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Nuclear Magnetic Resonance Spectroscopy.
Gamma, gamma-Dimethylallylmagnesium
Bromide

By George M. Whitesides, J. Eric Nordlander and John D. Roberts

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY.
 γ,γ -DIMETHYLALLYLMAGNESIUM BROMIDE¹

Sir:

The nuclear magnetic resonance (n.m.r.) spectrum of allylmagnesium bromide² 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

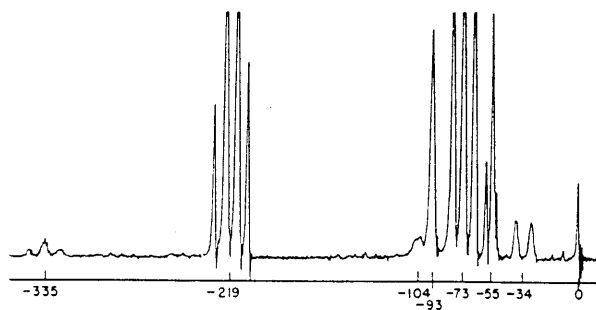
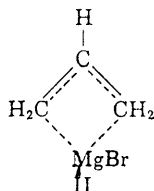
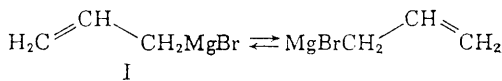


Fig. 1.—Nuclear magnetic resonance spectrum of γ,γ -dimethylallylmagnesium bromide in diethyl ether at 33° and 60 Mc./sec. with tetramethylsilane (0 cps.) as internal standard. The intense triplet and quartet centered at -73 cps. and -219 cps. are the resonances of the diethyl ether CH_3 and CH_2 . The 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_2 resonance at -93 cps.

Grignard reagent as either a rapidly equilibrating mixture of two equivalent classical structures (I) or a bridged structure with magnetically equivalent protons (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.

(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.

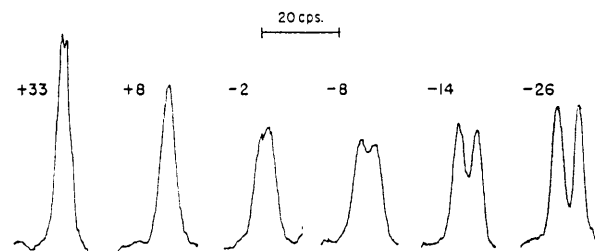


Fig. 2.—Methyl proton resonance of γ,γ -dimethylallylmagnesium bromide as a function of temperature.

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 Holm⁶ 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

(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).

the process leading to interchange of *cis* and *trans* methyl groups.⁷

If an appreciable amount of α,α -dimethylallyl-magnesium bromide were present in the solutions, a decrease in temperature would be expected to result in an increase in concentration of the more stable γ,γ -dimethylallyl isomer. The tempera-

(7) The magnitude of the uncertainty in these values reflects difficulties in obtaining an accurate value for the relaxation time T_2 of the methyl protons.

ture independence of this doublet and of the high-field doublet of the related butenyl Grignard reagent indicates that these Grignard reagents exist almost exclusively as the primary isomers.

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GATES AND CRELLIN LABORATORIES OF CHEMISTRY
CALIFORNIA INSTITUTE OF
TECHNOLOGY
PASADENA, CALIFORNIA

GEORGE M. WHITESIDES
J. ERIC NORDLANDER
JOHN D. ROBERTS

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