by alumina chromatography of the complex, formed red needles, m.p. 198–202°; $\lambda_{\max}^{\text{benzene}}$ 513 mμ (ϵ = 8700). Compound V is more stable in solution and less reactive as a diene than its oxygen analog IV. Although its reacts rapidly with tetracyanoethylene to give an adduct (XI), m.p. 268–280°, it did not react with N-phenylmaleimide on standing for sixteen hours in benzene solution at room temperature.

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[4] Fellow of the Alfred P. Sloan Foundation.

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PROTON SPIN-SPIN COUPLING CONSTANTS IN VINYLACETYLENES

Sir:

Kreevoy, Charman and Vinard[1] recently have presented coupling constants for the spin–spin splittings observed in the acetylenic region of the n.m.r. spectra for several monosubstituted acetylenes. In ten of these compounds the magnitude of the coupling between the acetylenic hydrogen and the α-hydrogen was found to fall in the range 2.1 cps. to 2.8 cps. Failure to observe a measurable splitting in the acetylenic peak of vinylacetylene and propynal, however, led these workers to conclude that the coupling was anomalous in these two molecules. As an explanation, it was proposed that π electrons centered on the α-carbon participate in such a manner as to yield a small coupling constant of non-measurable magnitude.

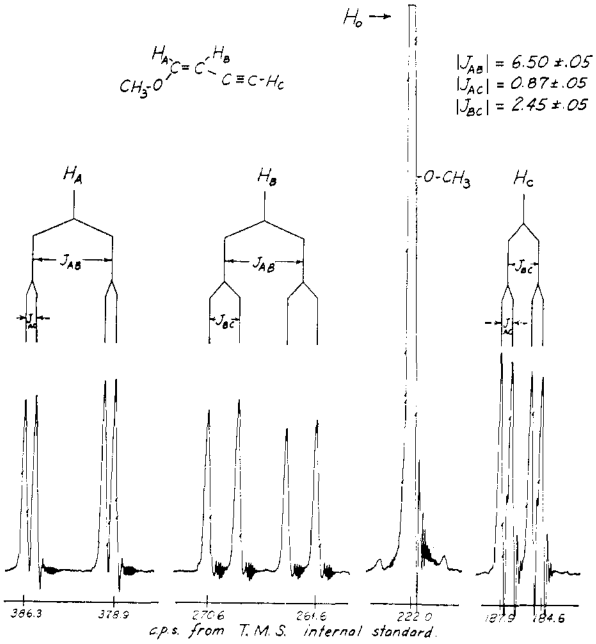

Fig. 1.—N.m.r. spectrum of 1-methoxy-1-buten-3-yne.

Work in this laboratory on vinylacetylenes indicates that the coupling constant in question has a magnitude in the prescribed range, 2.1 to 2.8 cps., and is not abnormally small as previously suggested. In the n.m.r. spectrum of *cis*-1-methoxy-1-butene-3-yne,[2] this splitting was measured to be 2.47 ± 0.05 cps. The essential features of the spectrum and the remaining spectral parameters are given in Fig. 1. As the multiplets are separated by relatively large chemical shifts, the coupling constants and chemical shifts can be taken directly from the experimental data. In addition to the chemical shift values which form a sufficient basis for the assignment, supporting evidence is found in the agreement of the 6.5 cps. vinyl coupling with the 6.4 and 6.8 cps. *cis*-couplings noted by Banwell and Sheppard,[3] respectively, for divinyl and methyl vinyl ethers. Furthermore, the 0.87 cps. long range acetylenic coupling is comparable with the values found in this laboratory for 2-methyl-1-butene-3-yne and vinylacetylene.

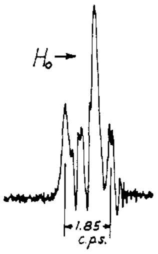

Fig. 2.—Acetylenic region of the n.m.r. spectrum of monovinylacetylene.

