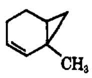
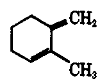
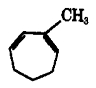
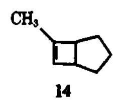
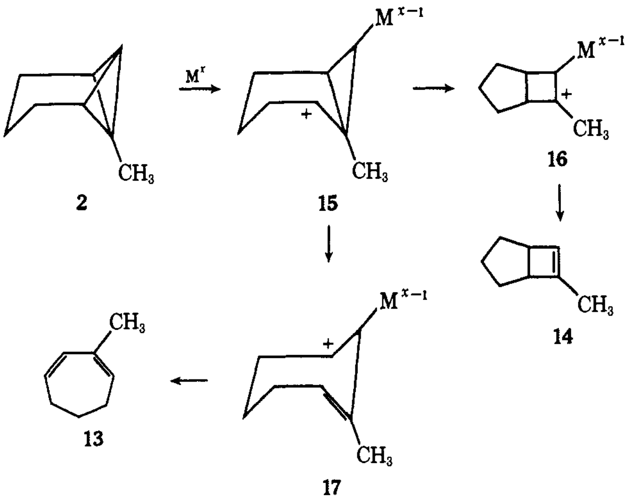
Table II. Metal-Promoted Isomerizations of 1-Methyltricyclo[4..1.0.$0^{2,7}$]heptane

		% yield of products			
Catalyst	Conditions temp, time, solvent	 11	 12	 13	 14
$[Rh(CO)_2Cl]_2$	25°, 15 min, $CHCl_3$		96		
$[Ir(CO)_3Cl]_2$	25°, 14 hr, $CHCl_3$		93		
$[(\pi\text{-allyl})PdCl]_2$	25°, 30 min, $CHCl_3$		93		
$[C_6F_5Cu]_4$	25°, 6 hr, $CHCl_3$		56		
ZnI_2	25°, 16 hr, Et_2O			48	12
$HgBr_2$	60°, 24 hr, Et_2O			24	42
$SnCl_2 \cdot 2H_2O$	60°, 24 hr, Et_2O	53			

This is the same ratio of ethers as was found in the methanolysis of **1** catalyzed by sulfuric acid.[13] This indicates to us that transition metal carbonyls can behave as Lewis acid catalysts. Furthermore, the trapping of a carbonium ion type intermediate by nucleophilic solvent tends to support our hypothesis that multiple bond cleavage promoted by transition metal catalysts is a stepwise process leading in some instances to **3**.

Table II lists the products observed in the reaction of various catalysts with **2**.[14] Comparison of Table I with Table II shows that the rearrangement of **1** was very similar to the rearrangement of **2** with most catalysts. The exceptions were zinc iodide and mercuric bromide which gave 6-methylbicyclo[3.2.0]hept-6-ene (**14**) as an added product. The formation of **14** adds support to the stepwise hypothesis advanced above. Initial attack of the catalyst on **2** would be expected to yield the cyclopropylcarbinyl cation **15**. A cyclopropylcarbinyl–cyclobutyl cation rearrangement would now produce the *tertiary* cation **16**,[15] which would yield **14** on the loss of M^x. The formation of **13** could be readily explained on the basis of a **2** → **15** → **17** → **13** reaction pathway.



We feel that the data presented in this communication offer support for the reasonable hypothesis that the transition metal promoted rearrangement of highly strained polycyclic systems is a stepwise process in which the transition metal complex acts like a Lewis acid. We feel that our observations indicate the inadequacy of those mechanisms for transition metal catalyzed rearrangements of certain highly strained polycyclics in which metal ions "promote facile [$_\sigma2_a$ + $_\sigma2_a$] skeletal rearrangement."

The major question which remains to be answered is how the different catalysts control the eventual product-forming step of the reaction. We are continuing to investigate this aspect of these intriguing rearrangements.

Acknowledgment. We are indebted to the National Science Foundation and to the Alfred P. Sloan Foundation for support of this work.

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[13] K. B. Wiberg and G. Szeimies, *J. Amer. Chem. Soc.*, **92**, 571 (1970).

[14] Satisfactory elemental analyses have been obtained on all new compounds. Compounds **11**, **13**, and **14** were independently synthesized. The details of these syntheses will be reported in a full paper.

[15] Alternately, **16** could be formed by the homoallylic participation of the double bond of **17**.

[16] National Science Foundation Trainee, 1968–1971.

Concerning the So-Called "Ladder Structure" of Equilibrated Phenylsilsesquioxane

Sir:

In a communication to this journal a decade ago,[1] the alkaline equilibration of phenylsilsesquioxane, $(PhSiO_{3/2})_x$, was reported to yield a highly ordered, thermodynamically stable, stereoregular, linear double-chain structure. Subsequent papers,[2] patents,[3] and textbook references[4] in the intervening years indicate that widespread acceptance this view has been achieved. The above notwithstanding, we report herein recent ob-

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[1] J. F. Brown, Jr., L. H. Vogt, Jr., A. Katchman, J. W. Eustance, K. M. Kiser, and K. W. Krantz, *J. Amer. Chem. Soc.*, **82**, 6194 (1960).

