Tetrahedron Letters No. 15, pp 1433 - 1436, 1972. Pergamon Press. Printed in Great Britain.

STEREOCHEMICAL EVIDENCE IN FAVOUR OF π-ALLYLNICKEL INTERMEDIATES IN THE FORMATION OF OLEFINS FROM ALLYLIC ALCOHOLS AND GRIGNARD REAGENTS, CATALYSED BY NICKEL COMPLEXES

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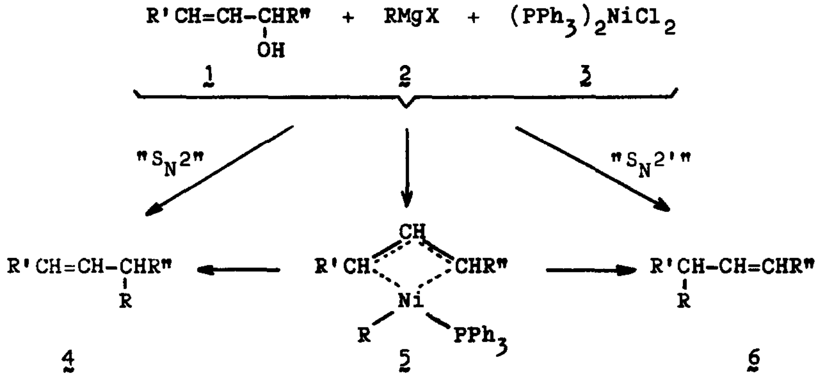
(Received in UK 14 February 1972; accepted for publication 2 March 1972)

In the presence of catalytic amounts of bis(triphenylphosphine)nickel dichloride 3, allylic alcohols 1 react with excess Grignard reagent 2 (R = Me, Ph, $PhCH_2$)[1] to form mixtures of isomeric olefins 4 and 6, generally in high

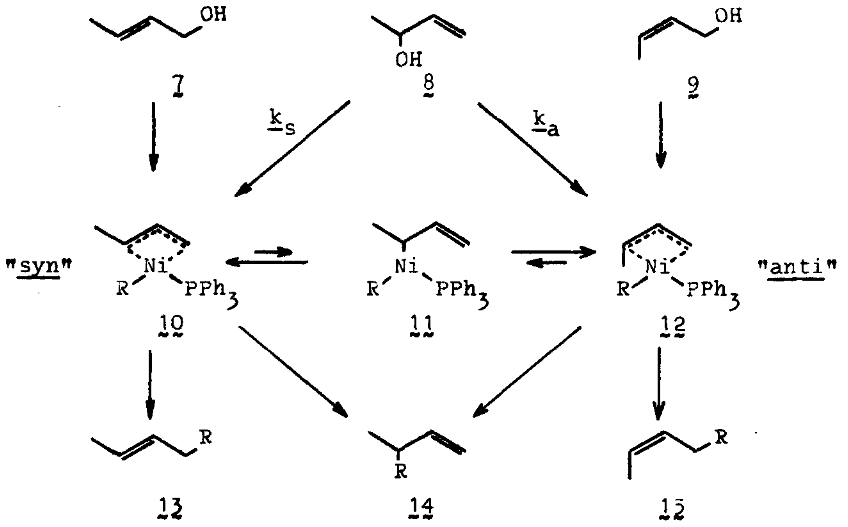


Scheme 1. The reaction between allylic alcohols and Grignard reagents, catalysed by the nickel complex 3: possible mechanisms.

yield.[2] As outlined in Scheme 1, this reaction could possibly occur either *via* π-allylnickel intermediates 5, or by a combination of "S_N2" and "S_N2'" processes, catalysed in some way by nickel (*e.g.*, *via* σ-allylnickel complexes). It is generally difficult to decide between these two possibilities in reactions such as this, in which the postulated intermediates (*e.g.*, 5) are too short-lived to be isolated. Here we report the use of a stereochemical criterion which indicates that the reaction shown in Scheme 1 occurs exclusively *via* π-allylnickel intermediates 5.

