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 BROMIDE

Sir:

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

\[
\text{H}_2\text{C} = \text{CH}_2\text{MgBr} \quad \text{II}
\]

Available data for allylmagnesium bromide and for butenylmagnesium bromide appear to favor the formulation of these Grignard reagents as rapidly equilibrating mixtures even at −80°C. 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.
the process leading to interchange of cis and trans methyl groups.\textsuperscript{7}

If an appreciable amount of $\alpha,\alpha$-dimethylallylmagnesium bromide were present in the solutions, a decrease in temperature would be expected to result in an increase in concentration of the more stable $\gamma,\gamma$-dimethylallyl isomer. The temperature 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.

\textsuperscript{7} The magnitude of the uncertainty in these values reflects difficulties in obtaining an accurate value for the relaxation time $T_1$ of the methyl protons.

\textbf{Contribution No. 2822} \hspace{1cm} \textbf{George M. Whitesides} \\
\textbf{Gates and Crellin Laboratories of Chemistry} \hspace{1cm} \textbf{J. Eric Nordlander} \\
\textbf{California Institute of Technology} \hspace{1cm} \textbf{Pasadena, California} \\
\textbf{Received March 7, 1962} \\

\textbf{Crellin Laboratories of Chemistry} \hspace{1cm} \textbf{John D. Roberts}