Fig. 2.—Oxidation rate of cumene vs. inverse square root of phenol concentration: 5.68 M cumene; $8 \times 10^{-3} M$ AIBN; 57°; 1 atm. of O_2; chlorobenzene diluent.

$\times 10^{-7}$ mole l.$^{-1}$ sec.$^{-1}$), the chain length approaching unity or the inhibitor concentration becoming so low that reliable initial rates cannot be determined.

The following supplementary observations aid in excluding some alternative explanations of the hydroperoxide effect.

1. Cumene hydroperoxide generated by oxidation before addition of inhibitor had exactly the same effect upon the inhibited rate as added hydroperoxide.

2. The inhibition periods with both phenol and diphenylamine are unchanged by hydroperoxide, showing that the observed effect is not due to chain initiation by hydroperoxide.

3. Direct chemical reaction between inhibitors and hydroperoxide is unimportant since the results are unchanged by aging their solutions prior to addition of initiator.

A number of alternative mechanisms have been examined with only one yielding calculated curves at all in agreement with experiment. This exception, which retains Boozer and Hammond's postulate, assumes that hydroperoxide forms a hydrogen bonded complex with inhibitor and that only free inhibitor reacts with $RO_2\cdot$ radicals. Agreement with experiment is obtained for an association constant of 300 l. mole^{-1}. However, infrared studies indicate an association constant between phenol and cumene hydroperoxide of only 12 l. mole^{-1} in carbon tetrachloride at 25°, making this explanation unlikely.

In addition to offering an explanation for the inverse square root inhibitor dependence so often observed with simple amines and phenols the hydroperoxide effect explains the lack of a deuterium kinetic isotope effect for diphenylamine even in the presence of excess deuterium oxide,[5] under which conditions Ingold[6] does find an isotope effect for 2,6-t-butyl cresol. It also explains why hindered phenols are more satisfactory inhibitors in autoxidation systems where chain initiation depends upon hydroperoxide.

By electron spin resonance techniques which permit the quantitative determination of cumylperoxy radical

(6) K. U. Ingold, Nature, **195**, 280 (1962).

concentration in oxidizing cumene,[3] attempts were made to observe the steady-state concentration of the phenoxy radical in phenol inhibited systems. These experiments showed the phenoxy radical concentration to be 10^{-6} M or less even with phenol concentrations as high as 1.0 M. With $k_1 = 4 \times 10^3$ l. mole^{-1} sec.$^{-1}$ from above, $k_3 \geq 4 \times 10^9$ l. mole^{-1} sec.$^{-1}$ and $k_2 \geq 2.3 \times 10^5$ l. mole^{-1} sec.$^{-1}$. The values of these rate constants, particularly that of k_2, seem implausibly large and are the source of some reservation in wholeheartedly adopting this mechanism.

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The Configurational Stability of Primary Grignard Reagents[1]

Sir:

The n.m.r. spectrum of the methylene hydrogens of 3,3-dimethylbutylmagnesium chloride[2] in diethyl ether
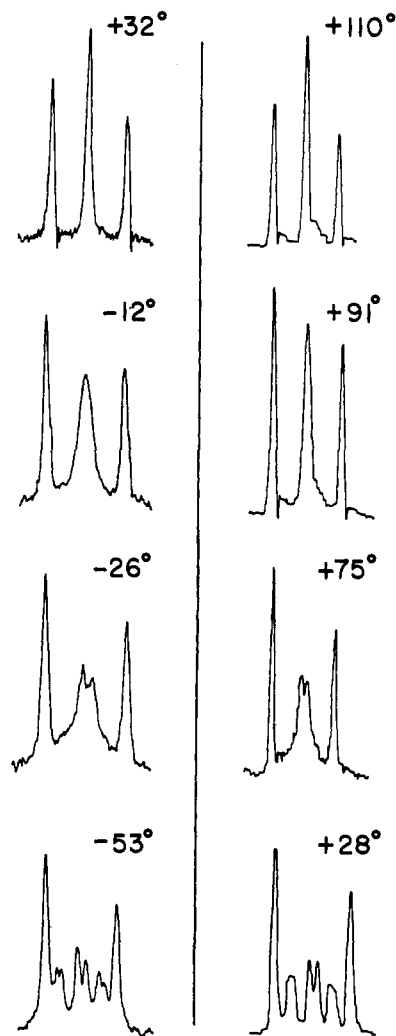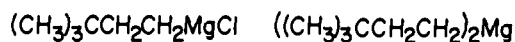
$(CH_3)_3CCH_2CH_2MgCl$ $((CH_3)_3CCH_2CH_2)_2Mg$

