Preparation of Triphenoxy-2,4,6-tribromophenoxy Phosphonium Bromide (XII).—2,4,4,6-Tetrabromocyclohexadien-1-one (9.4 g., 0.0229 mole) was suspended and stirred in 50 ml. of benzene, and a solution of triphenyl phosphite (7.4 g., 0.0239 mole) in 10 ml. of benzene was added. The reaction mixture became quite warm, the solid dienone dissolved, and then a second oily phase separated. After stirring for 30 min., the benzene layer was decanted, and the residual oil triturated with anhydrous ether. The product crystallized to a gummy yellow soil which was washed carefully with anhydrous ether and stored under ether or benzene. The yield was 12.5 g. (0.0177 mole, 75%).

Anal. Calcd. for $C_{24}H_{17}O_4Br_4P$: Ionic Br, 11.1. Found: Ionic Br, 11.3.

Attempted Reaction of Trimethyl Phosphite with 4-Methyl-4-dichloromethylcyclohexadien-1-one (XIII).—XIII (3.5 g.) was dissolved in 10 ml. of toluene, and trimethyl phosphite (7 ml.) was added. The solution was refluxed for 23 hr., and the solvent and trimethyl phosphite evaporated to give 3.5 g. of recovered XIII.

Attempted Reaction of Triethyl Phosphite with 2-Acetoxy-2,4,6-trimethylcyclohexadien-1-one.—A solution of triethyl phosphite (3.70 g., 0.0223 mole) and 2-acetoxy-2,4,6-trimethylcyclohexadien-1-one[16] (4.0 g., 0.0217 mole) in 20 ml. of benzene was refluxed for 3 hr. On evaporation of the solvent the residue was recrystallized from ether–petroleum ether to give 3.2 g. of the starting dieneone. Evaporation of the solvent from the mother liquor left 1.7 g. of yellow liquid, which showed strong unsaturated ketone and ester peaks in its infrared spectrum. It was not investigated further.

Reaction of Sodium Thiophenoxide with Ia.—A solution of thiophenol (11.0 g., 0.10 mole) and sodium methoxide (5.4 g., 0.10 mole) in 50 ml. of methanol was added to a suspension of Ia (17.25 g., 0.050 mole) in 50 ml. of methanol. The solid Ia immediately dissolved, and the solution became warm. Dilute hydrochloric acid (300 ml.) was added slowly, and the mixture extracted with methylene chloride. The methylene chloride was evaporated to give 22.1 g. of crude product, which was redissolved in methylene chloride, extracted with 10% sodium hydroxide solution, dried over magnesium sulfate, and the solvent evaporated to give 10.0 g. (0.046 mole, 92%) of diphenyl disulfide.

The sodium hydroxide washes were acidified with 6 *N* hydrochloric acid and extracted with methylene chloride, which was evaporated to give 11.0 g. (0.0415 mole, 83%) of 2,6-dibromo-4-methylphenol.

Reaction of Ia and Potassium O,O-Diethyl Phosphorodithioate.—A solution of potassium O,O-diethyl phosphorodithioate (6.53 g., 0.029 mole) in 100 ml. of acetone was added to a solution of Ia (10.0 g., 0.029 mole) in 50 ml. of acetone. The yellow cyclohexadienone color immediately disappeared. After stirring for 10 min., the solvent was evaporated. The residue showed no carbonyl absorption in the infrared. It was dissolved in methylene chloride, extracted with dilute sodium hydroxide, and the aqueous layer acidified with hydrochloric acid and extracted with methylene chloride. The methylene chloride layer was dried over magnesium chloride, and evaporated to give 6.65 g. (0.025 mole, 86%) of 2,6-dibromo-4-methylphenol.

Reaction of Dibutyl Sulfide with Ia.—The solid Ia (16.9 g., 0.048 mole) was suspended in 75 ml. of *tert*-butyl alcohol. Dibutyl sulfide (7.0 g., 0.049 mole) was added quickly to the stirred suspension. The solid dissolved almost immediately. After stirring for 10 min., the solution was dissolved in methylene chloride and extracted with 5% potassium hydroxide solution. The methylene chloride layer was washed with water, dried over magnesium sulfate, and evaporated to give 6.9 g. (0.043 mole 89%) of dibutyl sulfoxide, identical in infrared spectrum and v.p.c. retention time with a commercial sample. The potassium hydroxide solution was acidified with concentrated hydrochloric acid, extracted with methylene chloride, and dried over magnesium sulfate. Evaporation left 12.3 g. (0.043 mole, 89%) of 2,6-dibromo-4-methylphenol.

Reaction of Dibutyl Sulfide with 2,4,4,6-Tetrabromocyclohexadien-1-one (Ib).—The reaction was carried out exactly as described for Ia, using 10.5 g. (0.025 mole) of Ib and 3.55 g. (0.025 mole) of dibutyl sulfide, except that ethanol was used as the solvent. A 62% yield of dibutyl sulfoxide and a 91% yield of 2,4,6-tribromophenol were obtained.

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(16) F. Wessely and F. Sinwel, *Monatsh.*, **81**, 1055 (1950).

