mation (colorless needles): m.p. 79–80°; $\nu_{\max}^{\text{Nujol}}$ 3070 (cyclopropyl–hydrogen), 860, and 825 cm.$^{-1}$ (cyclopropyl ring).[13] The near-infrared spectrum (0.204 *M* CS_2 solution) displayed a maximum at 1.662 μ (ϵ 0.956) which is consistent with a nortricyclene-type structure.[11] The n.m.r. spectrum (in CS_2) shows no signals downfield from τ 6.0 while the signal farthest upfield has a τ value of 8.84 (triplet, cyclopropyl protons, integrated for two protons).

Anal. Calcd. for $C_{15}H_{24}N_2O_2$: C, 68.14; H, 9.15; N, 10.60. Found: C, 68.05; H, 9.41; N, 10.54.

Reaction of 5-Bicyclo[2.2.1]hepten-2-one (23) with Hexamethylenimine.—The reaction between 3.58 g. (0.033 mole) of 5-bicyclo[2.2.1]hepten-2-one[35] and 6.55 g. (0.066 mole) of hexamethylenimine in 75 ml. of xylene was carried out in the same manner as that described above for its reaction with morpholine. Five different products were found to be present upon distillation. Their structures and relative amounts were ascertained by using their infrared spectra and boiling points, and hydrolysis (of enamines) followed by isolation of the hydrolysis products. No nortricyclene-type compound was found among the products. The boiling point range, products isolated, and yields follow: b.p. 83–86° (0.45 mm.), 5-N-hexamethyleniminobicyclo[2.2.1]-hept-2-ene (8%) and 2-N-hexamethyleniminobicyclo[2.2.1]-hepta-2,5-diene (11%); b.p. 125–130° (0.25 mm.), 5-N-hexamethyleniminobicyclo[2.2.1]heptan-2-one (**18**) (7%); b.p. 163–172° (0.25 mm.), 2,5-bis(N-hexamethylenimino)bicyclo[2.2.1]-hept-2-ene (11%) and 2,5-bis(N-hexamethylenimino)bicyclo-[2.2.1]heptane (**19**) (10%).

3-N-Morpholinotricyclo[2.2.1.0^{2,6}]heptane (25).—A stirred mixture of 13.0 g. (0.12 mole) of tricyclo[2.2.1.0^{2,6}]heptan-3-one and 10.8 g. (0.12 mole) of morpholinium fluoroborate was refluxed in benzene with a Dean–Stark trap for 48 hr. The crude solid product was isolated by filtration. This solid salt was treated with an excess of lithium aluminum hydride in ether, and the stirred slurry was refluxed for 20 hr. The product was worked up in the usual manner, and upon distillation a total of 8.2 g. (38% yield) of colorless liquid product was obtained: b.p. 91–92° (2.9 mm.); $\nu_{\max}^{\text{film}}$ 3080 (cyclopropyl–hydrogen), 880 (s), 840 (m), and 810 (s, cyclopropane) cm.$^{-1}$. The near-infrared spectrum (0.537 *M* CS_2 solution) showed a maximum at 1.660 μ (ϵ 1.14) which further confirms the nortricyclene-type structure.[11]

Anal. Calcd. for $C_{11}H_{17}NO$: C, 73.71; H, 9.56; N, 7.82. Found: C, 73.92; H, 9.31; N, 7.87.

Nuclear Magnetic Resonance Spectra of the Bornyl and Norbornyl Grignard Reagents[1]

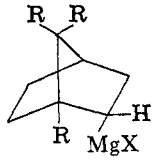
E. ALEXANDER HILL

School of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

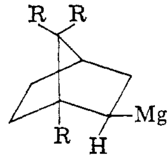
Received January 12, 1965

The n.m.r. spectra of the Grignard reagents from bornyl and norbornyl chlorides show that both Grignard reagents consist of a mixture of *exo* and *endo* isomers. The isomers of the bornyl Grignard reagent can be equilibrated by heating; no estimate has yet been obtained of the equilibration rate of the norbornyl isomers.