[2] (a) J. F. Brown, Jr., *J. Polym. Sci., Part C*, No. 1, 83 (1963); (b) K. A. Andrianov, G. A. Kurakov, F. F. Sushentsova, V. A. Myagkov, and V. A. Avilov, *Polym. Sci. USSR*, **7**, 1637 (1965); (c) V. N. Tsvetkov, K. A. Andrianov, Ye. L. Vinogradov, V. I. Pakhomov, and S. Ye. Yakushkina, *ibid.*, **9**, 1 (1967); (d) V. N. Tsvetkov, K. A. Andrianov, I. N. Shtennikova, G. I. Okhrimenko, L. N. Andreyeva, G. A. Fomin, and V. I. Pakhomov, *ibid.*, **10**, 636 (1968); (e) T. E. Helminiak, G. L. Benner, and W. E. Gibbs, *Polym. Prepr. Amer. Chem. Soc., Div. Polym. Chem.*, **8**, 284 (1967); (f) O. Quadrat, *Collect. Czech. Chem. Commun.*, **35**, 2564 (1970).

[3] (a) J. F. Brown, Jr., and L. H. Vogt, Jr., U. S. Patent 3,017,386, Jan 16, 1962; (b) A. Katchman, U. S. Patent 3,162,614, Dec 22, 1964; (c) K. W. Krantz, U. S. Patent 3,294,717, Dec 27, 1966; (d) K. W. Krantz, U. S. Patent 3,294,737, Dec 27, 1966; (e) K. W. Krantz, U. S. Patent 3,294,738, Dec 27, 1966; (g) K. W. Krantz, U. S. Patent 3,318,844, May 9, 1967; (g) K. W. Krantz, U. S. Patent 3,372,133, March 5, 1968.

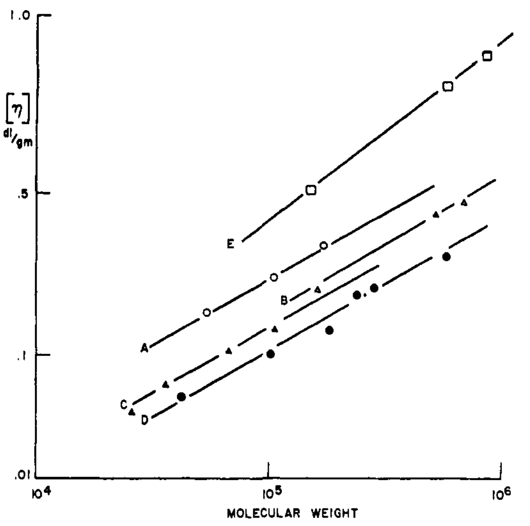

Figure 1. The relationship of molecular weight to intrinsic viscosity (25°, toluene) for fractionated silsesquioxanes equilibrated at different temperatures: (A) phenylsilsesquioxane equilibrated at 250° in diphenyl ether, (B) phenylsilsesquioxane equilibrated at 150° in *o*-xylene, (C) phenylsilsesquioxane equilibrated at 150° in diphenyl ether, (D) vinylsilsesquioxane equilibrated at 80° in benzene, and (E) polydimethylsiloxane.

servations that compel us to reject outright the validity of the previous structural conclusions.

Contrary to earlier claims,[1-4] *true* equilibration[5] of $PhSiO_{3/2}$ at high concentrations (>70%) does *not* yield a soluble product. Gelation of this system occurs reproducibly and reversibly whenever the critical gel point concentration is exceeded. Since the gel point should and does depend mainly on the volume fraction of the silsesquioxane solute, solvents of different density yield different gel points when the concentrations are expressed in terms of weight percentages. Thus the gel point in *o*-xylene (d_4^{20} 0.8968) at 150° is 58 wt %, while the gel point at the same temperature in diphenyl ether (d_4^{20} 1.0748) decreases to 54%. Although there may be some subtle polymer–solvent polar effects, when the solvent density differences are taken into account it is evident that these two solutions are gelling at comparable $PhSiO_{3/2}$ volume fractions. Similarly, the gel point is raised at higher temperatures, since the density of the system decreases with increasing temperature. Thus, the gel point in diphenyl ether expressed in terms of weight percentage of $PhSiO_{3/2}$ climbs to 67% at 250°; this gelation is easily reversible—*i.e.*, a solution just below the gel point at 250° gels upon lowering the temperature, and the gel which forms redissolves upon returning to the higher temperature. Consistent with the above discussion, gel permeation chromatography of aliquots of a given resin solution brought to equilibrium at each of several temperatures showed the anticipated shift of the molecular weight distribution to lower values at higher temperatures. In an attempt to determine whether this effect derives wholly from the decreased density accompanying the temperature increase, a catalyzed diphenyl ether solution of $PhSiO_{3/2}$ was divided into two equal portions at 250°, one of which was cooled to 150° and then adjusted to its "250° volume" with additional diphenyl ether; after reaching equilibrium at the indicated temperatures, these two equimolar solutions were then neutralized by the addition of Me_3SiCl. Subsequent gel permeation chromatographic analysis revealed a substantially lower molecular weight distribution for the 250° equilibrate, indicating the existence of a temperature effect over and above that expected for the volume change of just the solvent. This additional effect is attributable to the expansion of the resin itself; *i.e.*, the equilibrium volume of the individual $(PhSiO_{3/2})_x$ polymer molecules increases with increasing temperature. The net effect of this change in the "inherent density" of the solute is to shift the molecular weight distribution to an even lower value as the silsesquioxane skeleton of the polymeric substrate undergoes structural reorganization in order to utilize the increased available space more effectively. An inverse relationship between temperature and molecular weight in equilibrating systems is not without precedent,[6] and, in fact, we know of no instance in which the opposite obtains, *i.e.*, where increased temperature yields increased molecular weight distributions (at equilibrium).

