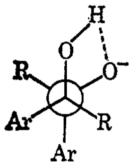
TABLE I
ELECTROLYTIC REDUCTION OF C_6H_5COR

Run	Electrode	Time, hr	Cathode potential (V)/ current (mA)	Medium[a,b]	Yield, % *dl*	Yield, % *meso*	Ratio *dl/meso*
			Benzaldehyde (R = H)				
1	Hg	20	−1.2/260	Acidic (A)	36.3	32.4	1.12
2	Hg	20	−1.6/290	Basic (B)	45.6	38.3	1.18
3[c]	Hg	15	−1.4/200	Basic (B)	45.5	41.0	1.11
4	Hg	1	−1.6/490	Basic (C)	48.9	37.5	1.30
5[c]	Hg	1	−1.6/500	Basic (D)	43.7	36.8	1.19
6	Cu[e]	20	−1.6/300	Basic (B)	39.1	33.7	1.16
7[c,d]	Hg	8	−/200	Basic (D)	96.5	<0.2	...
			Acetophenone (R = CH_3)				
8[c]	Hg	4	−1.2/450	Acidic (A)	39.9	31.3	1.27
9[c]	Hg	4	−1.2/200	Acidic (A)	43.4	34.6	1.25
			Propiophenone (R = C_2H_5)				
10	Hg	5	−1.2/300	Acidic (A)	31.3	22.3	1.40
11	Hg	7	−1.2/300	Acidic (A)	32.6	23.0	1.41
12	Hg	3.5	−1.6/300	Basic B	36.4	13.4	2.72
13	Hg	3	−1.6/450	Basic C	29.8	11.0	2.70
14	Hg	6.5	−1.6/300	Basic D	38.2	13.7	2.78
15	Cu[e]	4.5	−1.7/120	Basic B	18.0	5.5	3.25

[a] 80% EtOH in all cases. [b] (A) 1.7 *M* AcOH, 1.0 *M* LiCl; (B) 2 *M* KOAc; (C) 0.5 *M* Me_4NOH, 0.5 *M* Me_4NCl; and (D) 0.1 *M* KOH. [c] Nmr. [d] Stability study, pure racemate form used. [e] Smooth copper sheet, washed with dilute HNO_3 and rinsed thoroughly.

dimerizing phenyl hydroxymethyl radicals are sufficiently more reactive than the ketone-derived counterparts that the coupling process is less influenced by steric factors and generally less selective, or (b) the steric requirements of hydrogen are sufficiently less demanding than those of methyl or ethyl (see R in Table I) so as to limit the effectiveness of the following conformation (occuring at the time of dimerization)



in determining the resultant *dl/meso* ratio.[4] The present data is insufficient to choose between the two explanations at this time.

It may also be noted briefly that, as in the previously reported data for the acetophenone system, variations in time, current level, electrolyte, and choice of electrode did not make a significant contribution to the stereochemistry. The diastereomeric ratios appear to depend predominantly, if not exclusively, on the pH of the media.

Experimental Section

The purchase and purification, or preparation, of benzaldehyde-7-C^{14} and *meso*- and *dl*-hydrobenzoin have been previously described.[5] Propiophenone-7-C^{14} was purchased from Nuclear Research Chemicals, Orlando, Fla. *meso*- and *dl*-3,4-diphenyl-2,3-hexanediol were synthesized photochemically from propiophenone by standard techniques.

The general procedure has been reported in detail.[1] All runs contained 1 g of aldehyde or ketone in 60 ml of solution. In the isotope dilution studies, *meso*-hydrobenzoin was recrystallized to a final melting point of 136°, the *dl* form to 120°. For the propiophenone pinacols, the *meso* form was recrystallized to a melting point of 138° and the *dl* form to 86 or 114°.[6]

For nmr analyses, the basic media were first acidified with glacial acetic acid, and all reaction mixtures were quantitatively transferred with methanol. Following elimination of all alcohol on a rotary evaporator, the residue was extracted with dichloromethane (five 35-ml portions), the extract dried over anhydrous magnesium sulfate, and concentrated in an air stream on a steam bath. Carbon tetrachloride was added and concentration was continued to the exclusion of dichloromethane and essentially all of the tetrachloride. The nmr studies were conducted in deuteriochloroform. Nmr assignments for acetophenone pinacols have been reported;[3] for the hydrobenzoins, the *meso*-benzylic protons appear at 5.18 (2 H) and the *dl* at 5.32 (2 H).

Registry No.—Benzaldehyde, 100-52-7; propiophenone, 93-55-0; *meso*-hydrobenzoin, 579-43-1; *dl*-hydrobenzoin, 655-48-1; *meso*-pinacol of propiophenone, 16020-86-3; *dl*-pinacol of propiophenone, 16020-87-4.