The Grignard reagents (**1a** and **2a**) from bornyl and isobornyl chlorides have been investigated by Vavon, Riviere, and de Botton.[2] On the basis of product studies (primarily carbonation) under a variety of conditions, they concluded that these Grignard reagents are similar mixtures of the *exo* and *endo* isomers. These appeared to interconvert on heating in xylene and other high-boiling solvents, but to maintain their stereochemical identity at room temperature. Vavon and Thiec[3] concluded that the corresponding lithium compounds are more rapidly equilibrated. Walling and Buckler,[4] in a study primarily concerned with oxygenation of the Grignard reagent from bornyl chloride, confirmed part of the experimental work of Vavon and Riviere. However, since different product mixtures are formed in oxygenation and carbonation, they preferred the interpretation that the "isomerization" of the Grignard reagent by heating might rather involve a change in coordination of the Grignard reagent with change in solvent, which leads to an altered stereochemistry of carbonation.



1a, R = CH_3
b, R = H



2a, R = CH_3
b, R = H

Sauers[5] investigated the products from carbonation and oxygenation of the Grignard reagent (**1b** and **2b**) from norbornyl bromide. He suggested that his results might best be interpreted if the *exo* and *endo* forms of that Grignard reagent exist in a mobile equilibrium.

We have determined the n.m.r. spectra of the bornyl and norbornyl Grignard reagents, the former under a variety of conditions. Both of these consist of a mixture of *exo* and *endo* isomers. The two bornyl isomers are indeed quite slowly interconverted, but we have not obtained unambiguous information about the norbornyl Grignard, except their interconversion is slow enough at about 110° so as not to produce spectral broadening.

Results and Discussion

The α-hydrogen n.m.r. spectra of the norbornyl and bornyl Grignard reagents are reproduced in Figures 1a and b. These reagents were prepared in tetrahydrofuran (THF) from sublimed magnesium. In each case, the spectrum consists of two multiplets. By analogy with the relative chemical shifts and fine structure of other isomeric bicyclo[2.2.1]heptyl pairs, we assign the multiplet at higher field to the *endo* hydrogen of the *exo* isomer.[6] The difference in chemical shift, 0.40 p.p.m. in each case, is in the range previously

---

[1] Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

[2] (a) C. Riviere, *Ann. Chim.* (Paris), **1**, 157 (1946); (b) G. Vavon and C. Riviere, *Compt. rend.*, **220**, 286 (1945); (c) G. Vavon and M. de Botton, *ibid.*, **236**, 290 (1953); **237**, 729 (1953); (d) M. de Botton, *Ann. Chim.* (Paris), **10**, 455 (1955); (e) M. de Botton, *Bull. soc. chim. France*, 372 (1958).

[3] G. Vavon and J. Thiec, *Compt. rend.*, **233**, 1290 (1951); J. Thiec, *Ann. Chim.* (Paris), **9**, 51 (1954).

[4] C. Walling and S. A. Buckler, *J. Am. Chem. Soc.*, **77**, 6093 (1955).

[5] R. R. Sauers and G. T. Kwiatkowski, *J. Org. Chem.*, **27**, 4049 (1962).

[6] (a) J. I. Musher, *Mol. Phys.*, **6**, 93 (1963); (b) T. J. Flautt, and W. F. Erman, *J. Am. Chem. Soc.*, **85**, 3212 (1963).

found.[6] Approximate chemical shifts of the α-hydrogens of the norbornyl Grignard are τ 10.15 and 10.55. Those of the bornyl and isobornyl reagents are τ 9.8 and 10.2; methyl groups are at τ 9.15 and 9.2.

First-order analyses of the spin–spin splittings lead to the results in Table I.[7] Assignments are based on analogy with other bicyclo[2.2.1]heptanes.[6,8] Coupling constants to hydrogens on the 3-carbon are somewhat larger than those reported for other bicyclo[2.2.1]-heptanes, as should be expected from the low electronegativity of magnesium.[9] We note, as does Musher[6a] for substituted bicyclo[2.2.1]heptan-2-ols, that the *exo–exo* coupling constants are distinctly greater than the *endo–endo* ones. The smallest of three apparent coupling constants in the *endo*-norbornyl Grignard (~3.5 c.p.s.) might be assigned either to coupling to the bridgehead or to long-range coupling to the *exo*-6-hydrogen. The other of these is less than 1.5 c.p.s. We prefer assignment of the observed coupling constant to the bridgehead hydrogen, since this appears to be the larger in other substituted bicyclo[2.2.1]-heptanes.[6,8,10] It should be noted that the coupling constants reported may be somewhat in error if the coupling constant between the *exo* and *endo* 3-hydrogens is comparable with their difference in chemical shifts.[6] However, the similarity to the results of Musher,[6a] despite the substantial difference in electronegativity between magnesium and hydroxyl, makes it likely that the coupling constants are fairly reliable.

