

Preferential Formation of Products with *cis*-Double Bonds from the 1-Methylbut-2-enyl Grignard Reagent

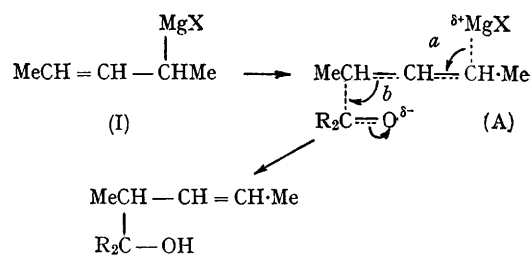
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THE protonation of "butenyl" magnesium bromide by various proton donors has been shown¹ to lead to mixtures of butenes in which the but-2-ene *cis/trans*-ratio is generally greater than 1, *i.e.*, considerably greater than the equilibrium ratio,² which is about 0.25.

We have found that the reactions, in ether, between the 1-methylbut-2-enyl Grignard reagent (I) and a variety of electrophilic substrates (see Table) also lead to products in which the *cis/trans*-ratio is invariably greater than the probable equilibrium ratio² ($\ll 0.25$), and is in most cases greater than 1. In other words, the "*cis*-preference" previously observed only in the protonation of allylic Grignard reagents,¹ appears to be a quite general phenomenon in the reactions of these reagents with electrophilic substrates.³

If *cis*-allylic carbanions are more stable than *trans*, as has recently been suggested,⁴ then the



preferential formation of products with *cis*-double bonds in these reactions is consistent with an S_E2' mechanism⁵ (with respect to the Grignard reagent), in the transition state of which the allylic moiety possesses substantial carbanionic character. This is depicted in transition state (A) for the reaction between the 1-methylbut-2-enyl reagent (I) and a ketone; bond breaking (*a*) is


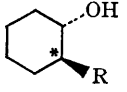
assumed to have progressed further than bond making (*b*), thus putting a partial negative charge on the allylic carbon atoms.

Structural features in the transition state (A) which assist *a* or impede *b* should increase the carbanionic character of the allylic moiety and

made more electrophilic, as in carbon dioxide, rather than less electrophilic, as in epoxycyclohexane. Bond breaking (*a*) is facilitated when X is electron-releasing, and bond forming (*b*) in the transition state is expected⁶ to have progressed to a lesser degree with the more electrophilic

TABLE

cis/trans-Ratios in the products (R = Me-CH=CH- $\overset{\bullet}{\text{C}}$ H-Me) from the 1-methylbut-2-enyl Grignard reagent

Substrate	Product ^a	Diastereoisomer	<i>cis/trans</i> -Ratio ^b	
			from RMgBr ^c	from R ₂ Mg ^d
CO ₂	R-CO ₂ H	—	5.6 ^e	—
(HCHO) _n	R*-CH ₂ OH	—	2.2	4.3
MeCHO	R-CH(OH)-Me	<i>threo</i>	4.4	6.5
			3.3 ^f	4.6 ^f
Me ₂ CO	R-COH-Me ₂	<i>erythro</i>	1.8	2.9
		—	2.4	3.0
		A ^g	0.3	1.4
		B ^g	0.5 ^f	1.9 ^f
			0.8	2.6

^a All the products had spectral properties (i.r. and n.m.r.) consistent with the structures assigned to them.

^b Determined by gas chromatography.

^c Reagent as prepared, in ether, from 2-bromopent-3-ene (40% yield).

^d Dioxan-precipitated reagent (halide-free).

^e Inverse addition at -78°.

^f Overall *cis/trans*-ratio.

^g Configurations not determined.

hence lead to an increased *cis/trans*-ratio in the product. Although the experimental conditions were not identical in all the reactions examined, and although the reasons for the very different *cis/trans*-ratios in the diastereoisomeric products from acetaldehyde and epoxycyclohexane are not yet understood, two general trends can nevertheless be discerned (see Table) which are in accord with the above reasoning: the *cis/trans*-ratio in the product is increased, on the one hand, when X in RMgX is made electron-releasing, as in R₂Mg, rather than electron-withdrawing, as in RMgBr, and, on the other hand, when the substrate is

substrates in these exothermic, low-activation-energy, reactions.

Both the overall "*cis*-preference," and the two trends just mentioned, suggest that the differences in the transition states on going from one electrophilic substrate to another are of degree rather than of kind; this is consistent with the conclusion⁵ that a cyclic transition state is *not* involved in the reactions between allylic Grignard reagents and carbonyl compounds.

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¹ K. W. Wilson, J. D. Roberts, and W. G. Young, *J. Amer. Chem. Soc.*, 1950, **72**, 215.

² A. Schriesheim and C. A. Rowe, *Tetrahedron Letters*, 1962, 405.

³ Oxidation of 1-methylbut-2-enylmagnesium bromide by oxygen afforded predominantly *trans*-pent-3-en-2-ol (*cis/trans*-ratio 0.3, close to the anticipated equilibrium ratio). Oxidation may be a radical process (C. Walling and S. A. Buckler, *J. Amer. Chem. Soc.*, 1955, **77**, 6032).

⁴ S. Bank, A. Schriesheim, and C. A. Rowe, *J. Amer. Chem. Soc.*, 1965, **87**, 3244.

⁵ H. Felkin and G. Roussi, *Tetrahedron Letters*, 1965, 4153.

⁶ G. S. Hammond, *J. Amer. Chem. Soc.*, 1955, **77**, 334.