Acknowledgment.—Financial assistance from the U. S. Atomic Energy Commission under Contract No. At-(40-1)-2833 (ORD-2833-19) is gratefully acknowledged. The nmr instrument utilized, an A-60 (Varian Corp.), was awarded Louisiana State University in New Orleans by the National Science Foundation under GP-3674.

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[4] In paper I of this series[1] it was proposed that the stereochemistry was determined by the characteristics of dimerizing free radicals in acid media and coupling between radicals and radical ions in alkaline media. The paper may be consulted for fuller details.

[5] J. H. Stocker and D. H. Kern, *J. Org. Chem.*, **33**, 291 (1968).

[6] The *dl*-pinacol is apparently polymorphic and the higher melting point is observed only with slow and particularly careful recrystallization.

The Acid-Catalyzed Dehydration–Condensation of 1,4-Cyclohexanediol[1a]

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The dehydration of a mixture of the *cis* and *trans* isomers of 1,4-cyclohexanediol (quinitol) with aqueous

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sulfuric acid has previously been used to prepare 3-cyclohexenol. Thus, it has been reported that quinitol, upon treatment with a catalytic amount of 65% sulfuric acid at 190–200°, yields a mixture of cyclohexadienes and 3-cyclohexenol.[2] A similar result was obtained by Senderens using a small amount of 50% sulfuric acid at 150°.[3]

We have found that when an aqueous solution of quinitol is slowly added to an excess of 45% sulfuric acid at 180°, through which is passed a vigorous stream of nitrogen in order to steam distil volatile products, the reaction takes an entirely different course. In this case, the major product is phenylcyclohexane accompanied by a mixture of higher boiling compounds.

In an attempt to gather information which might aid in elucidating the pathway taken by this reaction, a number of related compounds were subjected to the reaction conditions. In order to ascertain if the stereochemistry of the starting material was of importance, the *cis* and *trans* isomers of 1,4-cyclohexanediol were individually subjected to the reaction conditions. In each case, the crude reaction product consisted of a similar mixture of phenylcyclohexane and higher boiling materials. The stereochemistry of the starting diol is thus of no consequence. Based on this result, a likely intermediate, or precursor to an intermediate carbonium ion, is 3-cyclohexenol. That this possibility is correct is strengthened by our observation that 3-cyclohexenol, under the reaction conditions, yields a mixture of products similar in composition to that obtained from quinitol.

Two other possible intermediates, or precursors to intermediate carbonium ions, are 1,3- and 1,4-cyclohexadiene. Under the reaction conditions, both of these compounds yielded a mixture of phenylcyclohexane and higher boiling materials. However, the yield of crude product, and the percentage of phenylcyclohexane in the crude product, was appreciably lower than with the 1,4-cyclohexanediols or 3-cyclohexenol. These results suggest that the cyclohexadienes are not important intermediates, and thus that the condensation step precedes the possible double dehydration of quinitol.

A likely possibility for the condensation step involves addition to 3-cyclohexenol of either of the two carbonium ions resulting from the protonation of 3-cyclohexenol, to give one of four possible carbonium ions. In order for any of these four carbonium ions to be converted into phenylcyclohexane, a unit of unsaturation must be transferred from one ring to the other. In an attempt to gain information concerning this step, quinitol was treated with 45% D_2SO_4. The resulting phenylcyclohexane obtained from this experiment was extensively deuterated. Mass spectral analysis indicated the isotopic composition to be d_0–d_{11} 0%, d_{12} 1.6%, d_{13} 2.4%, d_{14} 8.5%, d_{15} 19.9%, and d_{16} 67.6%. That exchange had occurred in an intermediate rather than the product was shown by treating phenylcyclohexane with 45% D_2SO_4 under the reaction conditions. Mass spectral analysis of the recovered phenylcyclohexane indicated that only minor exchange had occurred (d_1 7%, d_2–d_5 approximately 2%, d_6 and above 0%). Thus, the aromatization process which forms phenylcyclohexane involves essentially complete exchange with solvent. This indicates to us a rather random process where many protonation–deprotonation steps occur prior to the formation of volatile phenylcyclohexane.

The ionic intermediates involved in the aromatization process could in principle add to another molecule of olefin to produce a trimeric species. To investigate this possibility, after removal of phenylcyclohexane the residual higher boiling material was distilled, and the distillate was analyzed by mass and nmr spectrometry and for elemental composition. The mass spectrum indicates the major components to be trimeric hydrocarbons (*m/e* 234, 236, 238, 240, 242, and 244) with the presence of smaller amounts of tetramers (*m/e* 318, 320, and 322) and pentamers (*m/e* 390, 392, and 394). A small amount of oxygen-containing material is indicated by direct oxygen analysis (4.1%) and mass spectral peaks at *m/e* 250, 252, 254, 256, 258, 260 (monooxygenated trimers).

