Tetrahedron Letters No. 24, pp. 2183-2186, 1971. Pergamon Press. Printed in Great Britain.

PROMOTION BY PRIMARY AND TERTIARY AMINE FUNCTIONS OF ADDITIONS OF GRIGNARD REAGENTS TO ALKENES AND ALKYNES[1]

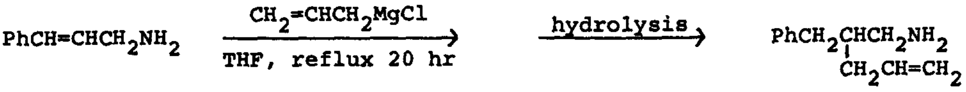
Herman G. Richey, Jr., Wayne F. Erickson, and Alan S. Heyn

Department of Chemistry, The Pennsylvania State University
University Park, Pennsylvania 16802

(Received in USA 19 April 1971; received in UK for publication 17 May 1971)

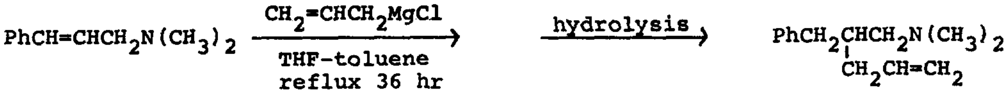
We have observed that an amine function in an alkene or alkyne can promote addition of a Grignard reagent to the multiple bond.

Reactions of an excess (3 moles) of allylmagnesium chloride with 1, 3, and



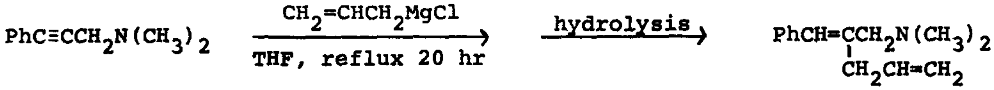
$$PhCH{=}CHCH_2NH_2 \xrightarrow[\text{THF, reflux 20 hr}]{CH_2{=}CHCH_2MgCl} \xrightarrow{\text{hydrolysis}} PhCH_2\underset{\displaystyle CH_2CH{=}CH_2}{\underset{|}{C}}HCH_2NH_2$$

1 2



$$PhCH{=}CHCH_2N(CH_3)_2 \xrightarrow[\text{THF-toluene reflux 36 hr}]{CH_2{=}CHCH_2MgCl} \xrightarrow{\text{hydrolysis}} PhCH_2\underset{\displaystyle CH_2CH{=}CH_2}{\underset{|}{C}}HCH_2N(CH_3)_2$$

3 4



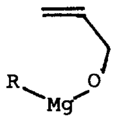
$$PhC{\equiv}CCH_2N(CH_3)_2 \xrightarrow[\text{THF, reflux 20 hr}]{CH_2{=}CHCH_2MgCl} \xrightarrow{\text{hydrolysis}} PhCH{=}\underset{\displaystyle CH_2CH{=}CH_2}{\underset{|}{C}}CH_2N(CH_3)_2$$

5 6

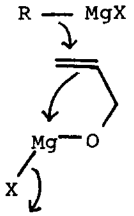
5 produced 2[2] (23%), 4[2,3] (44%), and 6[2] (51%) as the only compounds distilled in significant amounts.[4,5]

No evidence was found for addition of an excess of allylmagnesium chloride to the hydrocarbon components of mixtures of 1-phenyl-1-propene and 1, of 1-phenyl-1-propene and 3, or of 1-phenyl-1-butyne and 5, using conditions similar to those used for additions to 1, 3, and 5 alone. The failure to observe addition to related unsaturated hydrocarbons even when amine functions are present in other molecules in the solution, suggests that the amine functions promoted the additions to 1, 3, and 5, and moreover that promotion by an amine function was specifically for addition to the multiple bond contained within the same molecule.[6,7]

The addition of Grignard reagents to alkenes[8-11] and alkynes[11,12] is known to be promoted by the presence of hydroxyl functions near the multiple bonds. The additions must in some way be facilitated by the magnesium species coordinated with the oxygen in the reaction solutions. It has been suggested that proximity of the organic group (R) to the double bond afforded by attachment of R to the magnesium, as shown in 7, may favor the addition.[8,11] Alternatively, it has been suggested that the coordinated magnesium facilitates the addition of an external Grignard reagent, perhaps by acting as an electrophile as shown in 8.[9,10,13]

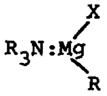


7



8

The promoting effect of a primary amino group is not surprising since this group should be present in a Grignard solution as RNHMgX and RNHMgR, isoelectronic with the ROMgX and ROMgR presumably responsible for the promoting effect of a hydroxyl group. However, a tertiary amino group cannot form analogous salts, and any promoting effect must be ascribed to complexes[14] (9) with



$R_3N{:}Mg(X)(R)$

9

Grignard reagents. In such complexes, -MgX and -MgR may have relationships to the multiple bond similar to those in ROMgX and ROMgR.

Acknowledgement: 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.

REFERENCES

1. Part of this material is taken from the M.S. Thesis of A. S. Heyn, The Pennsylvania State University, 1970.
2. The ir, nmr, and mass spectra of this new compound are in accord with the structural assignment.
3. The solution was prepared in tetrahydrofuran (THF), but then most of this solvent was replaced by toluene. The product (4) formed, but more slowly, in refluxing THF.
4. The yield figures are of quantities actually isolated from the reaction mixtures by distillation. Losses in work-up were significant since only a few g of amine were used for each reaction; therefore, the amounts of product formed are greater than the amounts isolated.
5. It has been reported that allylmagnesium bromide fails to add to 4-(N,N-dimethylamino)-1-butene, although allylic organozinc bromides add to this and to other alkenes containing tertiary amino functions [B. Mauzé, G. Courtois, and L. Miginiac, *C. R. H. Acad. Sci., Ser. C*, **269**, 1225 (1969)]. A reaction of allylmagnesium bromide and 4,4-diphenyl-4-anilino-1-butene furnished products of cleavage of the amine rather than of addition to the double bond [J. J. Eisch and R. L. Harrell, Jr., *J. Organometal. Chem.*, **21**, 21 (1970).]

6. Addition of tertiary amines to the reaction solutions does not increase rates of intramolecular additions of Grignard functions to carbon-carbon multiple bonds of unsaturated Grignard reagents [T. C. Rees, A. M. Rothman, and H. G. Richey, Jr., unpublished observations].
7. Allyl-, methallyl-, and crotyl-magnesium chlorides have recently been reported to add to ethylene and to 1-octene [H. Lehmkuhl and D. Reinehr, *J. Organometal. Chem.*, **25**, C47 (1970)].
8. J. J. Eisch and G. R. Husk, *J. Amer. Chem. Soc.*, **87**, 4194 (1965).
9. M. Chérest, H. Felkin, C. Frajerman, C. Lion, G. Roussi, and G. Swierczewski, *Tetrahedron Lett.*, 875 (1966).
10. H. Felkin and C. Kaeseberg, *Tetrahedron Lett.*, 4587 (1970).
11. J. J. Eisch and J. H. Merkley, *J. Organometal. Chem.*, **20**, P27 (1969).
12. H. G. Richey, Jr., and F. W. Von Rein, *J. Organometal. Chem.*, **20**, P32 (1969).
13. H. Felkin, G. Swierczewski, and A. Tambuté, *Tetrahedron Lett.*, 707 (1969).
14. E. C. Ashby, *Quart. Rev. Chem. Soc.*, **21**, 259 (1967).