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STEREOCHEMICAL AND MECHANISTIC ASPECTS OF THE NICKEL COMPLEX CATALYSED FORMATION OF OLEFINS FROM ALLYLIC ALCOHOLS AND GRIGNARD REAGENTS

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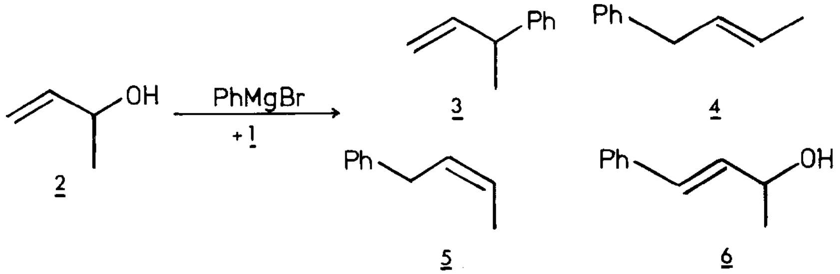
Abstract: The reaction of (+)-S-but-1-en-3-ol with phenylmagnesium bromide in the presence of bis(triphenylphosphine)nickel dichloride has been shown to proceed with inversion of configuration to yield (-)-R-3-phenylbut-1-ene.

We have previously shown that in the reaction of allylic alcohols with non-reducing Grignard reagents (i.e. those that do not bear a labile β-hydrogen), in the presence of bis(triphenylphosphine)nickel dichloride catalyst, substitution of the hydroxyl function by alkyl or aryl occurs.[1] The proposed mechanism for the nickel complex catalysed reaction of Grignard reagents with allyl alcohols is illustrated in figure 1. We have already demonstrated that the reaction proceeds exclusively through (η^3-allyl)nickel intermediates[2] and we report here evidence for another feature of this mechanism, namely that inversion of configuration at the carbon bearing the hydroxyl function occurs.

In the presence of the nickel complex (Ph$_3$P)$_2$NiCl$_2$ 1, racemic but-1-en-3-ol 2 reacts with PhMgBr to give a mixture of olefins 3, 4 and 5 in the ratio 44 : 40 : 16 respectively together with the alcohol 6.[2]



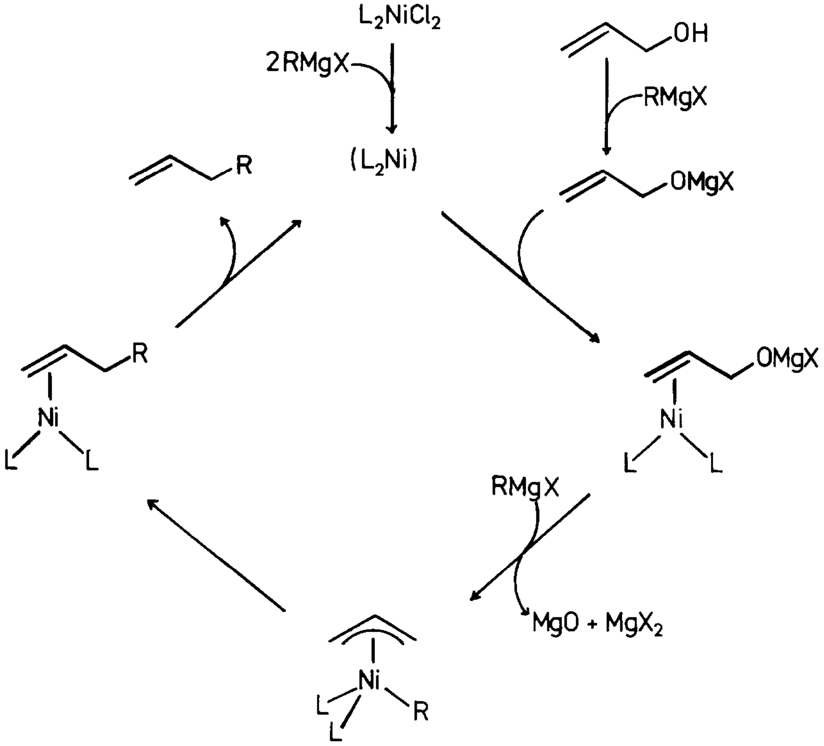


Figure 1. Mechanism of the L$_2$NiCl$_2$ catalysed formation of olefins from allylic alcohols and Grignard reagents. (L=tertiary phosphine).

The reaction of (+)-but-1-en-3-ol (12.5 mmole; 94% optical purity) with phenylmagnesium bromide (50 mmole; 1.44M in Et$_2$O) in the presence of 1 (1.25 mmole) gave, after 16h reflux, 42% of the olefins 3, 4 and 5 in the ratio 48 : 34 : 18. (-)-R-3-Phenylbut-1-ene,(-)-R-3, (9.2%, $[\alpha]_D^{25}$ = -1.47^{o} neat) was isolated by preparative g.l.c.[3] The reaction has therefore occurred with predominant (24.6%) inversion of configuration.[4]

Isolation of optically active 3 shows that the η^3-η^1(primary alkyl)-η^3 interconversions shown in figure 2 are not fast enough to lead to complete racemisation.[5] These reactions are, however, faster than the corresponding η^3-η^1(secondary alkyl)-η^3 interconversions since the amount of racemisation ($\sim$75%) is greater than the amount of syn-anti interconversion (<7%).[2,6] By analogy with the chemistry of other transition metal systems[7] the overall inversion of configuration clearly arises from inversion of configuration during formation of the (η^3-allyl)nickel complex followed by retention of configuration during the coupling reaction (figure 2).