It thus appears that after initial condensation to form a dimeric species, a competition exists between dehydration–aromatization to form the relatively volatile phenylcyclohexane and further condensation to yield higher molecular weight products.

Experimental Section[4]

The acid-catalyzed reactions were carried out by adding the substrate as a dilute aqueous solution to a large excess of hot 45% H_2SO_4, through which a vigorous stream of nitrogen was being passed. The resulting distillate was trapped by a series of flasks immersed in Dry Ice–acetone baths. The nitrogen flow was adjusted so that the addition rate and distillation rate were equal, thus maintaining the acid concentration constant. The cloudy aqueous distillate was extracted with CH_2Cl_2, and the dried organic layer was evaporated at room temperature.

In a typical run, 5.0 g of quinitol dissolved in 200 ml of H_2O was added over a 2.5-hr period, followed by 1 l. of water over an 8-hr period, to 500 ml of 45% H_2SO_4 heated to 180°.

The reactions of 1,3- and 1,4-cyclohexadiene were accomplished by periodically injecting 0.2-ml portions into a slower second stream of nitrogen which passed through a sintered glass disk into the sulfuric acid solution.

TABLE I

REACTION OF VARIOUS SUBSTRATES WITH 45% H_2SO_4

Substrate	Phenylcyclohexane in the crude product,[a,b] %
Quinitol	50
cis-1,4-Cyclohexanediol[c]	50
trans-1,4-Cyclohexanediol[c]	41
3-Cyclohexenol	40
1,3-Cyclohexadiene	13
1,4-Cyclohexadiene	25

[a] The yield of crude product, which consisted mainly of phenylcyclohexane and higher boiling material, generally ranged from 40 to 60% except in the cases of 1,3- and 1,4-cyclohexadiene where 5–10% was obtained. [b] The reproducibility of these results was approximately ±6%. Because of the difficulty of exactly duplicating experimental conditions, and the competing nature of the reaction coupled with the method of product removal, such agreement is considered excellent. [c] Obtained from quinitol by the method of H. C. Brown and G. Zweifel, *J. Org. Chem.*, **27**, 4708 (1962).

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[2] C. J. Gogek, R. Y. Moir, and C. B. Purves, *Can. J. Chem.*, **29**, 946 (1951).

[3] J. B. Senderens, *Compt. Rend.*, **180**, 790 (1925).

[4] Elemental analyses were performed by Schwarzkopf Laboratories, Woodside, N. Y. Mass spectral analyses were performed by Miss Vinka Parmakovich of Columbia University, New York, N. Y. Nmr spectra were determined in CCl_4 solution using a Varian Associates A-60 spectrometer with tetramethylsilane as internal standard.

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.

$$\begin{array}{l} \mathrm{CH_3MgI + C_6H_5CH_2Cl \longrightarrow C_6H_5CH_2CH_2C_6H_5 +} \\ \mathrm{C_6H_5CH_2CH_3 + CH_4 + C_2H_6 + C_2H_4} \quad 32\% \\ \quad 25\% \end{array} \tag{1}$$

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

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

where D = donor, and A = acceptor.

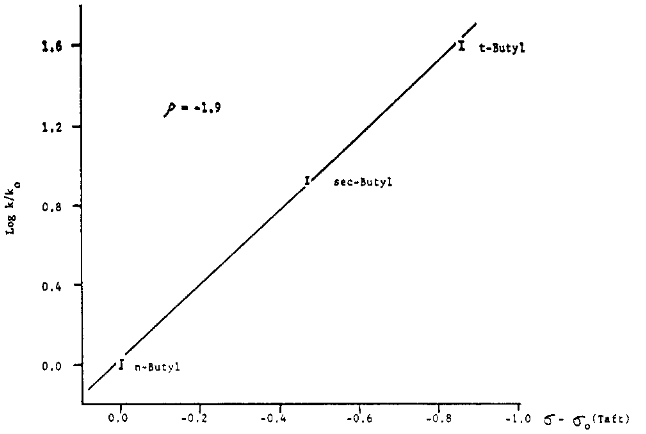
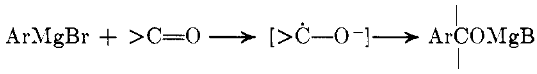


Figure 1.—Substituent effect in the reaction of grignard reagents with allyl bromide.

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.



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

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

(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.