TABLE I

SPIN–SPIN COUPLING CONSTANTS[a] OF THE 2-HYDROGENS OF BORNYL AND NORBORNYL GRIGNARD REAGENTS

		Coupled hydrogen				
Compd.	No.	1	*exo*-3	*endo*-3	*exo*-6	*anti*-7
Bornyl	**1a**	...	13	6	2.5	...
Isobornyl	**2a**	...	8	10.5	(0)	...
endo-Norbornyl	**1b**	*b*	12	6.5	*b*	(0)
exo-Norbornyl	**2b**	(0)	7.5	9.5	(0)	2

[a] Apparent coupling constants based on first-order analysis; probably ±0.5 c.p.s. [b] A coupling constant of 3.5 c.p.s. is observed, but assignment is not certain.

Several additional experiments were carried out with the Grignard reagent from bornyl chloride (**1a** and **2a**) for comparison with the carbonation studies of Vavon, *et al.*[2] For these, the reagent was prepared in ether, using "Grignard reagent" grade magnesium. A clear, very pale yellow solution could be removed by syringe after the dark suspended matter had settled overnight. To avoid the complication from the ether side bands, the solvent was replaced by tetrahydrofuran for observation of the spectra. Perturbation of the base line by the nearby strong methyl resonances made it impossible to obtain accurate measures of the relative amounts of the two isomers present, but the estimates given below are believed to reflect changes in composition semiquantitatively. For solutions which should be expected to have similar compositions, or for duplicate spectra on the same or identical solutions, estimates varied by about 5%. Absolute accuracy is undoubtedly poorer.[11]

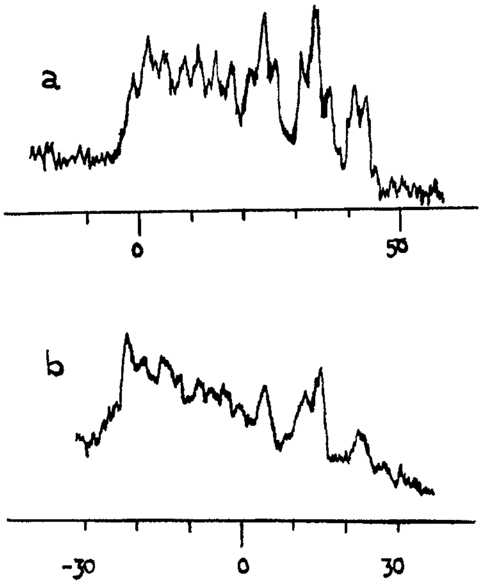


Figure 1.—Hydrogen resonance of (a) norbornylmagnesium chloride; (b) bornyl- and isobornylmagnesium chloride in tetrahydrofuran at 37°. Concentrations of both reagents are about 1.5 *M*. The scale is in cycles per second relative to tetramethylsilane. The spectra shown are somewhat saturated owing to high radiofrequency field levels.

The Grignard reagent as initially formed appeared to have the composition 40% *exo* and 60% *endo*. Ether and tetrahydrofuran preparations, either as formed initially or after replacement of solvent, gave agreement within a range of 5%. The carbonation experiments of Vavon, Riviere, and de Botton[2] yielded a mixture of acids which was 24–33% *exo*,[12] depending apparently upon the length of the carbonation period. The Grignard reagent from isobornyl chloride yielded an acid 35% *exo*.[2d]

A sample of the Grignard reagent was refluxed 7 hr. after replacement of the solvent by xylene. Again our reagent seemed somewhat higher in *exo* isomer (20%) than that reported from carbonation (5%).[2] However, our isomerization conditions were somewhat more vigorous than those used previously, and a new broad resonance at τ 10.7 appeared. There was some suspended matter, the solution was now orange in color, and the total bicyclic Grignard concentration appeared to have decreased.[13]

In the carbonation experiments, it was found that partial reaction with allyl bromide before carbonation produced an acid mixture which was enriched in the *exo* isomer, to the extent of as much as 41%.[2] When we added enough allyl bromide to react with about 65%

---

[7] (a) Results listed are averages of a large number of tracings of these spectra. Intensity and resolution seemed to be limited by solubility and by the viscosity of the solutions. Better resolution was obtained in ether, but unfortunately ^{13}C side bands of the ether fell in the region of interest. (b) We have been informed by Dr. M. Vogel of similar observations in ether solution.

[8] (a) F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961); (b) W. D. Kumler, J. N. Shoolery, and F. V. Brutcher, Jr., *J. Am. Chem. Soc.*, **80**, 2533 (1958); (c) P. Laszlo and P. v. R. Schleyer, *ibid.*, **86**, 1171 (1964).

