Nickel Complex-catalysed Reaction of Propylmagnesium Bromide with Butadiene. A Highly Stereoselective Synthesis of *cis*- and *trans*-(2-Vinylcyclopentyl)methylmagnesium Bromide

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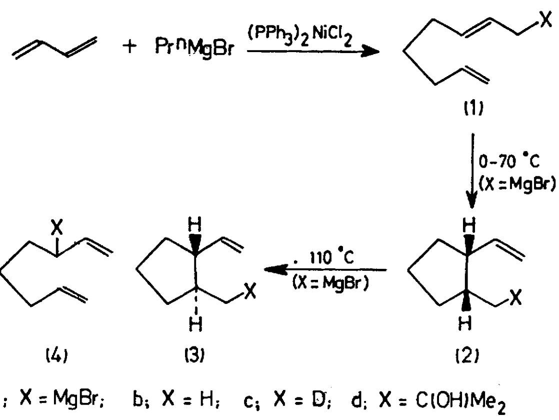
Summary Propylmagnesium bromide, butadiene, and catalytic amounts of [$(PPh_3)_2NiCl_2$] afford octa-2,7-dienylmagnesium bromide; this cyclises to *cis*-(2-vinylcyclopentyl)methylmagnesium bromide, which can be thermally epimerised to the *trans* isomer.

A number of nickel complex-catalysed telomerisations of butadiene with alcohols,[1] amines,[2] and active methylene compounds,[3] leading to 1-substituted octa-2,7-dienes (**1**) (X = OR, NR_2, or CHYZ) as the major products, have recently been described.

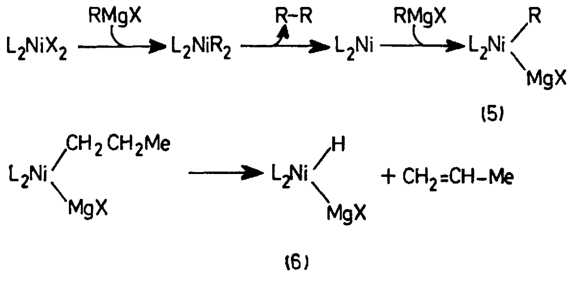
Here we report what is formally a telomerisation of butadiene with 'HMgBr': the formation of octa-2,7-dienylmagnesium bromide (**1a**) (and propene) from butadiene and n-propylmagnesium bromide in the presence of catalytic amounts of [$(PPh_3)_2NiCl_2$]. The open-chain Grignard reagent (**1a**) is unstable and smoothly cyclises[4] at room temperature to *cis*-(2-vinylcyclopentyl)methylmagnesium bromide (**2a**), and we have found that the latter can be epimerised to the more stable *trans* isomer (**3a**) (Scheme 1). Thus, bifunctional cyclopentane derivatives (**2**) and (**3**) may be prepared in a 'one-pot' reaction from butadiene with stereochemical purities which exceed 99% for the less stable *cis*-isomers (**2**) and 90% for the *trans*-isomers (**3**). Although a vast amount of work has been done on the reactions of butadiene with low-valent nickel species,[5] in only one other well authenticated case has a five-membered ring compound (2-methylenevinylcyclopentane)[6] been obtained.

[$(PPh_3)_2NiCl_2$] (5 mmol), butadiene (230 mmol), and Pr^nMgBr (1·9M; 250 mmol) in ether were mixed, in that order, at −78 °C, and allowed to warm to 0 °C with stirring. Hydrolysis of an aliquot portion of the orange solution after 18 h showed[†] that 41% of the butadiene had been converted into the open-chain Grignard reagent (**1a**), with almost no cyclisation to the *cis*-Grignard reagent (**2a**), and treatment of the solution with acetone gave the expected alcohol (**4d**).[‡] After 6 days at 0 °C, all the butadiene had been consumed and the solution contained approximately equal amounts of the uncyclised (**1a**) and cyclised (**2a**) Grignard reagents.



Scheme 1

When the reaction was carried out at reflux (room temperature, solid CO_2 condenser), no butadiene and very little uncyclised Grignard reagent (**1a**) remained after 24 h. Hydrolysis gave *cis*-2-methylvinylcyclopentane (**2b**)[4][‡] in 67% yield,[§] deuteriolysis gave the deuteriated hydrocarbon (**2c**),[‡] and treatment with acetone gave the *cis* alcohol (**2d**).[4][‡] The latter contained between 0·5 and 5% of its *trans* epimer (**3d**), depending upon the temperature (0—70 °C) at which the cyclisation of the open-chain Grignard reagent (**1a**) had been carried out. This cyclisation also occurs in the absence of nickel catalyst.[4]



Scheme 2

Heating (sealed tube; 110 °C; 24 h) a reaction mixture containing the *cis*-Grignard reagent (**2a**) gave the thermally more stable *trans*-Grignard reagent (**3a**) [(**3a**)/(**2a**) *ca.* 11]; this epimerisation probably takes place *via* the open-chain reagent (**1a**), and does not require the presence of a nickel catalyst. The *trans* compounds[‡] (**3b**), (**3c**), and (**3d**) were obtained from (**3a**) by hydrolysis, deuteriolysis, and treatment with acetone, respectively.

Various reactions of Grignard reagents are known which, like the one leading to (**1a**), only occur in the presence of catalytic amounts of phosphine nickel halides.[7] It has been suggested[8] that the activation of Grignard reagents by nickel complexes involves alkylnickelmagnesium halides (**5**), which may be formed as shown (Scheme 2). When R is propyl, β-elimination could lead to the hydride (**6**), and this may be the origin of the 'HMgX' in the telomerisation of butadiene reported here.

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[†] Analysis by g.l.c. of the hydrocarbons formed, using n-heptane as internal standard to determine the yields.

[‡] These compounds were isolated by distillation or preparative g.l.c.; their i.r., n.m.r., and, in the case of (**2c**) and (**3c**), mass spectra were consistent with the structures assigned.

[§] Small amounts (< 4%) of 4-vinylcyclohexene, cyclo-octa-1,5-diene, 2-methylenevinylcyclopentane, and octadienes [from (**1a**)] were also detected, and the total yield of C_8 hydrocarbons (including 12% of a number of other, unidentified, oligomers) was *ca.* 90%.

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