In consequence of the above solute density change (*i.e.*, the altered volume of the polymeric solute), silsesquioxane resins which have been equilibrated at greatly different temperatures may be expected to exhibit somewhat different physical properties (T_g, infrared absorption, rheology, intrinsic viscosity, etc.), even if fractions of similar molecular weight distribution are compared. Consistent with this expectation, $(PhSiO_{3/2})_x$ resins equilibrated just below the 250 and 150° gel points in diphenyl ether do indeed *appear* to be demonstrably different as evidenced by the parallel, but distinctly separate, intrinsic viscosity–molecular weight plots shown in Figure 1; *i.e.*, fractions of the higher temperature product *appear* able to occupy more volume than low-temperature fractions of comparable molecular weight. For purposes of comparison, a curve for an 80° $ViSiO_{3/2}$ equilibrate is also shown; the appreciably lower intrinsic viscosities (*i.e.*, tighter structures) of these fractions *may* be a consequence of the lower equilibration temperature. Future studies should be aimed at verification and demonstration of this presumably very general temperature effect on the physical properties of resinous equilibrates.

The ladder structure was offered not only to account for the *supposed* solubility of the "equilibrated" polymer, but also to explain the unusually steep slope of log–log plots of intrinsic viscosity *vs.* molecular weight.[1]

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(4) (a) R. J. Cotter and M. Matzner, "Ring-Forming Polymerizations, Part A," Academic Press, New York, N. Y., 1969, see especially pp 318–321; (b) O. J. Sweeting, Ed., "The Science and Technology of Polymer Films," Interscience, New York, N. Y., 1968, pp 219–220; (c) J. R. Van Wazer, "High Temperature Polymers," C. L. Segal, Ed., Marcel Dekker, New York, N. Y., 1967, p 36; (d) W. R. Sorenson and T. W. Campbell, "Preparative Methods of Polymer Chemistry," Interscience, New York, N. Y., 1968, pp 389–390.

(5) The equilibrations discussed herein employed KOH at a level of 1 K/300 Si. The end blocks produced by the catalyst at these low levels were shown to have negligible influence on the molecular weight distribution which is controlled predominantly by the variables of dilution and temperature. When the end-block level exceeds approximately 1/100 Si, their effect can then no longer be safely ignored. The effects of end-block level were conveniently assessed by the inclusion of appropriate amounts of $PhSi(OR)_3$ in the equilibrating system and subsequent gel permeation chromatography analysis of the resulting molecular weight distributions. Periodic gel permeation chromatography assay was used throughout this work to establish that equilibrium had indeed been achieved, the criterion being reproducible and constant molecular weight distributions for any set of conditions.

(6) C. L. Frye, *J. Org. Chem.*, **34**, 2496 (1969).

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.

Acknowledgment. We are pleased to acknowledge our indebtedness to our colleagues C. L. Lee and O. W. Marko for the determination of the solution properties[11] described herein.

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[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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Received May 21, 1971

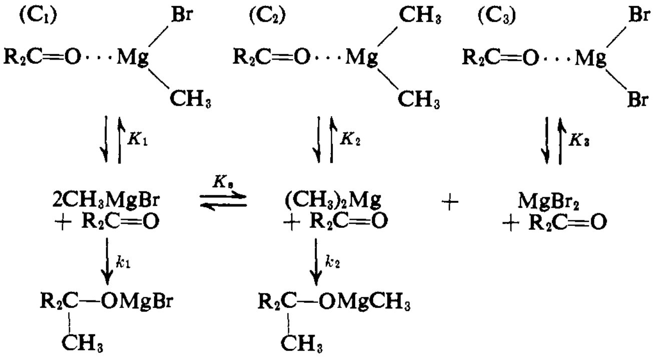
Direct Evidence for the Reactive Species, and Their Reaction Orders, in the Addition Reaction of Methylmagnesium Bromide Grignard to 2-Methylbenzophenone

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 $k_{obsd} = 0.0100 \pm 0.0004$ sec^{-1}).

The initial rate data were treated according to the model



where $K_s = 0.0022$, $K_1 = 1.35$ l. mol^{-1}, $K_3 = 4 \pm 1$ l. mol^{-1}, and $k_2 = 0.270$ l. mol^{-1} 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 $MgBr_2$

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[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).