Carbon–Carbon Bond Formation in the Dichlorobis(triphenylphosphine)nickel-catalysed Reaction between Grignard Reagents and Allylic Alcohols

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IN the presence of catalytic amounts of dichlorobis(triphenylphosphine)nickel,[1] the reaction between allylic alcohols (I) and an excess of n-propylmagnesium bromide leads to propene and a mixture of olefins (II) and (III).[2] We now report that the reaction of Grignard reagents RMgBr having

$$\underset{\text{(I)}}{R^1CH{=}CH{-}CHOHR^2} + Me{-}CH_2CH_2MgBr \xrightarrow{(PPh_3)_2NiCl_2} MeCH{=}CH_2 + \underset{\text{(II)}}{R^1{-}CH{=}CH{-}CH_2{-}R^2} + \underset{\text{(III)}}{R^1CH_2{-}CH{=}CHR^2}$$

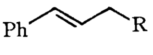
no β-hydrogen (R = Me, Ph, $PhCH_2$) with allylic alcohols (I), using the same catalyst, leads to olefins (IV) and (V) incorporating the entire R-group.

$$\text{(I)} + RMgBr \xrightarrow{(PPh_3)_2NiCl_2} \underset{\text{(IV)}}{R^1CH{=}CH{-}CHRR^2} + \underset{\text{(V)}}{R^1RCH{-}CH{=}CHR^2}$$

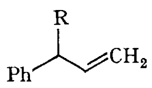
Grignard reagent (4 mol.) in ether was added to dichlorobis(triphenylphosphine)nickel (0·1 mol.); to the resulting red-brown solution the alcohol (I) (1 mole) was added, and the mixture was refluxed (1—120 hr.). The olefins (IV) and (V) either distilled out with the ether (C_4 and C_5 olefins), or isolated in the usual way. The yields were generally high.†

Under these conditions, allyl alcohol afforded but-1-ene (91%) with methylmagnesium bromide (1 hr. reflux), allyl benzene (68%) (uncontaminated with propenyl benzene) with phenylmagnesium bromide (1 hr.), and 4-phenyl-but-1-ene (90%) with benzylmagnesium bromide (72 hr.).

Both cinnamyl alcohol (VI) and α-phenylallyl alcohol (VII) with methylmagnesium bromide afforded the conjugated olefin (VIII) exclusively, no terminal olefin (IX) being formed. The yields were 81% and 75% respectively, after 2—3 hr. under reflux. With but-2-enol and α-methylallyl alcohol, however, the major product was the terminal olefin (X). From *trans*-but-2-enol the yield after 4 hr. under reflux was 87%, and the (X) : (XI) ratio was 51 : 49. The corresponding figures for α-methylallyl alcohol were 82% and 71 : 29; and 1·6% of *cis*-pent-2-ene was also formed.



(VI) R=OH
(VIII) R=Me



(VII) R=OH
(IX) R=Me

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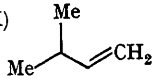
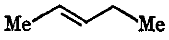
† All the olefins formed [except (XIV)] were shown to be identical with authentic samples. Gas chromatography was used to determine the proportions of isomeric olefins in all cases, and also the overall yields in the case of the C_4 and C_5 olefins.

These results are in sharp contrast to those obtained in the reactions between the same alcohols and *n*-propylmagnesium bromide,[2] which afforded, in both cases, only minor amounts of terminal olefin (but-1-ene), and, in the case of α-methylallyl alcohol, a considerable quantity of *cis*-but-2-ene.

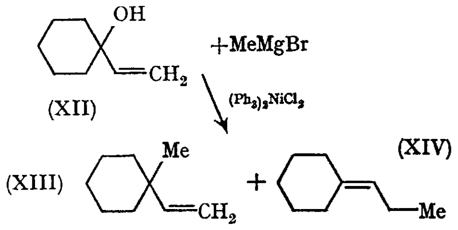
(X)



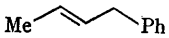
(XI)



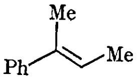
The propensity to form a terminal olefin is even more marked in the case of the disubstituted alcohol (XII) which led (in a much slower reaction) to a 78 : 22 mixture of the olefins (XIII) and XIV).



In only one case was there a side reaction: α-methylallyl alcohol and phenylmagnesium bromide gave only 25% of a mixture of the expected olefins [(IX) and (XV)] and 39% of γ-phenyl-α-methylallyl alcohol. *trans*-But-2-enol, however, gave a 77% yield of the olefins (IX) and (XV) (36 : 64). The corresponding conjugated olefins [(VIII) and (XVI)] were not formed in either case.



(XV)



(XVI)

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[1] L. M. Venanzi, *J. Chem. Soc.*, 1958, 719.

[2] H. Felkin and G. Swierczewski, *Compt. rend.*, 1968, **266**, *C*, 1611.