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).

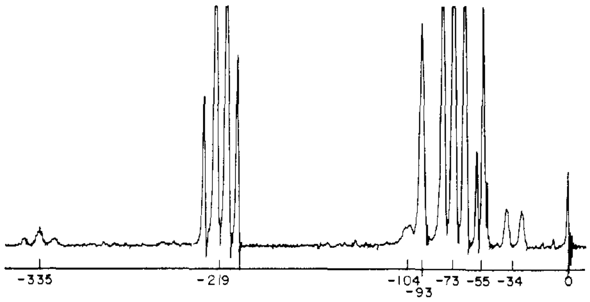
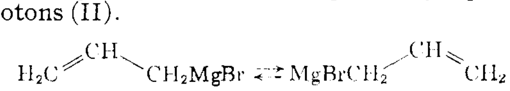
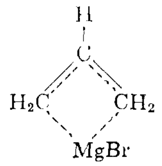


Fig. 1.—Nuclear magnetic resonance spectrum of γ,γ-dimethylallylmagnesium bromide in diethyl ether at 33° and 60 Mc./sec. with tetramethylsilane (0 cps.) as internal standard. The intense triplet and quartet centered at -73 cps. and -219 cps. are the resonances of the diethyl ether CH_3 and CH_2. The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

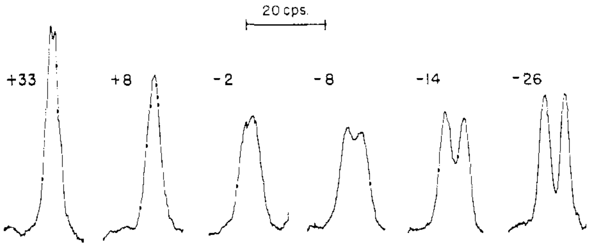


Fig. 2.—Methyl proton resonance of γ,γ-dimethylallylmagnesium bromide as a function of temperature.

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.

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[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).

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

If an appreciable amount of α,α-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 γ,γ-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.

[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.

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URANYL OXALATE ACTINOMETER FOR MICROPHOTOCHEMISTRY[1]

Sir:

Recently we have been studying photochemical reactions in aqueous solutions using volumes in the range of 1 to 10 microliters. After ultraviolet irradiation in sealed 1 mm. quartz tubes, about the size of melting point tubes, the cell is crushed and the entire sample vaporized into the carrier gas stream of a flame ionization gas chromatograph apparatus for analysis. For use with this technique, a suitable actinometric system was necessary. Consequently, we have developed a simplified method of uranyl oxalate actinometry based on the carbon monoxide formed rather than on the oxalate destroyed. The method is some 50 to 1000 times more sensitive than colorimetric or titration methods[2] and about three times as sensitive as the malachite green leucocyanide actinometer.[3]

Using the cells described above for actinometry, it is impossible to titrate the solutions for undecomposed oxalate. In our experiments, the concentration of uranyl oxalate was about 10^{-3} *M* to give the same optical density as the photochemical systems used, as required by Claesson's method of equivalent optical densities.[4,5] Consideration of the volumes involved and a suitable concentration change in the actinometer solution leads to the conclusion that the analytical method must be adequate for approximately 10^{-9} mole amounts, clearly outside the titration or colorimetric method range.

The reaction usually given[6] for the photodecomposition of oxalic acid in uranyl oxalate actinometry is

$$H_2C_2O_4 \longrightarrow H_2O + CO_2 + CO \qquad (1)$$

From the equation, it appears that it should be possible to relate the amount of CO to the oxalate destroyed and, hence, to the light absorbed.

This reaction does not, however, represent the experimentally determined stoichiometry. Carter and Weiss[7] consider also the reactions

$$H_2C_2O_4 \longrightarrow HCOOH + CO_2 \qquad (2)$$

$$H_2C_2O_4 + U^6 \longrightarrow H_2O + 2CO_2 + U^4 \qquad (3)$$

They observed that the relative proportions of the three reactions depend upon the acidity of the solution and upon the concentration of quenching ions present. Nevertheless, it may be concluded that it should be possible to establish a relationship between the quantum yield of CO formation and that of oxalate decomposition.

In our experiments, 10 microliter samples of uranyl oxalate solution containing a 10-fold excess of oxalic acid were sealed in the 1 mm. quartz reaction tubes. The tubes were maintained in a water thermostat at 30.0° and subjected to 2537 Å. radiation from a mercury resonance arc. The tubes were crushed and the contents were swept into a 5 Å. molecular sieve[8] gas chromatographic column. CO was determined at these low levels by a flame ionization detector after catalytic hydrogenation to methane.[9]

Experiments were performed to determine the effect of irradiation time and concentration on CO formation. With an initial concentration of 9.5×10^{-4} *M* uranyl oxalate, the quantum yield of CO formation was found to be independent of time up to 60% decomposition of the oxalate. The rate of carbon monoxide formation was found to be linearly dependent on concentration, Fig. 1. This result

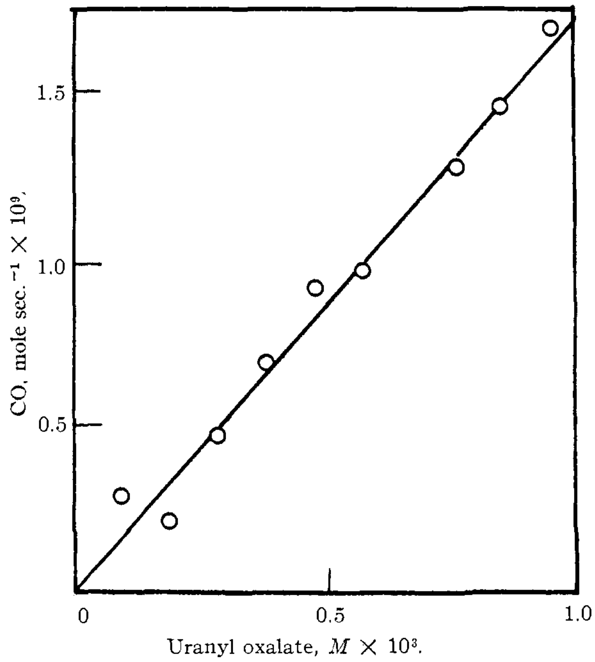

Fig. 1.—Rate of carbon monoxide formation as a function of uranyl oxalate concentration.

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[1] This research was supported by a grant from the U. S. Army Research Office (Durham).

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[3] J. G. Calvert and J. H. L. Rechen, *ibid.*, **74**, 2101 (1952).

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