Consider this reaction in the case of the three isomeric butenols 7, 8 and

9.[3] This system involves two possible *stereoisomeric* π-allylnickel intermediates 10 and 12.[4] The *trans* alcohol 7 is expected to lead first to the "*syn*" complex 10 and the *cis* alcohol 9 to the "*anti*" complex 12; α-methylallyl alcohol 8, on the other hand, can lead to both 10 and 12, which must then each af-



		13		14		15	
		R = Me	R = Ph	R = Me	R = Ph	R = Me	R = Ph
percentage proportion of olefin formed	from 7:	54.0	65.5	46.0	34.0	0	0.5
	from 8:	29.4	39.7	68.8	44.1	1.8	16.2
	from 9:	7.4	6.6	90.2	58.6	2.4	34.8
$\underline{k}_s/\underline{k}_a$ calc.[7]:		0.90	1.3	0.94	1.4	(-)[8]	1.2

Scheme 2. Postulated stereoisomeric π-crotylnickel intermediates in *the butenol* system, with the percentage proportions of olefins (13, 14 and 15, R = Me and Ph) formed in the reactions of the butenols 7, 8 and 9 with MeMgBr and PhMgBr (catalysed by the nickel complex 3),[6] and the calculated values of the rate ratio $\underline{k}_s/\underline{k}_a$.[7]

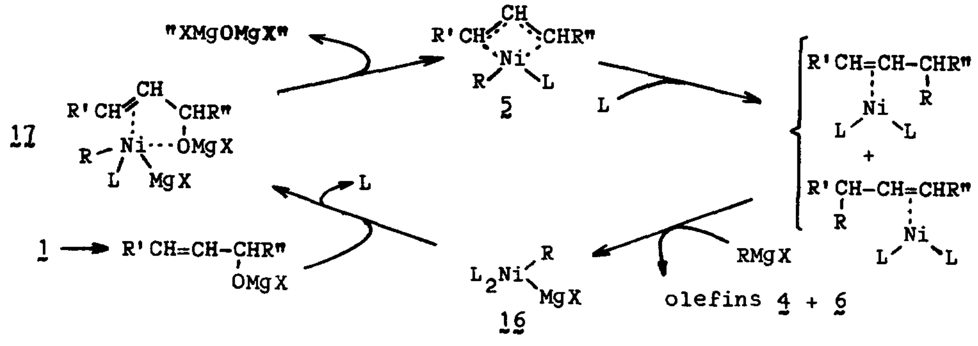
ford the *same* mixtures of olefins as are formed separately from 7 and 9, respectively. There is therefore a stereochemical corollary to the π-allyl mechanism in this system: if these reactions occur exclusively *via* the π-crotyl intermediates 10 and 12, as shown in Scheme 2, then the proportions of the three olefins (13, 14 and 15) formed from α-methylallyl alcohol 8 and a given Grignard reagent must be such that they each correspond to exactly the *same* weighted average of the proportions of the same olefins formed from the *cis* and *trans* alcohols 7 and 9, the common weighting factor being the rate ratio $\underline{k}_s/\underline{k}_a$.[5]

The proportions[6] of olefins (13, 14 and 15) formed in the reactions between the three isomeric butenols (**7**, **8** and **9**) and two Grignard reagents (MeMgBr and PhMgBr) are shown in Scheme 2, together with the weighting factors (k_s/k_a calc.)[7] calculated from them. It is apparent that these weighting factors are indeed identical, within experimental error, for all three olefins (about 0.9 with MeMgBr[8] and about 1.3 with PhMgBr). It seems quite inconceivable that such good agreement could occur fortuitously for two different Grignard reagents if these olefins were formed by a combination of "S_N2" and "S_N2'" mechanisms (Scheme 1); these data therefore constitute very strong evidence that the reactions take place *via* π-allylnickel intermediates **5**.[9]

The fact that the weighting factors (k_s/k_a calc.) are both close to unity shows that the two isomeric π-crotylnickel complexes **10** and **12** are formed at approximately equal rates from α-methylallyl alcohol **8**. Moreover, it seems that the interconversion of these intermediates (*via* **11**) occurs slowly with respect to their conversion to the products **13**,**14** and **15**. If such interconversion were rapid relative to conversion to olefin, the three isomeric alcohols **7**, **8** and **9** would all lead to the same mixture of olefins, and if there were no interconversion, the reactions would be stereospecific, *i.e.*, the *trans* alcohol **7** would lead only to **13** and **14**, and the *cis* alcohol **9** only to **14** and **15** (see Scheme 2). In fact, the situation is much closer to the second of these two extremes than to the first.

