

steric requirement for the novel type of long-range spin-spin coupling between 1,3-quasi-axial-axial protons.^{8-10a}

(8) The steric requirement is defined primarily in terms of the juxtaposition of $\beta\beta$ -H and $\delta\delta$ -H, although the juxtaposition of the benzylic $\beta\beta$ -H and the aromatic system cannot be a *priori* disregarded as an element of the steric requirement. The weak, and sterically unspecific, couplings between both benzylic ($\beta\alpha$ -H and $\beta\beta$ -H) protons with the aromatic (γ -H) proton could be regarded as evidence for the lack of strong σ - π interactions; this situation may be contrasted with the strong and sterically specific interactions between vinylic (γ -H) and allylic ($\beta\beta$ -H) protons, see ref. 1b and c. The juxtaposition of $\beta\beta$ -H and $\delta\delta$ -H is akin to the geometric arrangements, ref. 3d, Fig. 2 and 3, favorable for enhanced spin-spin coupling on the basis of overlap integrals of the C-H bond orbital wave functions calculated by Wiberg, *et al.*, ref. 3d. Our findings therefore appear to accommodate the predictions from this treatment based on Fermi contact potential. In view of environmental effects, other than geometry, which may influence J_{HH} values, ref. 7, it is not yet warranted to consider this a conclusive experimental confirmation of the theory.

(9) The concept of "virtual long range spin-spin coupling," developed by Musher and Corey, ref. 3f, describes a "coupling" between nonvicinal protons, which occurs when, for example, protons B and C, in a closed linear 3-spin system, are strongly enough coupled so that proton A can "see" the spin states of C although it experiences no coupling strength from C, *i.e.*, $J_{AC} = 0$. The XABC system described by us becomes a closed linear ABC system on decoupling of γ -H, Fig. 1 (B). As demonstrated by us, $J_{AC} \neq 0$, and this coupling is "real," not "virtual."

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An Electrochemical Method of Reducing Aromatic Compounds Selectively to Dihydro or Tetrahydro Products

Sir:

We hereby wish to report the development of the first successful electrochemical method of reducing aromatic compounds selectively to either dihydro or tetrahydro products.¹ A simple electrolytic cell shown in Fig. 1 was used.

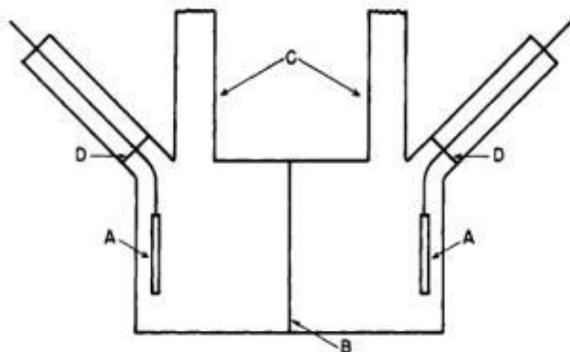
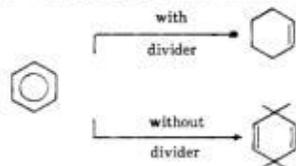


Fig. 1.—A, platinum electrodes; B, asbestos; C, condensers; D, glass seal.

When aromatic compounds dissolved in methylamine were reduced in this cell *without* the asbestos divider (*i.e.*, when the anode and cathode compartments were not separated) excellent conversions to dihydro products resulted. When the same aromatic compound



(1) A recent publication by H. W. Sternberg, R. Markby, and I. Wender, *J. Electrochem. Soc.*, **110**, 425 (1963), discloses the successful electrochemical reduction of benzene and tetralin. A mixture of reduction products was obtained and no increased selectivity was noted when an "anode compartment" was used.

TABLE I
ELECTROLYTIC REDUCTIONS OF VARIOUS AROMATIC HYDROCARBONS IN METHYLAMINE-LITHIUM CHLORIDE SOLUTIONS WITH AND WITHOUT CELL DIVIDER^a

Aromatic ^b	Yield, % ^c	Alkylcyclohexenes, %	Dihydrobenzenes, %	Recovered aromatic, %
Benzene ^d	49	4	95	1
Benzene ^e	49	100
Toluene ^d	64	5	94	...
Toluene ^e	44	86	...	14
Ethylbenzene ^d	73	4	93	...
Ethylbenzene ^e	63	96	...	4
Cumene ^d	82	6	78	13
Cumene ^e	75	89	...	11
<i>t</i> -Butylbenzene ^d	85	5	68	20
<i>t</i> -Butylbenzene ^e	81	53	...	47

^a In those runs where the asbestos divider was used, 0.4 mole of LiCl was employed in each compartment. With no divider, 0.8 mole of LiCl was used. About 50,000 coulombs was passed through the solution in each case. The amperage varied between about 1.2 to 2 and the time of reduction was about 7-9 hr. in each case. ^b The amount of aromatic in every instance was 0.1 mole. ^c The yield in each case was calculated so as to take into account the amount of aromatic recovered. The per cent conversion would hence be lower. ^d Without asbestos cell divider. ^e With asbestos cell divider.

was reduced *with* the asbestos divider in place, equally excellent conversions to tetrahydro products resulted. Thus, benzene can be reduced to either cyclohexane or 1,4-dihydrobenzene by the simple device of carrying out the electrolytic reduction in the presence or absence of the cell divider.

