As shown in Figure 1, very ordinary intrinsic viscosity-molecular weight slopes not greatly different from those of polydimethylsiloxane[7] were obtained, except, of course, that the viscosity for a given molecular weight is much lower for the resin system, as was to be expected.[8] The high slope observed by Brown possibly resulted from the incompletely equilibrated nature of his products. We suspect that his high molecular weight fractions were of the 250° variety and that the lower molecular weight fractions were the accompanying "prepolymer" previously prepared at much lower temperature. Attempts to fit a line between such fractions could easily account for the steep slope reported.

It is thus evident that the soluble resins which Brown, et al., obtained by equilibration (sic) at high solids were not, in fact, true equilibrates. They were instead materials which had been equilibrated at lower concentrations, but which had not yet actually reached equilibrium at the higher concentrations employed for the preparation of the so-called high molecular weight ladder structure. This accounts for the anomalous nature of the previous work in which yields and molecular weight of the soluble polymer were a function of equilibration time.

The weight of our evidence supports a more or less randomly linked array of polycyclic cages for the structure of polymeric $PhSiO_{3/2}$. At sufficiently high dilutions, equilibration results in a high proportion of oligomeric cages which are completely closed, zero-functional entities (i.e., the lower oligomers T_{8-14}). The polymer is built up largely from random combinations of incompletely closed cages, the functionality of which can vary, i.e., they can be monofunctional, difunctional, trifunctional, etc.[9] While the average functionality of the polycyclic components in these soluble polymers must be 2.0 or less, at the critical gel point their average functionality exceeds 2.0 and gel phase appears.[10] This view has the added virtue of assigning common structural features to both the oligomer and polymer portions of the resin solution. In contrast to the highly ordered nature of the ladder structure, the structure herein proposed exhibits only short-range order (i.e., the partially opened polycyclic cage moieties) while being essentially random on a larger scale.

(7) (a) A. J. Barry, *J. Appl. Phys.*, **17**, 1020 (1946); (b) P. J. Flory, L. Mandelkern, J. B. Kinsinger, and W. B. Shultz, *J. Amer. Chem. Soc.*, **74**, 3364 (1952).

(8) F. P. Price, S. G. Martin, and J. P. Bianchi, *J. Polym. Sci.*, **22**, 41 (1956).

(9) While the zero-functional cages must necessarily involve an even number of T units, the mono- or trifunctional cages must be made up of an odd number of units (e.g., monofunctional PhT_9).

(10) Additional evidence for this view rests on related work with $ViSiO_{3/2}$ equilibrates which will be documented in a subsequent paper by J. C. Saam, W. T. Collins, and C. L. Frye.

(11) Details of this and related silsesquioxane characterization will be published elsewhere by C. L. Lee and O. W. Marko.

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Direct Evidence for the Reactive Species, and Their Reaction Orders, in the Addition Reaction of Methylmagnesium Bromide Grignard to 2-Methylbenzophenone

Sir:

We report here the first direct determination of the reaction order of a Grignard reagent in its reaction with a ketone. In the reaction of methylmagnesium bromide with 2-methylbenzophenone the reaction proceeds by two paths, one first order in CH_3MgBr and the other first order in $(CH_3)_2Mg$.

When methylmagnesium bromide is allowed to react with excess 2-methylbenzophenone, an absorption band appears immediately in the 400–600-mμ region of the spectrum, a region in which neither ketone nor methylmagnesium bromide absorb. The rate of disappearance of this band, attributed to a complex between ketone and CH_3MgBr, was measured at 410 mμ, and through quenching experiments it was shown that the initial rate of formation of the product was equal to the initial rate of disappearance of the absorption band at 410 mμ. Although the change in absorbance over the entirety of the reaction did not adhere to any simple integral order behavior, meaningful rate constants were obtained by treating the initial disappearance of the complex in a pseudo-first-order fashion. The validity of this treatment is demonstrated by the constancy of initial rate constants obtained with varying concentrations of methylmagnesium bromide at constant excess ketone ($[K]_0 = 0.445$; $[G]_0 = 0.0236-0.00748 M$; initial $k_{obsd} = 0.0100 \pm 0.0004 \text{ sec}^{-1}$).