+32°   +110°

−12°   +91°

−26°   +75°

−53°   +28°

Fig. 1.—N.m.r. spectra of the $-CH_2-Mg$ protons of 3,3-dimethylbutyl Grignard reagent and bis-(3,3-dimethylbutyl)-magnesium in diethyl ether solution as a function of temperature.
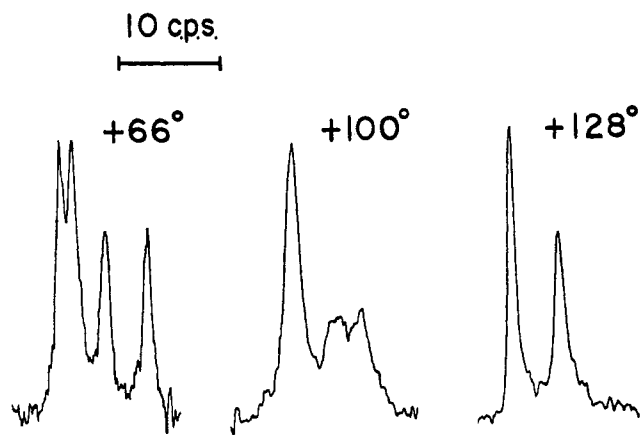
Fig. 2.—N.m.r. spectra of the CH_2–Mg protons of 2-phenyl-3-methylbutyl Grignard reagent in tetrahydrofuran solution as a function of temperature. Only four of eight theoretical lines for the AB part of the spectrum have sufficient intensity to be observed.

solution changes from an A_2X_2-type spectrum at $+33°$ to an $AA'XX'$-type at $-50°$ [3] (Fig. 1). The observation of two distinct vicinal coupling constants at low temperatures indicates that inversion of configuration at the $-CH_2$–Mg center is slow on the n.m.r. time scale, and strongly suggests that the populations of the three conformations (I–III) are not equal
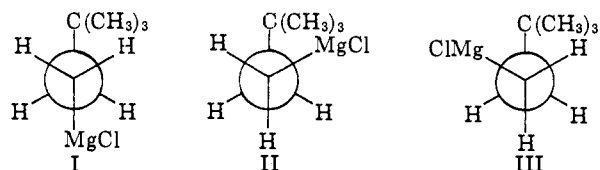
The averaged vicinal coupling constants observed at room temperature might be the result of either rapid inversion of configuration at the carbon carrying the magnesium (such inversion interchanging the relative positions of the hydrogens at the α-carbon of I, II and III) or else a change in populations of the conformations. Incursion of a Schlenk equilibrium,[4] eq. 1, at

$$2RMgX \rightleftarrows R_2Mg \cdot MgX_2 \rightleftarrows R_2Mg + MgX_2 \quad (1)$$
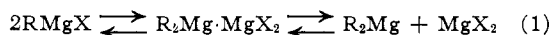
the higher temperature clearly is not responsible for the variation in the spectra, because bis-(3,3-dimethylbutyl)-magnesium[5] shows spectral behavior similar to that of the Grignard reagent (Fig. 1).

We have previously suggested[3] that changes in the rate of inversion were responsible for the changes in the appearance of the spectrum; we now report further evidence supporting this suggestion.

Ten of the twelve theoretical lines for the A part of an $AA'XX'$ spectrum[6] can be identified in the low-temperature spectra in Fig. 1. The 1,2 and 3,4 transitions are easily identified on the basis of intensity and position as the strong outer lines in these spectra; their separation is equal to the sum of the two vicinal coupling constants $J + J'$.[6] On the reasonable assumption

magnesium chloride. For recent discussions of the structure of Grignard reagents, see E. C. Ashby and W. E. Becker, J. Am. Chem. Soc., 85, 118 (1963); G. E. Stucky and R. E. Rundle, ibid., 85, 1002 (1963), and references therein.

