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A CONVENIENT PREPARATION OF TRANS (OR CIS)-1-CHLOROALKENES FROM TRANS (OR CIS)-1,2-DICHLOROETHYLENE : A NEW SYNTHESIS OF THE SEX PHEROMONE OF LOBESIA BOTRANA.

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Abstract : Trans (or cis)-dichloroethylene leads to trans (or cis)-1-chloroalkenes when treated with Grignard reagents and to trans (or cis)-1-chloro-1-en-3-ynes when treated with terminal acetylenes. A simple synthesis of (7E, 9Z)-dodecadien-1-yl acetate has been realized .

Halogenoalkenes are useful precursors for the synthesis of olefins and several methods for their preparations have been described [1].

We now report a simple synthesis of 1-chloroalkenes from the commercially available trans and cis 1,2-dichloroethylenes which proceeds with high stereospecificity [2].

Thus, when treated with n-octyl magnesium chloride (1 equiv.) and 0.01 equiv. of tetrakis (triphenylphosphine)nickel [3] in ether : benzene (80 : 20) 30 mn at 10°C followed by 2.5 h at room temperature, (E)-1,2-dichloroethylene (5 equiv.) gave (E)-1-chlorodecene 3a(⩾99% isomeric purity) in 72% yield [4].

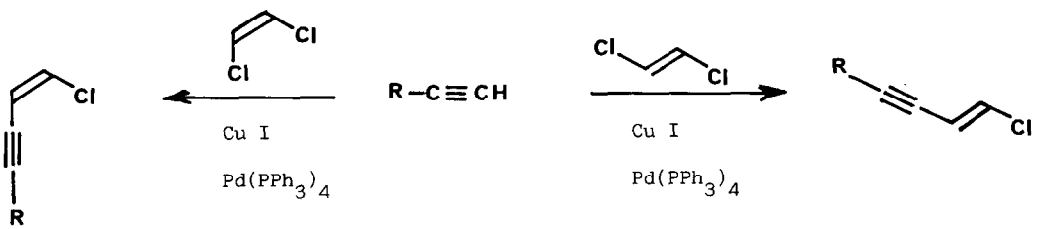
Under the same conditions, (Z)-1,2-dichloroethylene [5] gave (Z)-1-chlorodecene 1a (⩾96% isomeric purity) in 65% yield.

1 2 3

	R	yield (%) of 1	3
a	$n\text{-}C_8H_{17}$	65	72
b	$C_6H_5(CH_2)_3$	60	68

Dichloroethylenes are also efficient precursors for the preparation of chloroenynes :

Thus, when treated in benzene with terminal acetylenes 5 (1 equiv.), in the presence of tetrakis(triphenylphosphine)palladium (5%), copper iodide (5%) and n-butylamine (1.5 equiv.) [6] for 5 h at room temperature, Z (or E)-1,2-dichloroethylene (5 equiv.) gives 1-chloro-1-en-3-ynes 4 (or 6) [4] (> 99% isomeric purity) in high yield.

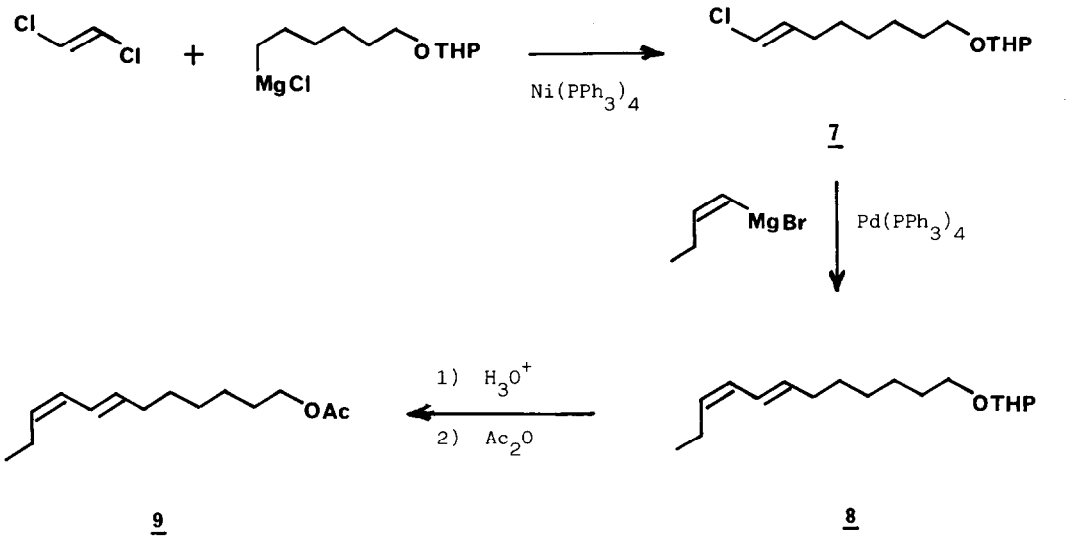


4 5 6

R	yield (%) of 4	6
$n\text{-}C_5H_{11}$	95	98
CH_2OTHP	95	95
CH_2OAc	72	65
CH_2SCH_3	95	100

The new procedure reported here has been applied to an efficient synthesis of the sex pheromone of Lobesia botrana which is a major pest of vineyards [7] :

Reaction of the Grignard reagent of 6-chloro-1-hexanol pyrannyl ether (1 equiv.) with (E)-1,2-dichloroethylene (5 equiv.) for 2 hr at room temperature in ether : benzene under nickel-catalyzed conditions led to the chloride 7 (33%). Treatment of 7 (1 equiv.) with (Z)-butenylmagnesium bromide (1.2 equiv.) and a catalytic amount of tetrakis (triphenylphosphine) palladium [8] gave the diene 8 (96 % isomeric purity) in 96% yield. Hydrolysis with "Amberlite" resin (IR 120) and acetylation gave the pheromone 9 in 95 % yield.



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Notes and References.

1) For syntheses of vinylchlorides, see : G. ZWEIFEL, W. LEWIS, H.P. ON, J. Amer. Chem Soc., 101, 5101 (1979) ; V. REUTRAKUL and P. THAMNUSAN, Tetrahedron Lett., 617(1979) and references therein.

2) The nickel-catalyzed reaction of 1,2-dichloroethylene with Grignard reagents to give 1,2-substituted ethylenes has been previously reported :
a) R.J.P. CORRIU and J.P. MASSE, J. Chem. Soc., Chem. Comm., 144 (1972) ;
b) K. TAMAO, K. SUMITANI, M. KUMADA, J. Amer. Chem. Soc., 94, 4374 (1972) ;
c) K. TAMAO, M. ZEMBAYASHI, Y. KISO and M. KUMADA, J. Organomet. Chem. 55, C91(1973)

3) Prepared in situ according to : J.F. FAUVARQUE and A. JUTAND, J. Organomet. Chem., 177, 273 (1979).

4) The products were purified by chromatography on silica gel (elution with pentane for the chlorides 1 and 3, with a mixture of pentane : ether (80 : 20) for the chlorides 4 and 6). All new compounds exhibited satisfactory spectral and physical properties.

5) The authors thank Dr. D. DAUZONE for gas chromatography analyses.

6) K. SONOGASHIRA, Y. TOHDA and N. HAGIHARA, Tetrahedron Lett., 4467 (1975).

7) For a recent synthesis of 9, see : G. DRESSAIRE and Y. LANGLOIS, Tetrahedron Lett., 67 (1980) and references there in.

8) H.P. DANG and G. LINSTRUMELLE, Tetrahedron Lett., 191 (1978).

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