The initial rate data were treated according to the model
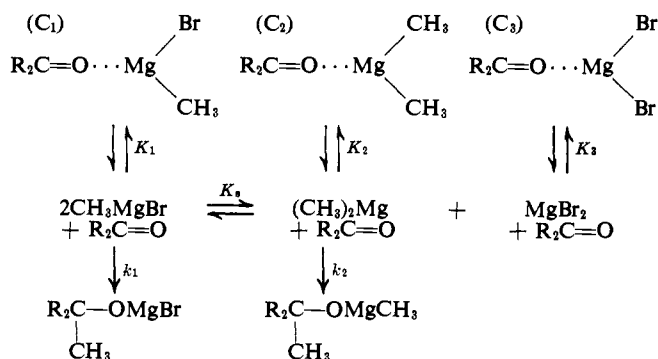
where $K_s = 0.0022$, $K_1 = 1.35 \text{ l. mol}^{-1}$, $K_3 = 4 \pm 1 \text{ l. mol}^{-1}$, and $k_2 = 0.270 \text{ l. mol}^{-1} \text{ sec}^{-1}$. In experiments in which the absorbance at 410 mμ is measured, it is assumed that in the initial stages of the reaction the absorption is due solely to C_1. According to this model the initial rate of change of absorbancy is given by eq 1.

$$-\frac{d[C_1]}{dt} = \frac{(k_2\sqrt{K_s(1 + K_3[K])} + k_1)[K]}{(1 + K_1[K] + 2\sqrt{K_s(1 + K_3[K])}}[C_1]_0 \quad (1)$$

The value of the equilibrium constant K_1 was obtained from the kinetic data by extrapolating the absorbancy values to zero time, and relating these values to the reactant concentrations by methods similar to those in the literature.[1] Since mixtures of $MgBr_2$

(1) (a) R. L. Scott, *Recl. Trav. Chim. Pays-Bas*, **75**, 787 (1956); (b) J. Billet and S. G. Smith, *J. Amer. Chem. Soc.*, **90**, 4108 (1968).
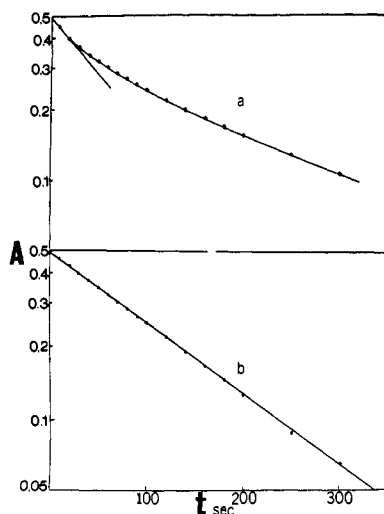
Figure 1. Plot of the reaction of 0.462 M 2-methylbenzophenone with 0.124 M methylmagnesium bromide: (a) with no added magnesium bromide; (b) in the presence of 0.0480 M magnesium bromide demonstrating the first-order behavior of the species CH_3MgBr.

and ketone do not absorb at 410 mμ, the equilibrium constant K_3 could not be evaluated in the media of high ketone concentration, but could be evaluated from spectral data at 305 mμ using 0.00088 M ketone and 0.0232–0.116 M magnesium bromide. The value of the rate constant k_2 was taken from our earlier work with dimethylmagnesium.[2] Variations in the zero time absorbancy caused by addition of $MgBr_2$ indicated a value of 0.0022 for the Schlenk constant K_s.

