Tetrahedron Letters No. 41, pp 3785 - 3787, 1971. Pergamon Press. Printed in Great Britain.

ADDITIONS OF THE ALLYL GRIGNARD REAGENT TO ALLENOLS

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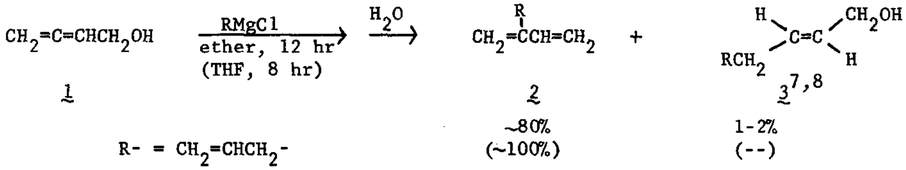
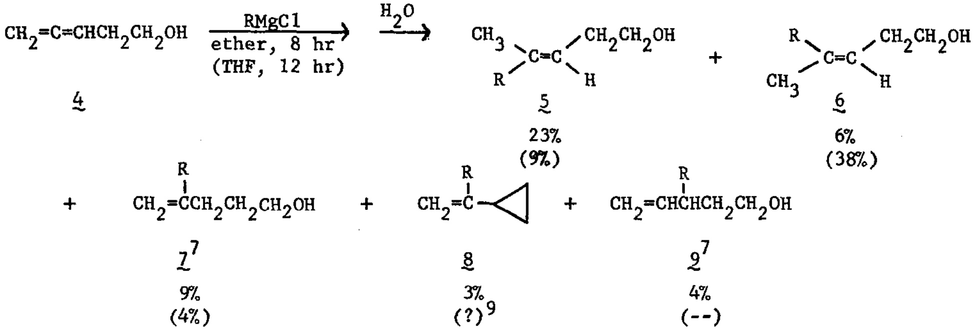
(Received in USA 22 June 1971; received in UK for publication 7 September 1971)

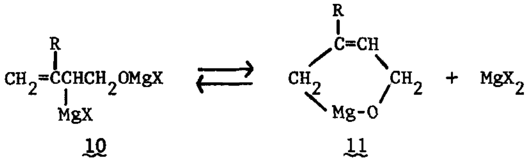
We have observed additions of allylmagnesium chloride to allenols, reactions related to the additions to alkenols[1,2] and alkynols[2-4] that are promoted by the hydroxyl function.[5,6] In addition to providing interesting products, this investigation indicates that the products obtained from additions of Grignard reagents to alkynols would be accompanied by products resulting from additions to the allenols sometimes formed by isomerization of the alkynols.[5]

The products of addition of allylmagnesium chloride to 1 and 4 in ether and in tetrahydrofuran

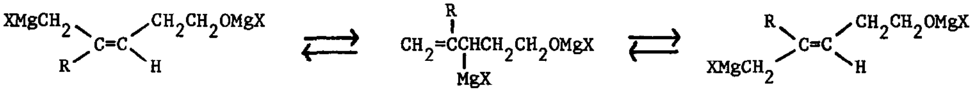




(THF) result predominantly from C—C bond formation at the central carbon of the allene function; only minor products 3 and 9 result from addition to a terminal allene carbon.[10] Hydrocarbon 2, the principal product obtained from 1, presumably forms by loss of magnesium and oxygen from specie such as 10 or 11.[11] Though the relative amounts of 5, 6, 7, and 9 in the product mixtures obtained from 4 do not alter significantly with time, the relative amount of 8, observed in reactions in ether, increases with increasing reaction time. Probably 8 is formed by 1,3-elimination from some species such as 13. The assignment of configuration to 5 and 6 is described in the preceding communication.[12] Whatever the stereochemistry associated with the initial Grignard addition, the observation of both isomers is not surprising, since equilibria such as 12 ⇄ 13 ⇄ 14 can interchange precursors of the *cis* and *trans* isomers.[13]

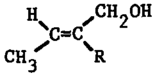


10 11



12 13 14

Allenol 4 when recovered from its reactions is accompanied by 3-pentyn-1-ol and 4-pentyn-1-ol. This isomerization to alkynols, much more significant in THF than in ether, presumably has the same mechanistic origin as the formation of 4 in reactions of allylmagnesium chloride and 3-pentyn-1-ol.[4] Indeed, hydrolysis with D_2O furnishes 5 and 6 from a reaction in ether that are largely monodeuterated, but from a reaction in THF that are largely undeuterated, consistent with their Grignard precursors serving in part as bases for the isomerization. However, the addition products reported here could not have formed significantly from addition to the alkynols;[5] 15 and 16, the major products obtained from reactions of allylmagnesium chloride with 2-butyn-1-ol and 3-pentyn-



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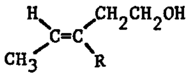

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1-ol, respectively, were not detected.[3,4] The failure to detect products of addition to alkynols is not surprising, since crude kinetic observations indicate that the addition of allylmagnesium chloride to 4 is at least ten-fold faster than to 3-pentyn-1-ol, which through most of the reaction is present in much smaller amounts than is 4.

Acknowledgements: We are grateful to the National Science Foundation for support of this research and for aiding in the purchase of the nmr spectrometers that were used.

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2. J. J. Eisch and J. H. Merkley, J. Organometal. Chem., 20, P27 (1969).
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5. Although it is convenient to speak of additions to alcohols, the hydroxyl functions are present as magnesium salts in the Grignard solutions.
6. It is not certain that the hydroxyl groups of 1 and 4 are exerting a large promoting effect on the additions. In control experiments (run under the same conditions except that no alcohol was present or 1-propanol was the alcohol) allylmagnesium chloride added to 3-methyl-1,2-butadiene, though much more slowly than to 1 and 4.
7. The spectral properties of each new compound are in accord with the structural assignment.
8. Due to its small amount and its contamination by an unidentified product, the stereochemistry of 3 is not established.
9. This compound would not have been detected in this reaction.
10. In all reactions, the molar ratio of Grignard reagent to allenol exceeded 3 and the reaction temperature was 50°. The course of a reaction was followed and yields assigned by glc and nmr analysis of aliquots.
11. A similar elimination may have occurred in the addition of a Grignard reagent to an alkenol.[2]
12. H. G. Richey, Jr., and F. W. Von Rein, Tetrahedron Lett., p. 3781, 1971.
13. Species 12 and 13 probably are also in equilibrium with cyclic species (analogous to 11). Protonation of 13 (or of a related cyclic species) might also lead to both 5 and 6.