(3) J. D. Roberts, paper presented at the Symposium on High-Resolution Nuclear Magnetic Resonance, Boulder, Colorado, July 3, 1962.

(4) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Non-metallic Substances," Prentice-Hall Inc., New York, N. Y., 1954, pp. 104–109.

(5) Prepared from the Grignard reagent by precipitating the magnesium chloride with an excess of dioxan.[4]

(6) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Chapter 6.

that the trans and gauche coupling constants, J_t and J_g, have the same respective values for each conformation (I–III), the separation of the outer lines for I should be $(J_t + J_g)$, while the corresponding separation for a rapidly interconverting mixture of II and III would be $\frac{1}{2}(J_t + 3J_g)$. Therefore, if the averaging of coupling constants observed in the high-temperature spectra is a consequence of changes in conformational populations, the separation of the outer lines would be expected to change appreciably with temperature.[7] Experimentally, no such temperature variation is observed—the separation of the outer lines of the Grignard reagent changes only from 18.2 to 18.4 c.p.s. over the temperature range of Fig. 1; the corresponding separation of the dialkylmagnesium compound remains unchanged at 18.0 c.p.s. We believe these data are incompatible with significant temperature-dependent variation in populations of the conformations.

The n.m.r. spectrum of the methylene group of 2-phenyl-3-methylbutylmagnesium chloride also shows a temperature variation suggesting changes in rate of inversion (Fig. 2). In this case, the inversion at the $-CH_2$–Mg center is slow even at $+66°$ and the two methylene protons are magnetically non-equivalent due to their proximity to a center of molecular asymmetry.[8] As the temperature is increased, the rate of inversion increases until at about $+120°$ the ABX spectrum collapses to an A_2X spectrum.[9] The rates and thermodynamic parameters for the processes which result in the simplification of spectra of these Grignard reagents will be discussed in later papers.

(7) This would be true only, of course, if J_t is substantially different from J_g but this must be so in the present case because otherwise the low-temperature spectrum could only be of the A_2X_2 type.

(8) G. M. Whitesides, F. Kaplan, K. Nagarajan and J. D. Roberts, Proc. Natl. Acad. Sci., 48, 1112 (1962), and references therein.

(9) It has been suggested that the observation of an A_2-type spectrum for the methylene protons of 2-phenylpropylmagnesium bromide indicates that this Grignard reagent is inverting rapidly at room temperature: cf. G. Fraenkel, D. G. Adams and J. Williams, Abstracts of Papers, 143rd National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963, p. 4 M. We have examined the spectrum of this compound and of bis-(2-phenylpropyl)-magnesium at $-75°$ and find that the methylene protons are still magnetically equivalent, although inversion in the latter compound is very probably slow at this temperature. We believe, therefore that no conclusions can be drawn about the rate of inversion of this Grignard reagent from its n.m.r. spectrum.

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The Deamination of Tertiary Carbinamines

Sir:

We wish to report an oxygen-18 and stereochemical study of the nitrosoamide and nitrous acid deaminations of 2-phenyl-2-butylamine. Only one other example of the deamination of an optically active, acyclic, tertiary carbinamine has been reported in the literature; in that study, Arcus, Kenyon and Levin found that the nitrous acid deamination of optically active phenyltolylnaphthylcarbinylamine yielded inactive alcohol.[1]

In the present work, 2-phenyl-2-butylamine was fully resolved via the tartrate salt,[2] and the salt was converted into optically pure N-(2-phenyl-2-butyl)-benzamide ($[\alpha]^{25}D$ $+19.2°$ for one enantiomer and $-19.2°$ for the other (c 7.0, $CHCl_3$)). The rotation of the free amine was determined (less accurately) to be $[\alpha]^{25}D$ $-15.7°$ (neat, 1 dm.). $(+)$-2-Phenyl-2-methylbutanoic acid

(1) C. L. Arcus, J. Kenyon and S. Levin, J. Chem. Soc., 407 (1951).

(2) We thank Professor C. H. DePuy for furnishing seed crystals of the partially resolved material.