[9] (a) R. E. Glick and A. A. Bothner-By, *J. Chem. Phys.*, **25**, 362 (1956); (b) K. L. Williamson, *J. Am. Chem. Soc.*, **85**, 516 (1963).

[10] It is perhaps possible that there are two coupling constants of ~3 c.p.s. and that a part of the multiplet is hidden by the multiplet of the other isomer.

[11] Relative concentrations were estimated by cutting out and weighing tracings of spectra.

[12] Compositions given for the carbonation products are based on revised values of the optical rotations of the acids given later by de Botton.[2e]

[13] Carbonation of a sample produced an acid mixture which contained additional strong n.m.r. peaks which do not correspond to either of the bornanecarboxylic acids. The results may suggest metalation of the xylene.

of the carbon–magnesium bonds present, a precipitate was formed. The supernatant solution showed a slight increase in *exo* content (to about 47%).

Precipitation with a 10% excess of dioxane produced a heavy suspension, which was stirred for 2 days. Only a part of the supernatant solution could be recovered after centrifuging. It appeared from the n.m.r. spectrum that the *exo* content in solution had decreased to about 33%. It is likely that much of the organometallic was present in the precipitate. Similar spectra were obtained for the dialkylmagnesium in 1,2-dimethoxyethane. Riviere found that the acids produced by carbonation of the precipitate and of the filtrate had the same rotation and concluded that they were identical mixtures similar in composition to the Grignard reagent.[2a] Chemical shifts of the 2-hydrogens were the same within 0.1 p.p.m. as those for the Grignard solutions. However, there appeared to be new absorption under the multiplet for the *exo* compound.

Heating of the dialkylmagnesium solution in THF produced isomerization of the *exo*-magnesium to the *endo* position. Equilibration appears to be complete within less than 1 hr. at 110°. At that time, the *exo* content was reduced to about 15%. Estimation was made difficult by the presence of the "extra" peak (see above) lying at about τ 10.2. This peak remained constant after 43 hr.

The Grignard reagent in THF was also isomerized to a mixture containing about 25% *exo* isomer. With the Grignard formed from "Grignard reagent" magnesium, the reaction was apparently complete in less than 1 hr. at 110°. A sample of about the same concentration (*ca.* 1.3 *M*) prepared with sublimed magnesium isomerized with approximate half-life of 0.75 hr. at 110°. Impurities in the magnesium thus appear to promote the equilibration,[14] although it is possible that the difference in behavior might have resulted from slight differences in concentration or in the handling of the reagents.

The present results definitely confirm the conclusions of Vavon, Riviere, and de Botton that the bornyl Grignard undergoes configurational change slowly once it is formed, although considerable isomerization (probably through a free carbanion or radical intermediate) does occur in the formation step. Quantitative differences between their carbonation results and our spectral studies may result from slight differences in technique, from uncertainties in estimating n.m.r. curve areas, and from the slow carbonation of the highly hindered isobornyl magnesium compounds.[2d] Since oxygenation yields mixtures of alcohols which are markedly different from either the carbonation products or the Grignard reagent composition as estimated by n.m.r., it is very likely that a different mechanism, probably free radical, is involved there.[5] It is not yet certain whether the slow inversion observed with the bornyl Grignard reagent is typical of secondary carbon–magnesium bonds or whether it is abnormally slow owing to bond-angle strain of the ring or to steric hindrance to a bimolecular reaction. Both factors may contribute to the lack of racemization observed by Walborsky for the 1-methyl-2,2-diphenylcyclopropyl Grignard reagent.[15]

It was not possible to obtain an estimate of the rate of equilibration of the *exo*- and *endo*-norbornyl reagents in the same way. No significant change was noted from a composition of 50% (+3%) *exo* either after heating for 43 hr. at 110° or 5 hr. at 148°. At the latter temperature, appreciable cleavage of solvent occurred. After 18 hr. at 148°, the organometallic had been largely destroyed, but the remaining weak absorption was not markedly changed in appearance.

