Phenylcyclohexane was identified by comparison with an authentic sample. The percentage of phenylcyclohexane in the crude reaction products was determined by glpc analysis on a 20% DC 550 column, using 1-phenylhexane as internal standard. Typical results are summarized in Table I.

After removal of phenylcyclohexane, the residue was subjected to short-path distillation at 0.1 mm and 200° bath temperature. The nmr spectrum of the distillate ((CCl_4), δ 0.7–3.2 (broad overlapping multiplet with highest point at about δ 1.5), δ 6.5–7.4 (broad overlapping multiplet)) strongly resembles that of an asphaltene.[5]

Anal. Found: C, 86.54; H, 9.52; O, 4.1.

Registry No.—*cis*-1,4-Cyclohexanediol, 931-71-5; *trans*-1,4-cyclohexanediol, 6995-79-5.

[5] N. F. Chamberlain, F. C. Stehling, K. W. Bartz, and J. J. R. Reed' "Nuclear Magnetic Resonance Data for Hydrogen-1," Esso Research and Engineering Co., Baytown, Texas.

Radical Mechanisms in Reactions of Grignard Reagents

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The coupling reactions of Grignard reagents with organo halides or with another molecule of Grignard reagent have been reviewed by Kharasch and Reinmuth.[2a] They concluded that in the absence of agents such as cobalt(II) chloride, and at temperatures lower than 100°, free-radical mechanisms are not involved except in reactions with aryl-substituted methyl halides which can give rise to relatively stable free radicals. For example, the reaction in eq 1 appears to involve a free radical mechanism, but Kharasch and Reinmuth[2a] have argued convincingly that the reaction of Grignard reagents with allyl halides, α-halo ethers, and other organic halides that give rise to condensation product (R-R′) in high yield, are not free-radical reactions.

$$\begin{aligned}&\mathrm{CH_3MgI} + \mathrm{C_6H_5CH_2Cl} \longrightarrow \mathrm{C_6H_5CH_2CH_2C_6H_5} + \\ &\quad \underset{25\%}{\mathrm{C_6H_5CH_2CH_3}} + \mathrm{CH_4} + \mathrm{C_2H_6} + \mathrm{C_2H_4}\ \ 32\% \qquad (1)\end{aligned}$$

Recent studies by Russell[3] and others have indicated that the occurrence of radical mechanisms in the reactions of Grignard reagents may be more common than previously thought.

Russell[3] has shown that butylmagnesium bromide in tetrahydrofuran solution will form radical anions with benzophenone, fluorenone, and a variety of nonbenzenoid aromatic compounds. He formulates the general reaction as shown in eq 2

$$\mathrm{D}^- + \mathrm{A} \longrightarrow [\mathrm{D}\cdot^- + \mathrm{A}\cdot]\ \underset{\text{cage}}{\text{solvent}} \longrightarrow \mathrm{DA}^- \qquad (2)$$

where D = donor, and A = acceptor.

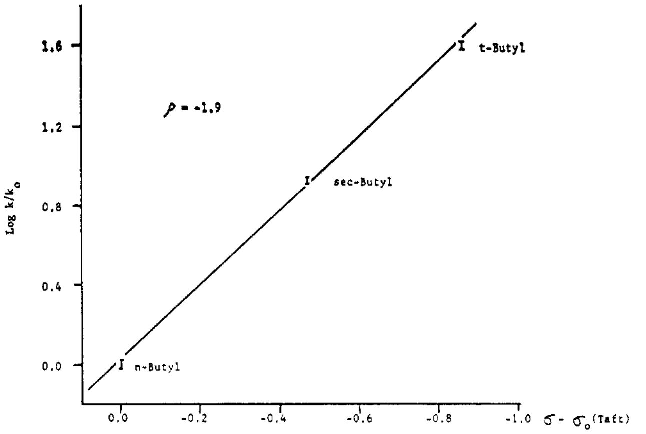

Figure 1.—Substituent effect in the reaction of grignard reagents with allyl bromide.

