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INVERSION RATE IN A PRIMARY GRIGNARD REAGENT

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There is a wealth of chemical evidence concerning carbanion inversion phenomena in organometallic reagents. (1-6)

We now report a direct physical measurement of the inversion rate in a primary Grignard reagent using the techniques of NMR (7,8,9)

The Grignard reagent in ether was prepared from 2-methyl-butyl bromide. (10) The NMR absorption at 60 Mc and -30° of the CH_2-Mg···hydrogens in the Grignard reagent is illustrated in Fig. 1a; it consists of the AB portion of the familiar ABX system (11) where $J_{AB} = \pm 12.4$, $J_{AX} = +7.65$ and $J_{BX} = +4.35$ cps respectively and $\delta_A - \delta_B = 0.170$ ppm. The methylene hydrogens are magnetically non-equivalent because H_A is always in an environment different from that around H_B regardless as to the rate of rotation about the CH_2-C (asymmetric) bond. (12-14) Only by exchanging places simultaneously can H_A and H_B become magnetically equivalent. Such an effect could be accomplished by inversion at the Mg-CH_2 - carbon atom. (15) This is indeed the case for with increasing temperature the CH_2-Mg multiplet in the Grignard NMR spectrum collapses to a doublet, A_2X (16) by 70°. See Fig. 1a - e.

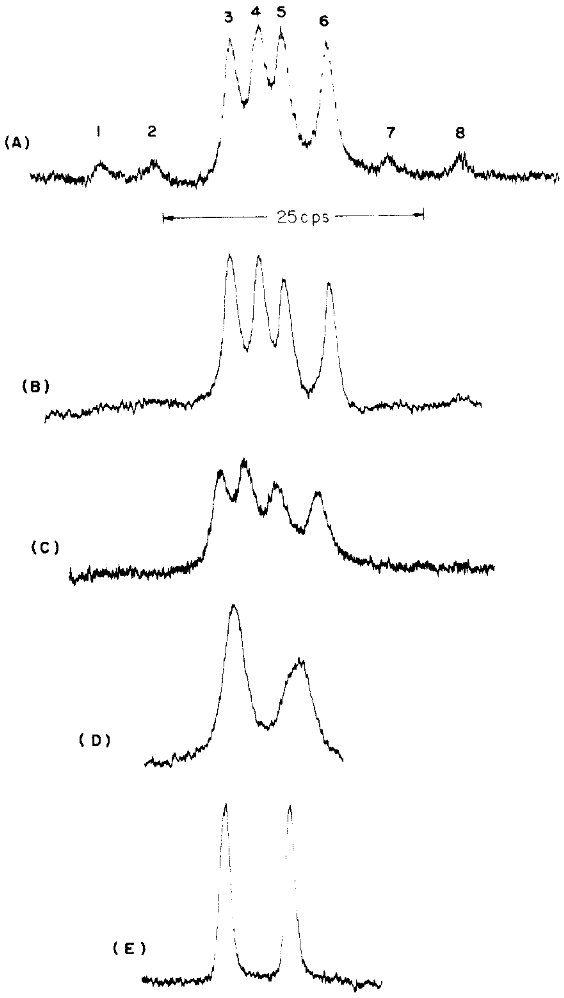

FIG. 1

NMR absorption of CH_2Mg multiplet in 2-methyl-butylmagnesium bromide, 1M, a, -30°; b, -5°; c, 21.5°; d, 40°; e, 70°.

We have calculated inversion frequencies from the line-shapes of the collapsing CH_2-Mg multiplet. At -30° the latter consists of two overlapping AB quartets generated by the spin-states of H_X, $-\overset{|}{C}H_XCH_2Mg$. They are lines 1,3,4, and 7 and lines 2,5,6, and 8 in Fig. 1a. The distance between the quartet centers is $\frac{1}{2}(J_{AX} + J_{BX})$. It is assumed that during an inversion the spin states of the methylene hydrogens do not change. Hence with rapid inversion the quartets collapse independently to single lines at their center. (17) Using Saunders' computor program for determining the line-shape of an AB system undergoing $H_A \rightleftharpoons H_B$ exchange at different rates (18) we have superposed the line-shapes for the two collapsing quartets described above and compared the calculated spectra with the observed results. At 25° the mean lifetimes between inversions is 2.4×10^{-2} sec, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are 12 ± 1 kcal and -17 ± 3 eu.

We have obtained very similar results for 2-methyl-butyllithium in pentane.

These results indicate that primary Grignard reagents and organolithium compounds undergo rapid inversion at ordinary temperatures.

The kinetics of these processes will be reported later. **Elucidation of the mechanisms of these inversion processes must await completion of these kinetic studies.**

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