A spectrum of the norbornyl Grignard reagent was run at about 110°.[16] This spectrum was essentially unchanged in appearance, and, if anything, had somewhat narrower lines than the spectrum at room temperature. The absence of any broadening of spectral lines indicates that the lifetime of the isomeric molecules must be at least 0.5 sec. at this temperature. The most reasonable interpretation seems to be that the norbornyl Grignard reagent undergoes a configurational inversion at least as rapidly as the bornyl Grignard, but that a nearly equilibrium mixture is formed initially. The approximately 50:50 equilibrium mixture is a bit surprising, since the equilibrium mixture of the norborneols is 80% *exo* at 100°.[17] However, the increased bond length between carbon and a second row element such as magnesium might be more effective in relieving strain in the *endo* compounds than it would in relieving the repulsion with the *syn*-7-methyl group in isobornylmagnesium derivatives **2a**.

In their carbonation studies with the norbornyl Grignard in ether, Sauers and Kwiatkowski found that the *exo*:*endo* ratio of the carboxylic acids formed increased from 7:3 at 25° to 9:1 at Dry Ice temperature.[5] They suggested that a rapidly equilibrating mixture of *exo* and *endo* reagents yields predominantly *exo* product *via* a transition state of lower energy than that leading to *endo* product. At higher temperature, the product distribution then shifts toward the *endo* product. Comparison of their results with ours is rather uncertain owing to differences in solvent, halide (chloride *vs.* bromide), and perhaps the magnesium. It seems reasonable that equilibration could be rapid enough, at least at room temperature, to allow a distribution of products different from the equilibrium Grignard composition. It might be noted that, at least in THF, the Grignard *exo*:*endo* ratio does not seem to vary by more than a few per cent from a 1:1 ratio either at 37 or 110°, and that this does not closely resemble the carbonation product ratios.

Cleavage of tetrahydrofuran by the norbornyl Grignard apparently proceeds to a considerable extent by a fragmentation route to ethylene and the enolate ion of acetaldehyde. Such fragmentation has been observed by Letsinger and Pollart for 2-phenyltetrahydrofuran with organosodium and -lithium compounds, and by Rembaum, Siao, and Indictor for tetrahydro-

---

[14] A "typical analysis" for the sublimed magnesium indicates amounts of impurities such as Al, Cu, Fe, Mn, and Ni in the range of 1–20 p.p.m. A qualitative emission spectrographic analysis indicated parts per million traces of Cu, Ag, and Fe, while similar analysis of the "Grignard reagent" magnesium indicated about 0.1% of Mn and 0.01% of Fe. We are indebted to Dr. W. Erickson of Minneapolis Honeywell Regulation Co. for the emission analyses and to Dr. R. S. Busk of the Dow Metal Products Co. for the sample of sublimed magnesium and the typical analysis.

[15] H. M. Walborsky and A. E. Young, *J. Am. Chem. Soc.*, **86**, 3288 (1964).

[16] We are indebted to Dr. W. B. Schwabacker for running this spectrum on the Varian HR-60 spectrometer.

[17] C. F. Wilcox, Jr., M. S. Sexton, and M. F. Wilcox, *J. Org. Chem.*, **28**, 1079 (1963).

furan with ethyllithium.[18] The n.m.r. spectrum of the strongly heated sample showed a very sharp new resonance at τ 4.64, identical in position (±0.02 p.p.m.) with the resonance of ethylene dissolved in a Grignard solution. The size of the signal was sufficient to account for about 15% of the Grignard reagent which had reacted. The other fragmentation product, the enolate of acetaldehyde, was not identified, though there were some additional resonance absorptions in the vinyl region which were less well defined than the ethylene resonance. In previous reports of cleavage of tetrahydrofuran by Grignard reagents, only the products of nucleophilic attack on the α-carbon of the tetrahydrofuran ring have been reported.[19]

Experimental Section

Materials.—Bornyl chloride of unknown origin was recrystallized from ethanol, m.p. 132°, $[\alpha]^{23}\text{D}$ +22.5° (ethanol). The n.m.r. spectrum was consistent with that reported previously,[6b] and showed no contamination with isobornyl chloride. The infrared spectrum showed the absence of any detectable ethanol of crystallization (<1 mole %), and so the chloride was used without the toluene distillation previously reported.[2,4] We are indebted to Mr. R. Theissen for a sample of norbornyl chloride.

Anhydrous reagent grade ether was used directly from a fresh can. Tetrahydrofuran and 1,2-dimethoxyethane were refluxed over potassium hydroxide and distilled under a stream of nitrogen from lithium aluminum hydride. Dioxane was treated with hydrochloric acid and sodium, and distilled under nitrogen from lithium aluminum hydride. Xylene was dried by partial distillation. Allyl bromide was redistilled. "High purity dry" nitrogen was used for most purposes. Magnesium was Fisher "for Grignard Reaction" (lot no. 794064) or sublimed magnesium furnished by the Dow Metal Products Co.[14]

N.m.r. spectra were obtained on a Varian A-60 spectrometer. Analyses for relative concentrations of the isomers were made by cutting out and weighing tracings. The coupling constants reported were obtained by averaging measurements on a large number of spectra.