Maruyama[4] has found that arylmagnesium bromides react with ketones to form ketyls, presumably as shown in eq 3. In addition Lamb[5] demonstrated that a radical mechanism must occur in the reaction of Grignard reagents with oxygen, and Seyferth[6] suggested a free-radical mechanism for the reaction of methylmagnesium bromide with 7,7-dibromobicyclo[4.1.0]heptane.

$$\mathrm{ArMgBr} + {>}\mathrm{C{=}O} \longrightarrow [{>}\dot{\mathrm{C}}\mathrm{{-}O^-}] \longrightarrow \mathrm{Ar}\overset{|}{\underset{|}{\mathrm{C}}}\mathrm{OMgBr} \qquad (3)$$

This paper reports evidence which suggests that even in the reactions of simple allylic bromides with alkylmagnesium halides, a radical mechanism is operative.

Results and Discussion

Relative rate data on the reaction of allyl bromide with Grignard reagents (Table I) gives a good fit to a Hammett plot[7] (Figure 1).

TABLE I

REACTION OF ALKYLMAGNESIUM HALIDES WITH ALLYL BROMIDE

Grignard reagent	Relative rate at 0° in ethyl ether
C_6H_5MgBr	1.00
n-C_4H_9MgCl	2.77
sec-C_4H_9MgCl	22.6
t-C_4H_9MgCl	107

The relative rates in Table I were calculated from the relative amounts of analogous products, $RCH_2CH=CH_2$, arising from competition reactions between two Grignard reagents for the allyl bromide.

The value of ρ, -1.9, (Figure 1) indicates that the α carbon of the Grignard reagent has a lower electron density in the transition state than in the ground state.

A second observation was the isolation of 2,2,3,3-tetramethylbutane as a reaction product from the reaction of *t*-butylmagnesium chloride and allyl bromide. Since 2,2,3,3-tetramethylbutane is undoubtedly formed in the preparation of *t*-butylmagnesium halide, it was necessary to determine if a significant amount of

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[1] (a) Abstracted from a portion of the Ph.D. Thesis of R. G. G. (1967). (b) To whom all correspondence should be addressed.

[2] M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954 (a) pp 1048–1053 and 1058–1059, (b) p 1078, (c) p 124.

[3] G. A. Russell, E. G. Jansen, and E. T. Strom, *J. Amer. Chem. Soc.*, **86**, 1807 (1964).

[4] K. Maruyama, *Bull. Chem. Soc. Jap.*, **37**, 897, 1013 (1964).

[5] R. C. Lamb, P. W. Ayers, M. K. Toney, and J. F. Garst, *J. Amer. Chem. Soc.*, **88**, 4261 (1966).

[6] D. Seyferth and B. Prokai, *J. Org. Chem.*, **31**, 1702 (1966).

[7] J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 85.

the total of 2,2,3,3-tetramethylbutane was formed during the coupling reaction. By means of a control reaction it was established that a 16% increase in the amount of 2,2,3,3-tetramethylbutane resulted during the coupling reaction with allyl bromide.

Finally, it was possible to observe an esr signal that was shown conclusively to occur during the reaction of n-butylmagnesium chloride and allyl bromide and was not present in the reagents. The signal is transient and difficult to observe but it is reproducible.

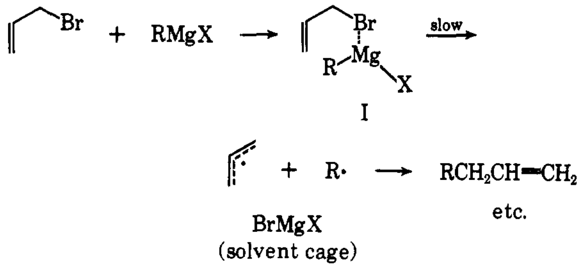
These three observations, plus the reactivity sequence, $t\text{-}C_4H_9 > sec\text{-}C_4H_9 > n\text{-}C_4H_9 > C_6H_5$, suggest a free-radical mechanism.

Assuming the validity of a free-radical process, a mechanism such as in eq 4 does not appear consistent

$$RMgX \longrightarrow R\cdot + \cdot MgX \xrightarrow{CH_2{=}CHCH_2Br} RCH_2CH{=}CH_2 + MgXBr \quad (4)$$

with the high yields of $RCH_2CH{=}CH_2$ (85–90%) observed here and in previous studies.[2c] It is known[8] that important reaction paths for alkyl radicals under these conditions are hydrogen abstraction from ether, dimerization, and disproportionation.

