hexane under argon, an evolution of gas occurs and a dark brown solution results. A solution of the alkyl halide (1 equiv.) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (2 equiv.) in dry THF is added by syringe and the mixture is stirred at room temperature overnight. Removal of the solvent on a rotary evaporator, trituration of the residue with light petroleum (or diethyl ether, depending on the solubility of the alkene produced), and chromatography of the tritrate on silica gel produces the alkene.

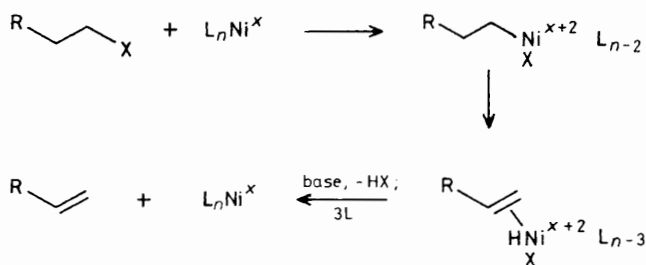


The examples given in Table 1 show that: (i) the method proceeds without difficulty in the presence of benzyl ether, ketone, ester, and hydroxy groups, (ii) a bromotetrahydro-

Table 1.

RX	Yield of alkene (%)
PhCH ₂ O(CH ₂) ₄ I	56
PhCH ₂ O(CH ₂) ₄ Br	68
PhCH ₂ O(CH ₂) ₄ Cl	0 ^a
THPO(CH ₂) ₆ Br	12 ^b
Me(CH ₂) ₁₅ Br	77 ^c
MeC(O)(CH ₂) ₃ I	49 ^{d,e}
EtOC(O)(CH ₂) ₃ Br	77 ^{e,f}
(1)	50 ^{e,g}
HO(CH ₂) ₁₁ Br	82 ^h

^a Starting material recovered (100%). ^b Plus recovered starting material (80%). ^c Plus a mixture of internal alkenes (20%). ^d Product is *trans*-pent-2-en-3-one. ^e Some loss of product occurs owing to volatility. ^f Product is ethyl *trans*-but-2-enoate. ^g Product is the terminal alkene, (2). ^h Plus a mixture of internal alkenes (14%).



pyranyl (THP) ether proved more resistant to elimination, (iii) alkyl chlorides appear to be unreactive, (iv) in suitable cases conjugation of the resultant double bond occurs, and (v) only in two cases of long chain alkyl halides have we observed some random migration of the double bond.

Additionally it should be noted that (a) carboxylic acids prevent the reaction, (b) DBU is the most efficient of a number of bases tried, and (c) bromides on the whole are the better halides to choose since we have found them less prone to react with DBU to give an unproductive quaternary ammonium salt.

This elimination procedure was devised on the premise that oxidative addition of a primary alkyl halide to a low valent nickel complex followed by β -elimination would both be ready processes (Scheme 1).

Our results suggest that the situation is more complicated than this and we are currently attempting to identify the

intermediates in the reaction and to make the reaction catalytic in nickel complex.

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References

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 - 2 If the primary halide has a 2-alkyl side chain, nucleophilic attack by DBU becomes prohibited and elimination proceeds well, see S. Wolff, M. E. Huecas, and W. L. Agosta, *J. Org. Chem.*, 1982, **47**, 4358.
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