Grignard Reagent Preparation.—The reagent using ordinary magnesium was prepared under nitrogen in the conventional manner from 5.0 g. of magnesium and 25.0 g. of bornyl chloride in 100 ml. of ether; 0.10 ml. of methyl iodide was used to help initiate the reaction. Reflux was continued for 2 hr. after completion of addition, the stirrer was removed, and the solution was allowed to settle overnight under nitrogen. Samples were removed from this flask for various experiments over a period of approximately 1 week. Shortly after formation, acid titration gave a concentration of 1.08 *M*. At the end of these experiments, a second titration showed a base concentration of 1.14 *M*, and iodine titration for active alkyl groups yielded a concentration of 1.12 *M*.[20] Care was taken to use dry benzene and dry resublimed iodine[21] and to carry out addition of the Grignard reagent to excess iodine solution under a nitrogen atmosphere. In one case, the concentration of Grignard reagent was also determined by comparing the area of the α-hydrogen resonance with that of a solution of bornyl chloride of similar concentration.

The Grignard reagents from bornyl and norbornyl chlorides with sublimed magnesium were prepared from about 0.004 mole of chloride and a slight excess of magnesium in 2 ml. of tetrahydrofuran under nitrogen in a flask sealed to a reflux condenser.

Grignard reagents were transferred by syringes which had been previously dried at 170°. Vessels to which they were transferred had also been dried and filled with nitrogen. N.m.r. tubes were flamed out under vacuum, filled in a stream of nitrogen, and sealed off with somewhat less than 1 atm. of nitrogen pressure.

The ether solvent was replaced with tetrahydrofuran by solvent distillation under high vacuum at room temperature and adding new solvent by syringe under a nitrogen stream. In some cases, after standing for several days, a precipitate formed in the tetrahydrofuran solutions of the Grignard reagent; this did not redissolve readily.

Heating in Xylene.—The ether solution of the Grignard reagent (20 ml.) was added to 20 ml. of dried xylene and distilled under a slow nitrogen stream until the temperature reached 135°. It was refluxed for 7 hr. and cooled, and a 10-ml. portion of the resulting yellow suspension was transferred to another flask. The solvent was removed and replaced by tetrahydrofuran. The solution was cloudy, but partly cleared on standing, with deposition of a small amount of yellow solid; the solution was orange.

Precipitation with Dioxane.—To 30 ml. of the Grignard solution (1.08 *M*) was added 3.0 ml. of dioxane. A gelatinous mass formed. Addition of 15 ml. of tetrahydrofuran allowed the mixture to be stirred with a magnetic stirrer. After 2 days 36 ml. of the suspension was centrifuged, and 14 ml. of clear supernatant liquid was transferred to another flask for replacement of solvent by tetrahydrofuran. After n.m.r. tubes had been prepared, the solvent was again replaced by 1,2-dimethoxyethane, in which the solubility of the dialkylmagnesium was considerably higher.

Reaction with Allyl Bromide.—To 10 ml. of Grignard solution (1.12 *M*) was added 1.0 g. of allyl bromide. After an initial exothermic reaction, the solution was allowed to cool and was centrifuged. The supernatant solution was removed, and solvent was replaced by tetrahydrofuran.

---

[18] (a) R. L. Letsinger and D. F. Pollart, *J. Am. Chem. Soc.*, **78**, 6079 (1956); (b) A. Rembaum, S.-P. Siao, and N. Indictor, *J. Polymer Sci.*, **56**, No. 163, S17 (1962); (c) Additional examples of analogous cleavages of other rings are reported by F. Weygand and H. Daniel [*Chem. Ber.*, **94**, 1682, 3145, (1961)] and by G. Wittig and W. Tochtermann [*ibid.*, **94**, 1692 (1961)].

[19] (a) F. R. Jensen and R. L. Bedard, *J. Org. Chem.*, **24**, 874 (1959); (b) H. Normant, *Compt. rend.*, **239**, 1510 (1954).

[20] A. Job and R. Reich, *Bull. soc. chim. France*, [4] **33**, 1414 (1923).

[21] W. C. Pierce and E. L. Haenisch, "Quantitative Analysis," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1954, p. 243.