

tained when lithium is dissolved in methylamine. Hence, it is our tentative opinion that the actual reducing agent in this system is lithium metal generated at the cathode by the electric current. This hypothesis receives some substantiation from our observation that the electrolyte solution can be reused several times for further reductions without replenishing the lithium chloride. We wish to emphasize, however, that the exact nature of the electrode reactions, as well as the function of the asbestos divider, are under active investigation in our Laboratory. We hope to elucidate these points in future publications as well as to report further on the scope of these reductions.

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The Structure of the Pyrrole Grignard Reagent

Sir:

There has been considerable controversy on the nature of the pyrrole Grignard reagent.¹ Largely on the basis of chemical evidence, pyrrolymagnesium halides have been formulated as C-MgX,^{1,2} N-MgX,³ or ionic species.¹ The present communication presents physical evidence, primarily in the form of n.m.r. spectra,⁴ which suggests that in diethyl ether *pyrrolymagnesium chloride consists predominantly of an N-MgX or ionic species.*

A 10% solution of pyrrolymagnesium chloride was prepared by adding distilled pyrrole to a 10% excess of butylmagnesium chloride⁵ in ether with the usual precautions against air and moisture. The theoretical amount of butane was liberated.

The n.m.r. spectrum⁶ of a 10% solution of pyrrolymagnesium chloride (Fig. 1) consists of two triplets (2.90 and 3.63 τ ; $J = 2$ c.p.s.) of equal area whose general appearance is very similar to those found in the n.m.r. spectra of pyrrole-N-*d*⁷ and pyrrolysodium (3.16 and 3.74 τ ; $J = 2$ c.p.s.).⁸ No absorption which might be attributed to an N-H group could be detected in either the n.m.r. or infrared spectrum of the Grignard reagent although such peaks were observed for pyrrole itself.

On the basis of chemical evidence^{1-3,9} the pyrrole Grignard reagent might be represented by any of the structures I-VI or a mixture thereof.¹⁰ The occur-

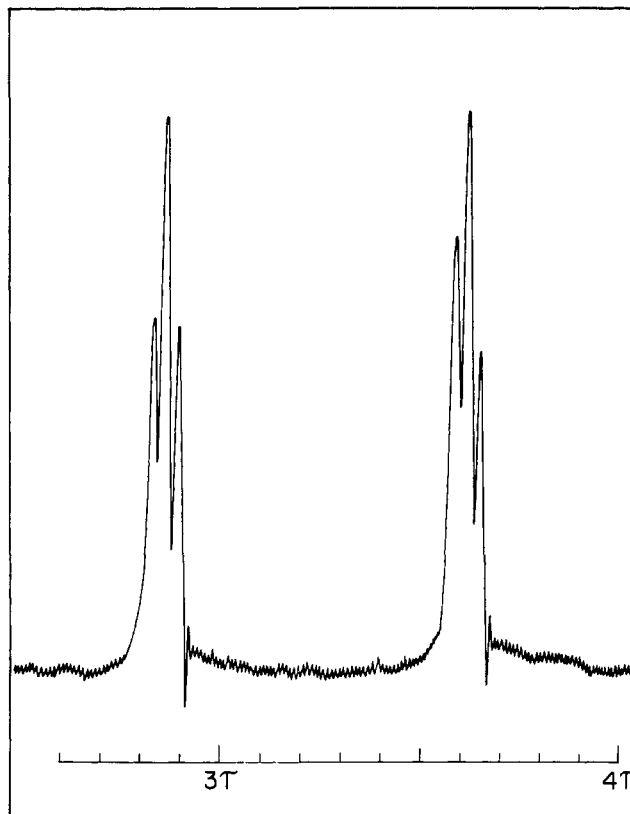
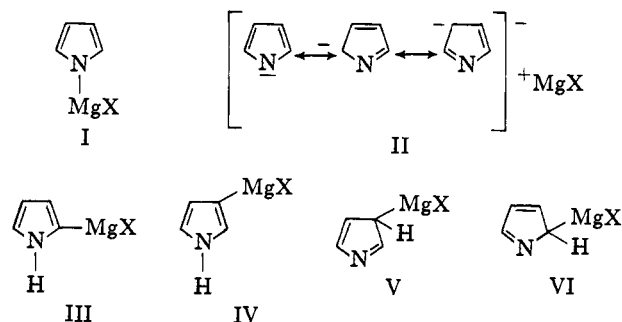


Fig. 1.—N.m.r. spectrum of a 10% solution of pyrrolymagnesium chloride in diethyl ether.