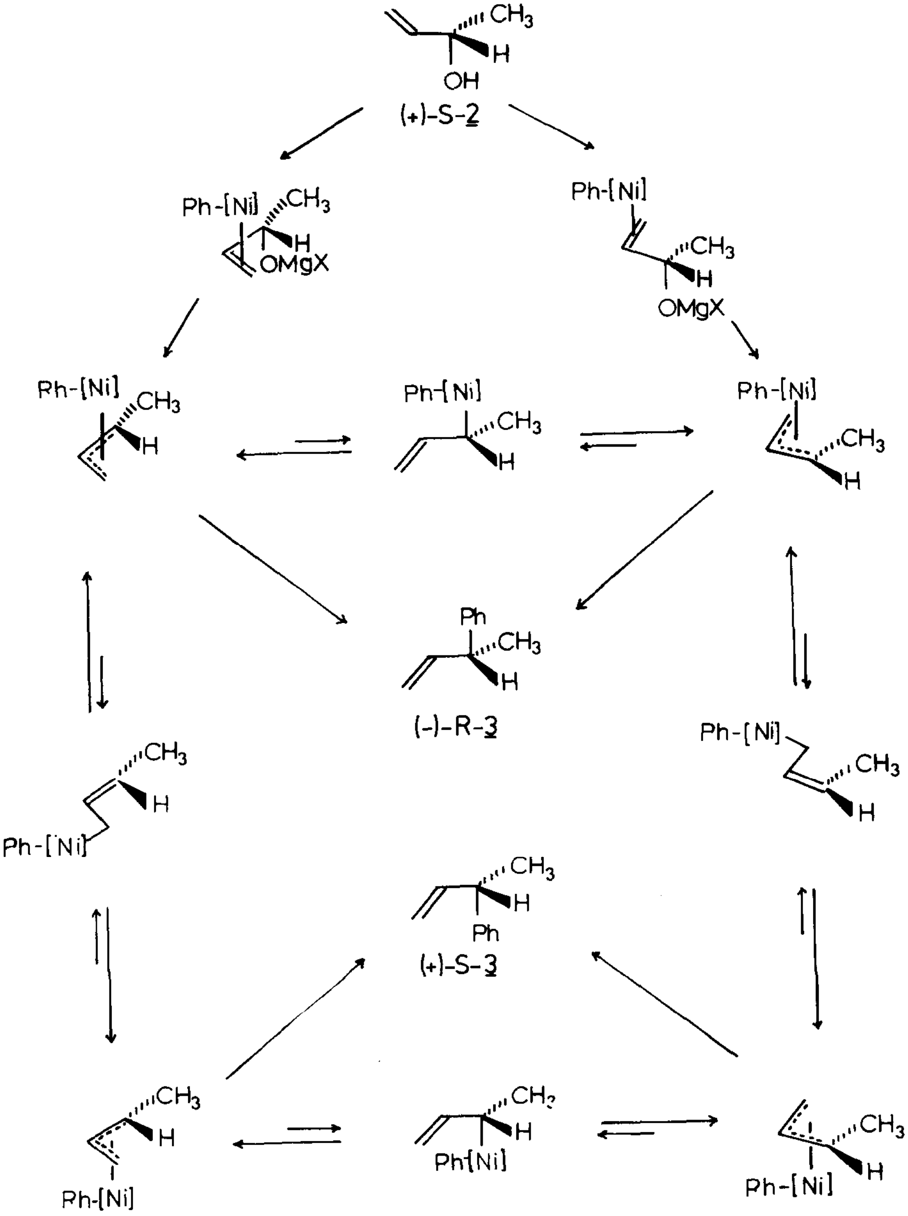
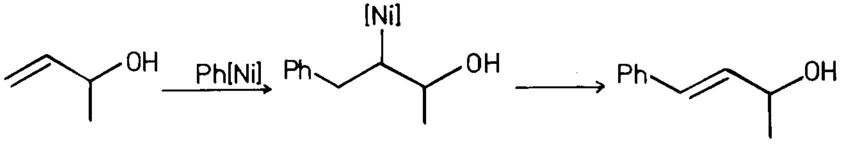


Figure 2. Formation of (-)-R-3-phenylbut-l-ene from (+)-S-but-l-en-3-ol and the mechanism of racemisation.

The alcohol 6, formed in 25% yield, is presumably produced by a reaction analogous to the Heck reaction catalysed by palladium complexes.[8]



2 6

In the formation of 6 the asymmetric centre of the alcohol 2 is not involved and therefore 6 must possess the same configuration as (+)-S-but-1-en-3-ol. The rotation of 6 after recrystallisation is $[\alpha]_D^{22} = -34.8^{\circ}$ (C=5, $CHCl_3$ containing 0.5% EtOH).[9]

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