Alternatively, we suggest the mechanism in eq 5.



(5)

Typically, in free-radical reactions involving the production of a free radical from a neutral species, ρ is in the range of -0.5 to -1.0.[9] The larger value, in an absolute sense, of ρ in the Grignard coupling reaction is probably a reflection of the fact that in the proposed complex (I), the alkyl group R possesses appreciable anionic character.

For the scheme in eq 5, relative rates calculated from the relative amounts of $RCH_2CH{=}CH_2$ would be valid only if the fraction of the caged species that goes on to $RCH_2CH{=}CH_2$ is constant for each R group. This appears reasonable since the yield of $RCH_2CH{=}CH_2$ is 90% for n-butylmagnesium halide and 85% for t-butylmagnesium halide.[2b]

The proposed reaction course suggests the formation of RH and R–R as minor by-products. Limitations in experimental design precluded the detection of the gaseous hydrocarbons and an effort to detect n-octane from the reaction of n-butylmagnesium halide and allyl bromide was not successful.

Experimental Section

The butyl halides used for this study were free of isomeric halides, as established by gas chromatography under conditions shown to separate the isomeric butyl halides.

A. Typical Competition Reaction.—A 300-ml, three-necked, round-bottomed flask was fitted with a condenser, magnetic stirrer, and serum-type rubber stopper. Purified argon provided an inert atmosphere into which 0.050 mol of each of the competing, clear, water white, Grignard reagents was placed. The mixture was cooled to 0° and allyl bromide (0.025 mol) was added by means of a hypodermic syringe. After stirring at 0° for 30 min, the mixture was slowly poured into 200 cc of crushed ice. The mixture was acidified and the organic products were extracted with ether and dried over anhydrous magnesium sulfate. Concentration of the ethereal solution was achieved by distilling the ether through a 6-in. column packed with glass helices. The ratio of the products was determined by gas chromatography using a 6-ft column packed with 10% XE-60 on Gas Chrom R, 60–80 mesh. The column was calibrated using known quantities of independently prepared reference compounds having the structures of the expected products.

B. Determination of the Amount of 2,2,3,3-Tetramethylbutane Formed during the Allylic Coupling Reaction.—Two identical aliquots, A and B, were taken from the same solution of t-butylmagnesium chloride. To each aliquot was added an equal amount of biphenyl to serve as an internal, quantitative gas chromatography standard. Allyl bromide was added to one aliquot (A) and both aliquots were subjected to identical reaction conditions and work-up procedures. By quantitative gas chromatographic analysis it was established that sample A contained 1.16 ± 0.02 times as much 2,2,3,3,-tetramethylbutane as sample B.

C. A Typical Esr Experiment.—To a serum-capped, nitrogen-filled, esr tube, an ethereal solution of allyl bromide was added by hypodermic syringe. This was frozen in liquid nitrogen and a solution of n-butylmagnesium chloride was added and frozen. By keeping the reagents frozen, mixing and reaction were prevented. The tube was placed in the spectrometer and the solids were allowed to melt. No signal was observed from the completely melted solutions at $-40°$. However, when the tube was removed from the spectrometer, inverted several times to cause mixing of the layers, and replaced in the spectrometer at $-40°$, a signal was observed. The signal was transient and disappeared before a well-characterized spectrum could be obtained. However, it was reproducible.

Registry No.—C_6H_5MgBr, 100-58-3; $n\text{-}C_4H_9MgCl$, 693-04-9; $sec\text{-}C_4H_9MgCl$, 15366-08-2; $t\text{-}C_4H_9MgCl$, 677-22-5; allyl bromide, 106-95-6.

Acknowledgments.—Appreciation is expressed to the American Petroleum Institute for partial support of this research and to the National Science Foundation for funds which aided in the purchase of the esr spectrometer.

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The Ozonation of Pyrene. A Monomeric Monoozonide formed in Polar Solvents

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Since it was first reported by Vollman[1] in 1937, the reaction of ozone with pyrene to give 4-formyl-5-phenanthrenecarboxylic acid has been investigated repeatedly[2-6] but the mechanism has not heretofore been

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