The high resolution n.m.r. spectrum of the acetylenic proton of 30% by volume vinylacetylene[4] dissolved in chloroform is presented in Fig. 2 as evidence that the splittings in this compound are not less than 0.5 cps. (the proposed limit of resolution for data presented in ref. 1). By first obtaining the vinyl couplings from the deuterated compound, $CH_2{=}CH{-}C{\equiv}C{-}D$, the spectrum of $CH_2{=}CH{-}C{\equiv}C{-}H$ was fitted[5] numerically with an high speed digital computer. Using a system of labeling where X and A, B, C are, respectively, the acetylenic and three vinyl protons with A *cis* to B and *trans* to C, the spectral parameters and their relative signs were found as follows: $\nu_0\delta_{AB}$ = 13.7 cps., $\nu_0\delta_{AC}$ = 2.9 cps., $\nu_0\delta_{AX}$ = 168.3 cps., J_{AB} = 11.5 cps., J_{AC} = 17.3$_5$ cps., J_{BC} = 2.0$_5$ cps., J_{AX} = −2.1 cps., J_{BX} = 0.8 cps. and J_{CX} = 0.7 cps. The acetylenic multiplet was 88.6 cps. downfield from cyclohexane. A standard deviation of 0.047 cps. was obtained from the difference in the positions of the experimental and the theoretical lines.

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[1] M. M. Kreevoy, H. B. Charman and D. R. Vinard, *J. Am. Chem. Soc.*, **83**, 1978 (1961).

[2] This sample was obtained from L. Light and Company.

[3] C. N. Banwell and N. Sheppard, *Mol. Phys.*, **3**, 351 (1960).

[4] Dr. H. E. Schroeder of E. I. du Pont de Nemours and Co. provided this sample.

[5] This calculation was finished during the interim between submitting the original and revised forms of this communication. As such, the calculations of Snyder, Altman, and Roberts in the accompanying manuscript predate ours. The difference in the two sets of parameters exceeds slightly the limits of error of both calculations. We have noted, however, that the parameters are very sensitive to the determined positions of the experimental lines, and minor errors in these values might account for the variation. Our spectrum was obtained on a Varian A-60 console used in conjunction with the standard 12 inch magnet.

The above data suggest that hybridization of the α-carbon does not significantly influence the spin-spin coupling mechanism which leads to an α-hydrogen splitting in the acetylenic resonance, and that π electrons, centered on the α-carbon, probably can be ignored in any theoretical consideration.

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RECEIVED JANUARY 5, 1962

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY. γ,γ-DIMETHYLALLYLMAGNESIUM BROMIDE[1]

Sir:

The nuclear magnetic resonance (n.m.r.) spectrum of allylmagnesium bromide[2] is characterized by a simplicity inconsistent with any single classical structure; notably, the α and γ protons occupy magnetically equivalent positions. This observation may be accommodated by formulating the Grignard reagent as either a rapidly equilibrating mixture of two equivalent classical structures (I) or a bridged structure with magnetically equivalent protons (II).

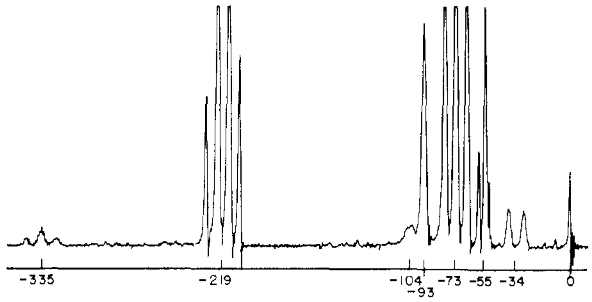
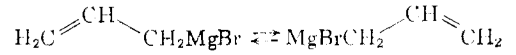
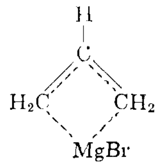