rence of two peaks of equal area in the n.m.r. spectrum of pyrrolymagnesium chloride indicates either that one species with equal numbers of two kinds of hydrogen atoms is predominant (*i.e.*, I or II) or that any mixture of species is in rapid equilibrium so that only two dif-



ferent average magnetic environments of the hydrogen atoms are produced. The failure to detect an N-H group eliminates the presence of significant quantities of III or IV in such an equilibrium. Furthermore, the fact that the triplets in the n.m.r. spectrum of pyrrolymagnesium chloride occur at lower fields than the quartets of pyrrole (3.27 and 3.86 τ ; $J = 2$ c.p.s.) suggests that appreciable amounts of V and VI are also absent, since both the presence of the magnesium atom¹² and the rehybridization of the carbon atom to which it is attached¹³ from sp^2 to sp^3 would be expected to produce a pronounced diamagnetic shift of the resonance of the hydrogen on this carbon atom and thus in the time averaged resonances as well.¹⁴ Finally, the striking similarity of the n.m.r. spectra of the pyrrole Grignard reagent, pyrrole-N-*d*,⁷ and pyrrolysodium is most easily

(1) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, New York, N. Y., 1954, pp. 75-78.

(2) C. D. Nenitzescu, *Bull. Soc. Chim. Romania*, **11**, 130 (1930); *Chem. Abstr.*, **24**, 2458 (1930).

(3) H. Gilman and I. Heck, *J. Am. Chem. Soc.*, **52**, 4949 (1930).

(4) For other applications of this method of determining the structure of ambident Grignard reagents see (a) G. M. Whitesides, J. E. Nordlander, and J. D. Roberts, *Discussions Faraday Soc.*, **34**, 185 (1962); (b) M. G. Reincke, H. W. Johnson, and J. F. Sebastian, *Tetrahedron Letters*, 1183 (1963).

(5) The magnesium turnings used were 99.99% pure and are available from A. D. Mackay, Inc., New York, N. Y.

(6) All n.m.r. spectra were taken at room temperature on a Varian Associates Model DP-60 high resolution spectrometer operating at 56.4 Mc./sec. Chemical shifts were determined by the audiofrequency side-band technique with tetramethylsilane as an internal reference ($\tau = 10.0$) and are accurate to at least ± 0.04 τ .

(7) R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **37**, 1056 (1959).

(8) Prepared by refluxing an ether solution of pyrrole with an excess of sodium hydride.

(9) P. S. Skell and G. P. Bean, *J. Am. Chem. Soc.*, **84**, 4655 (1962).

(10) For the purposes of this paper the Grignard reagent is written as RMgX although the authors recognize that this formulation is not necessarily correct.¹¹

(11) G. D. Stucky and R. E. Rundle, *J. Am. Chem. Soc.*, **85**, 1002 (1963); E. C. Ashby and W. E. Becker, *ibid.*, **85**, 118 (1963); R. E. Dessy, G. S. Handler, J. H. Wotiz, and C. A. Hollingsworth, *ibid.*, **79**, 3476 (1957).

(12) D. F. Evans and J. P. Maher, *J. Chem. Soc.*, 5125 (1962).

(13) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 238.

(14) Ref. 13, p. 218.

interpreted if pyrromagnesium chloride is represented as the N-MgX derivative I or the ionic, but not necessarily highly dissociated, resonance hybrid II.

Although a clear choice between these two alternatives cannot be made at this time, it should be pointed out that the lack of complete identity of the n.m.r. spectra of pyrromagnesium chloride and the presumably ionic¹⁵ pyrrosodium (see chemical shift data) need not argue against the ionic structure II, since these differences might simply be due to variations in the solvation or degree of association of the two metals. Hopefully, studies which are presently underway in this laboratory to clarify this point will also shed some light on the marked differences in the chemical reactivity of the Grignard reagents⁹ and alkali metal salts¹⁶ of pyrrole.

Acknowledgment.—This research was supported by grants from the research committee of the University of California.

(15) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p. 93.

(16) C. F. Hobbs, C. K. McMillin, E. P. Papadopoulos, and C. A. VanderWerf, *J. Am. Chem. Soc.*, **84**, 43 (1962).

(17) Lockheed Graduate Research Fellow in Chemistry, summer, 1963.

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RECEIVED JULY 23, 1963

Solvent Effect on *cis-trans* Isomerization in Grignard Reagent Formation from β -Bromostyrenes

Sir:

We have found that a Grignard reagent prepared in the dark from *cis*- or *trans*- β -bromostyrene shown to be free from the counter isomer of the bromide by infrared and n.m.r. spectra gives a mixture of *cis*- and *trans*- β -*d*₁-styrenes by addition of heavy water as can be seen in Fig. 1 and in Table I. Though n.m.r. signals due to the β -protons of β -*d*₁-styrenes overlap with β -proton signals¹ of styrene contained in the β -*d*₁-styrene mix-