In conclusion, the stereochemical criterion outlined above indicates that the reactions discussed proceed exclusively through π-allylnickel intermediates. This criterion, which does not appear to have been employed previously, may be found useful in other systems, involving allylic intermediates, in which the same kind of mechanistic problem arises.

Addendum.- Reasons given elsewhere in this Journal[10] prompt us to outline in Scheme 3 a possible catalytic cycle for the reaction between allylic alcohols and Grignard reagents, catalysed by nickel complexes. The two key intermedia-



Scheme 3. Possible catalytic cycle involving π-allylnickel intermediates **5** (L = PPh_3, PEt_3 ; R = Me, Ph).

tes in this cycle are the π-allylnickel complex **5** and a complex **16** with a nickel-magnesium bond; the stage **17**→**5** is assumed to be rate determining. Experiments which support this scheme will be the subject of a forthcoming paper.

We thank Drs J.K.Crandall and M.L.H.Green for many helpful discussions, and the D.G.R.S.T. (Paris) for support.

Footnotes and references

1. *i.e.*, Grignard reagents devoid of β-hydrogens; Grignard reagents with β-hydrogens, like nPrMgBr, lead to olefins (**4** and **6**) in which R = H [H.Felkin and G.Swierczewski, *Compt.rend.*, *266C*, 1611 (1968)].
2. C.Chuit, H.Felkin, C.Frajerman, G.Roussi and G.Swierczewski, *Chem.Commun.*, 1604 (1968).
3. We thank Dr. C.Georgoulis (Paris) for a generous gift of this compound.
4. Strictly speaking, *four* isomeric intermediates should be considered, since the "*syn*" and "*anti*" complexes **10** and **12** are diastereoisomeric. Our results, however, indicate either that the members of each pair of diastereoisomers **10** and **12** are formed in the same proportions from **8** as they are from the *trans* and *cis* alcohols **7** and **9**, or that both members of each pair lead to the same proportions of olefins (**13** and **14** from **10**, and **14** and **15** from **12**), or both.
5. This must be true whether or not the isomeric π-crotyl complexes **10** and **12** are interconverted (*e.g.*, *via* the σ-complex **11**), and whatever the relative rate of this interconversion (if it occurs); slow (*anti*→*syn*) interconversion of π-crotylnickel complexes has been observed recently by C.A.Tolman, *J.Amer.Chem.Soc.*, *92*, 6777 (1970).
6. All the reactions were carried out under standard conditions: molar ratios of **1**:**2**:**3** = 1:3:0.1, in ether, at room temperature in a vacuum line with R = Me, and at reflux with R = Ph. The olefins formed were identified by their retention times and, in the case of the major (> 10%) constituents, by their ir and nmr spectra. The percentage proportions shown in Scheme 2 were determined (and in some case redetermined: cf. ref. 2) by GC, and are thought to be accurate to within ± 0.5 percentage unit.
7. k_s/k_a calc. = $(X_8 - X_9)/(X_7 - X_8)$, where X_n stands for the percentage proportion of any one olefin X (X = **13**, or **14**, or **15**, R = Me or Ph) formed from the alcohol *n* (*n* = **7**, **8**, **9**).
8. The proportions of *cis*-2-pentene **15** (R = Me) formed are so close together that it is not possible to calculate a significant value of k_s/k_a for this olefin (see ref. 7).
9. This conclusion does not appear to apply to Grignard reagents with β-hydrogens (G.Swierczewski, unpublished work; cf. ref. 1).
10. Instructions to Contributors, *Tetrahedron Letters*, cover, p.iii: "An odd number of pages results in a blank page, which costs almost as much to produce as a full page. Consequently, authors are requested to send papers of 2 or 4 pages."