Using the values for the constants as stated above, k_1, the bimolecular rate constant for the reaction of CH_3MgBr with 2-methylbenzophenone,[3] was computed. A consistent value for k_1 should arise in separate experiments if the model properly describes the system and if all the constants employed are accurate. The results shown in Table I give a surprisingly consistent

Table I. Rate Constants, k_1, Calculated for the Reaction of CH_3MgBr with 2-Methylbenzophenone[a]

$[K]_0$	Initial k_{obsd}, sec^{-1}	k_1, l. mol^{-1} sec^{-1}
0.128	0.00445	0.0284
0.230	0.00685	0.0253
0.343	0.00879	0.0215
0.448	0.0108	0.0213
0.563	0.0138	0.0245
0.668	0.0149	0.0222
0.892	0.0217	0.0314
1.10	0.0262	0.0349
	Av	0.0261 ± 0.004

[a] $[G]_0 = 0.0124 \ M$, $K_s = 0.0022$.

value for k_1 in experiments in which the ketone concentration is varied.

If this model is correct, it should be possible to obtain more directly an experimental value for k_1 by adding

(2) J. Laemmle, E. C. Ashby, and H. M. Neumann, *J. Amer. Chem. Soc.*, in press.
(3) This does not imply that the reaction of CH_3MgBr with ketone occurs exclusively by bimolecular collision as this cannot be determined by kinetics. It is convenient for computational purposes to use the bimolecular constant. If reaction occurs by rearrangement of the complex, then the unimolecular constant $k_u = k_1K_1$.

additional magnesium bromide to the reaction mixture, thus driving the Schlenk equilibrium far enough to the left so that the amount of dimethylmagnesium is insignificant. As magnesium bromide is increased in amount in a set of experiments at a constant excess of ketone, two effects are observed: (1) the observed initial rate constants decrease to a certain value, then remain constant regardless of the excess of magnesium bromide employed, and (2) the first-order plots become linear. The results of such a set of experiments are shown in Table II, and two individual experiments are

Table II. Reaction of 0.124 M Methylmagnesium Bromide with 0.462 M 2-Methylbenzophenone in the Presence of Added Magnesium Bromide

$[MgBr_2]$	Initial k_{obsd}, sec^{-1}	Ratio of $MgBr_2$:Gri-gnard	k_1,[c] l. mol^{-1} sec^{-1}
0.0480	0.00680[a]	4:1	0.0251
0.0250	0.00672[a]	2:1	0.0243
0.0120	0.00672[b]	1:1	0.0239
0.00623	0.00693		
0.00268	0.00872	Av	0.0244 ± 0.0004
0.00156	0.00930		
0.000	0.0105		

[a] First-order plot linear for >80% reaction. [b] First-order plot linear for 30% reaction. [c] Calculated by use of the equation $k_1 = k_{obsd}(1 + K_1[K])/[K]$ where [K] is a corrected value which takes into account the ketone which is complexed by $MgBr_2$.

shown in Figure 1.

The absolute amount of free ketyl formed in the reaction is apparently very small since product studies under the actual conditions of the kinetics gave 100% yield of addition product. In addition, uv analysis shows that the rate of formation of the ketyl is much slower than the rate of alkylation. These conclusions apply strictly to the system studied.

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2,3,4,4-Tetramethyloxetene. Kinetics of Rearrangement Compared to Cyclobutene–Butadiene Conversions

Sir:

Molecules in which a methylene group is replaced by an oxygen atom sometimes possess properties very different from those of their all-carbon analogs. Some examples are α-pyranes[1] which, contrary to cyclohexadienes, exhibit photo- and thermochromic behavior in certain compounds, oxirenes[2] which are orders of magnitude less stable to unimolecular rearrangement than cyclopropenes, and dioxetanes[3] which fragment with the production of light, whereas cyclobutanes fragment with much larger activation energies without luminescence.

(1) J. B. Flannery, Jr., *J. Amer. Chem. Soc.*, **90**, 5660 (1968), and examples cited therein.
(2) G. Frater and O. P. Strausz, *ibid.*, **92**, 6654 (1970).
(3) (a) K. R. Kopecky and C. Mumford, *Can. J. Chem.*, **47**, 709 (1969); (b) E. H. White, J. Wiecko, and D. R. Roswell, *J. Amer. Chem. Soc.*, **91**, 5194 (1969); (c) P. D. Bartlett and A. P. Schaap, *ibid.*, **92**, 3223 (1970); (d) S. Mazur and C. S. Foote, *ibid.*, **92**, 3225 (1970).