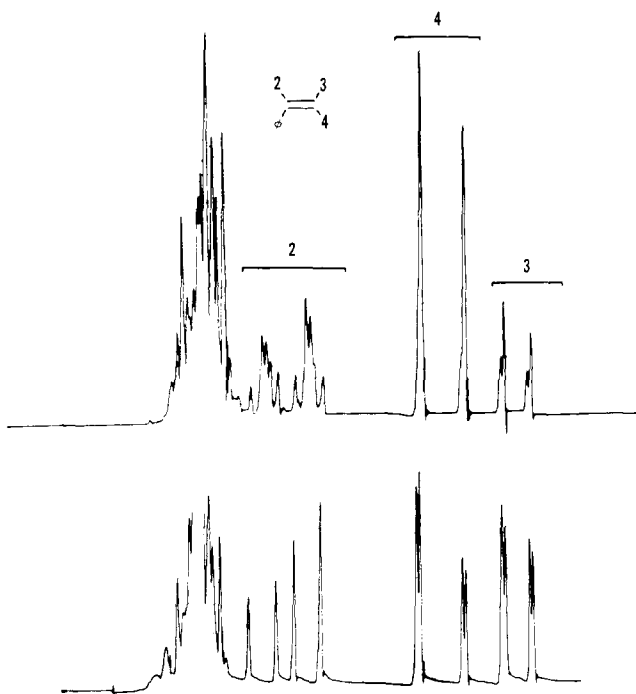


Fig. 1.—The n.m.r. spectrum (60 Mc.) of β -*d*₁-styrene mixture obtained by the addition of heavy water to the Grignard reagent prepared from *trans*- β -bromostyrene in tetrahydrofuran. The n.m.r. spectrum of styrene is also given for comparison.

TABLE I

THE *cis/trans* RATIOS IN β -*d*₁-STYRENE MIXTURES OBTAINED BY ADDITION OF HEAVY WATER TO GRIGNARD REAGENTS PREPARED^a FROM *cis*- OR *trans*- β -BROMOSTYRENE IN VARIOUS SOLVENTS

| Solvent | From <i>cis</i> - β -bromostyrene | From <i>trans</i> - β -bromostyrene |
|---------------------------|---|---|
| Tetrahydrofuran | 10:1 | 1:10 |
| 1:1 Mixture of THF and EE | 10:1 | 1:5 |
| Ethyl ether | ... | 1:1 |

^a Bromostyrene in solvent was added to Mg metal in 90 min. at 26° and the mixture was stirred for 15 min.

ture, the highest and lowest field signals of the α -proton quartet¹ of styrene are separate from the α -proton signals of β -*d*₁-styrenes as seen in an example shown in Fig. 1. We can, therefore, easily estimate the amount of styrene contained in the mixture and make a correction for the β -proton signals. The *cis/trans* ratios thus obtained for the β -*d*₁-styrene mixtures from these corrected areas of the β -proton signals are shown in the Table.

The *cis/trans* ratios are higher for the products from *cis*- β -bromostyrene than those from the *trans* compound. However, the ratios are dependent on the solvent species used for preparing the reagents. If the Grignard reagent is prepared from *trans*- β -bromostyrene, the original *trans* configuration is much more completely preserved in the β -*d*₁-styrene mixture with the reagent prepared in tetrahydrofuran than with the reagent prepared in ethyl ether. The use of a 1:1 mixture of tetrahydrofuran and ethyl ether as solvent affords a product with a *cis/trans* ratio intermediate between those for the single solvents, though the ratio for the mixed solvent is closer to that for tetrahydrofuran. If a Grignard reagent is prepared from *cis*- β -bromostyrene using tetrahydrofuran or the 1:1 mixture as solvent, the β -*d*₁-styrene mixture obtained is much more abundant in *cis*- β -*d*₁-styrene than in the *trans* isomer. *cis*- β -Bromostyrene does not form a Grignard reagent in ethyl ether at temperatures up to the boiling point of the solvent. The yields of β -*d*₁-styrene mixtures in the other cases were in a range of 30–50% based on β -bromostyrenes, when the Grignard reagents were prepared at 26°.

It can clearly be concluded from the following experiment that the isomerization and the solvent effect on it take place in the course of Grignard reagent formation but not in addition of heavy water. When the Grignard reagent prepared in ethyl ether from *trans*- β -bromostyrene is diluted with tetrahydrofuran, the *cis/trans* ratio of β -*d*₁-styrenes obtained is equal to that from the same Grignard reagent diluted with ethyl ether. The *cis/trans* ratio is also unchanged by dilution with ethyl ether of the Grignard reagent prepared in tetrahydrofuran from *cis*- or *trans*- β -bromostyrene.

The *cis/trans* ratio is unchanged by the difference of time intervals up to 5 hr. at 20° between the Grignard reagent formation, the dilution by solvent, and the addition of heavy water. This experimental result and the high degree of retention of original *cis* or *trans* configuration in tetrahydrofuran show that the Grignard reagent is stable in tetrahydrofuran, in which prompt isomerization of vinyl lithium reagents is reported² to take place.

If the temperature is allowed to rise to the boiling point of the solution in the preparation of the Grignard reagent, the yield of β -*d*₁-styrene decreases. (β -*d*₁-Sty-

(1) As for the assignment of proton signals of styrene, see J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 240.

(2) D. Y. Curtin and W. J. Koehl, *J. Am. Chem. Soc.*, **84**, 1967 (1962).