Table I lists the results obtained when a representative series of aromatic hydrocarbons was reduced electrolytically both in the presence and absence of the cell divider. An electrolyte consisting of lithium chloride was used in each case.

All of the electrolyses were carried out under similar conditions. The preparation of 2,5-dihydroisopropylbenzene and the isopropylcyclohexenes which follows can be considered as typical.

An electrolysis cell (Fig. 1) 170 mm. in length by 100 mm. in diameter was fitted with two Dry Ice condensers, platinum electrodes (2 × 5 cm.), and an asbestos divider. Cumene (12 g., 0.1 mole) was placed in the cathode compartment. Lithium chloride (17 g., 0.4 mole) and 450 ml. of anhydrous methylamine were placed in *each* compartment. A total of 50,000 coulombs (2.0 amp.; 90 v.) was passed through the solution in 7 hr. The solvent was then allowed to evaporate and the mixture was hydrolyzed by the slow addition of water. After extraction with ether, drying, and removal of solvent, there was obtained 9.0 g. (75%) of product boiling at 149-153°. Analysis by v.p.c. (Aerograph, 14 ft. β , β' oxydipropionitrile column; 75°; 16 p.s.i. He) showed the presence of 89% isopropylcyclohexenes and 11% cumene.

When the same cell was used without the divider, 12 g. (0.1 mole) of cumene was reduced, using 34.0 g. (0.8 mole) of lithium chloride and 900 ml. of methylamine. Again, 50,000 coulombs (2.0 amp.; 85 v.) was passed through the mixture in 7 hr. Using the same work-up as described earlier, there was collected 9.8 g. (82%) of product boiling at 152-157°. Analysis by v.p.c. showed the presence of 6% isopropylcyclohexenes, 3% of an unidentified diene, 13% cumene, and 78% 2,5-dihydroisopropylbenzene.

When the reductions are carried out in the presence of the asbestos cell divider, the amine solution in the cathode compartment becomes deep blue in color. This color is highly reminiscent of the blue color ob-

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, pyrrolylmagnesium 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 pyrrolylmagnesium chloride consists predominantly of an N-MgX or ionic species.

A 10% solution of pyrrolylmagnesium 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 pyrrolylmagnesium 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-d⁷ 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-

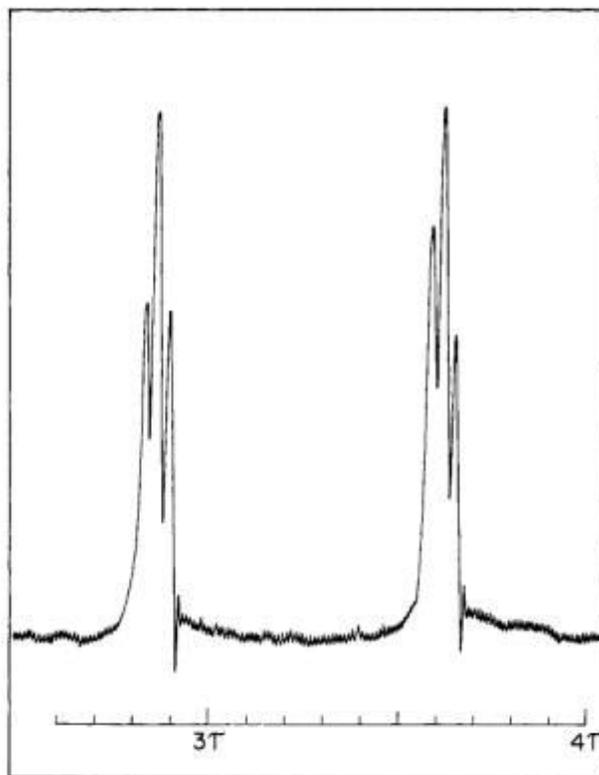
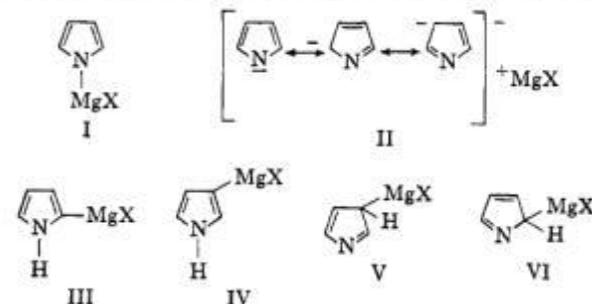


Fig. 1.—N.m.r. spectrum of a 10% solution of pyrrolylmagnesium chloride in diethyl ether.

rence of two peaks of equal area in the n.m.r. spectrum of pyrrolylmagnesium 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 pyrrolylmagnesium 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 L. 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. P. 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 $\pm 0.04 \tau$.

(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.