Fig. 1.—Nuclear magnetic resonance spectrum of γ,γ-dimethylallylmagnesium bromide in diethyl ether at 33° and 60 Mc./sec. with tetramethylsilane (0 cps.) as internal standard. The intense triplet and quartet centered at -73 cps. and -219 cps. are the resonances of the diethyl ether CH_3 and CH_2. The complex of lines at -55 cps. is due to isoöctane. Residual coupling products from the preparation of the Grignard reagent give rise to the resonance at -104 cps. The α-CH_2 doublet of the Grignard reagent comes at -34 cps.; the β-CH triplet at -335 cps.; the γ-CH_3 resonance at -93 cps.



$$H_2C{=}CH{-}CH_2MgBr \rightleftarrows MgBrCH_2{-}CH{=}CH_2$$

I



II

Available data for allylmagnesium bromide[2,3] and for butenylmagnesium bromide[3,4] appear to favor the formulation of these Grignard reagents as rapidly equilibrating mixtures even at $-80°$. We now wish to report evidence which we interpret as excluding the symmetrical structure for γ,γ-dimethylallylmagnesium bromide, and by analogy for allyl- and butenylmagnesium bromides.

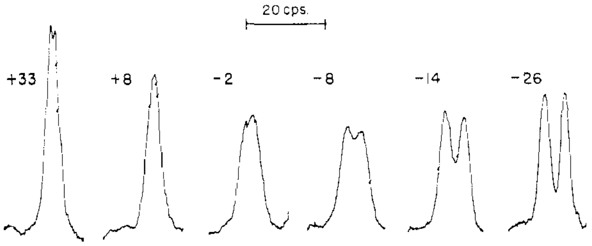


Fig. 2.—Methyl proton resonance of γ,γ-dimethylallylmagnesium bromide as a function of temperature.

The Grignard reagent of γ,γ-dimethylallyl bromide was prepared by reaction of a highly dilute solution of halide in diethyl ether with a column of amalgamated magnesium turnings.[3] The reaction product was seriously contaminated with coupling products; these were conveniently removed by concentration of the solution and extraction with dry isoöctane.

At room temperature, the n.m.r. spectrum of γ,γ-dimethylallyl Grignard reagent (Fig. 1) consists of a triplet in the vinyl proton region, a high field doublet, and a sharp singlet at slightly lower field than the ether methyl quartet. These resonances have areas approximately in the ratio 1:2:6 and can be assigned, respectively, to the single β proton, the two α protons, and the six methyl protons of γ,γ-dimethylallylmagnesium bromide, on the assumption that the *cis* and *trans* methyl groups experience averaging of their chemical shifts through what amounts to rotation around the double bond as the result of interconversions with α,α-dimethylallylmagnesium bromide (present only in very low concentrations).

Upon lowering the temperature of the sample, the methyl proton singlet broadens and then splits symmetrically into two equal components (Fig. 2). Neither the vinyl proton resonance nor the high field doublet significantly changes form or position. Clearly, at the lower temperatures, the lifetime of a methyl group in a *cis* or *trans* position is increased, and the magnetic environment of protons on the methyl groups is no longer averaged.[5]

The observation of two methyl resonances at low temperatures excludes a symmetrical structure analogous to II for this Grignard reagent. The methyl groups in a symmetrical structure would be static; hence a decrease in temperature would not be expected to produce the observed separation.

Application of the procedure of Gutowsky and Holm[6] to the variation of the line shapes of the methyl resonances from -55 to $+33°$ gave $\Delta H^* = 7 \pm 3$ kcal./mole, and $A = 10^3$ to 10^8 sec.$^{-1}$ for

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[1] Supported in part by the Office of Naval Research.

[2] J. E. Nordlander and J. D. Roberts, *J. Am. Chem. Soc.*, **81**, 1769 (1959).

[3] J. E. Nordlander, Ph.D. Thesis, California Institute of Technology, 1960.

[4] J. E. Nordlander, W. G. Young and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 494 (1961).

[5] J. D. Roberts, "Nuclear Magnetic Resonance," McGraw-Hill Book Company, Inc., New York, N. Y., 1959, Chap. 4.

[6] H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).