The Chemistry of Carbanions. II. The Reaction of Organomagnesium Compounds with α,β-Unsaturated Ketones[1a]

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From product studies of the reactions of *trans*-3-penten-2-one and *trans*-4-phenyl-3-buten-2-one with dimethylmagnesium, diethylmagnesium, and diphenylmagnesium, the following conclusions may be drawn about factors affecting conjugate and normal addition. (1) The presence of magnesium bromide only slightly enhances normal addition. (2) The ratio of conjugate to normal addition is not dependent on the concentration of the dialkylmagnesium, implying that the two reactions are of the same kinetic order. (3) Added cuprous chloride enhances conjugate addition with both dialkylmagnesium and alkylmagnesium bromide. (4) Neither the copper-catalyzed nor the uncatalyzed conjugate addition is diminished by the presence of excess isoprene, indicating that neither conjugate addition process involves free radicals which are reactive toward isoprene.

This paper reports a study (Chart I) of several factors which might be expected to influence the proportions of conjugate addition (or 1,4-addition to form **6**) and normal addition (or 1,2-addition to form **5**) obtained from the reaction of unsaturated ketones **8** with organomagnesium compounds **7**.[2]

The Effect of Magnesium Bromide.—The presence or absence of magnesium bromide in reaction mixtures involving organomagnesium compounds has been reported to affect the course or rate of a variety of reactions. Among these effects are the elimination of epoxide rearrangements in the absence of magnesium bromide,[3] an enhanced rate of reaction of diethylmagnesium with 1-hexyne in the absence of magnesium bromide,[4] an enhanced rate of reaction of dimethylmagnesium with acetone[5] and with benzophenone[6,7] in the absence of magnesium bromide or iodide, a de-

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(1)(a) This research has been supported in part by the National Science Foundation grant no. G-5107 and in part by grant no. 594A from the Petroleum Research Fund; (b) supported by the U. S. Air Force Academy.

(2) For a discussion of earlier work with leading references, see (a) E. G. Rochow, D. T. Hurd, and R. N. Lewis, "The Chemistry of Organometallic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1957; (b) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954.

(3) N. G. Gaylord and E. I. Becker, *Chem. Rev.*, **49**, 413 (1951).

(4) (a) J. H. Wotiz, C. A. Hollingsworth, and R. E. Dessy, *J. Org. Chem.*, **21**, 1063 (1956); (b) J. H. Wotiz, C. A. Hollingsworth, and R. E. Dessy, *J. Am. Chem. Soc.*, **78**, 1221 (1956); (c) R. E. Dessy, J. H. Wotiz, and C. A. Hollingsworth, *ibid.*, **79**, 358 (1957).

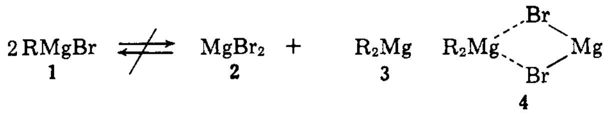
(5) J. G. Aston and S. A. Bernhard, *Nature*, **165**, 485 (1950).

(6) N. M. Bikales and E. I. Becker, *Chem. Ind.* (London), 1831 (1961).

(7) (a) M. Anteunis, *J. Org. Chem.*, **26**, 4214 (1961); (b) M. Anteunis, *ibid.*, **27**, 596 (1962).

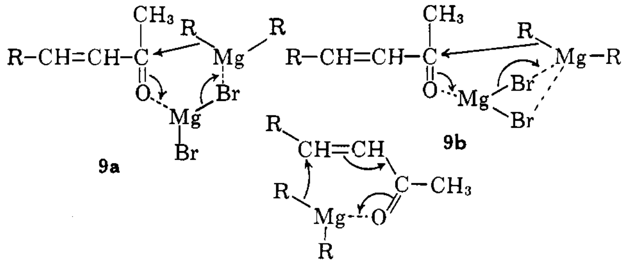
creased rate of addition of dialkylmagnesium compounds to nitriles in the absence of magnesium bromide,[8-10] a decreased amount of enolization and reduction as side reactions in the addition of propylmagnesium bromide to diisopropyl ketone when excess magnesium bromide was present,[11] an increased amount of enolization in the reaction of acetomesitylene with dimethylmagnesium when magnesium iodide was absent,[12] and a decreased amount of enolization and reduction in the reaction of diisopropyl ketone with dialkylmagnesium compounds in the presence of magnesium bromide.[13,14]

Following the experimental demonstration[15-17] that the magnesium atoms of magnesium bromide **2** and dialkylmagnesium compounds **3**[18] are not readily exchanged, the classical formulation of the Grignard reagent as **1** (and the supposed[2b] associated equilibrium) has been abandoned[6,7b,10,13] in favor of a dimeric (or polymeric[19]) structure such as **4**. Other data[20,21] have established that at least one molecule of solvent is closely associated with the reagent. After making suitable modifications to avoid the presence of a monomeric Grignard reagent **1**, the transition states proposed for normal and conjugate addition may be represented as **9**[2b,8,11,13,21] and **10**.[2b,22,23]



$2RMgBr \not\rightleftharpoons MgBr_2 + R_2Mg$

1 **2** **3** **4**



9a **9b** **10**

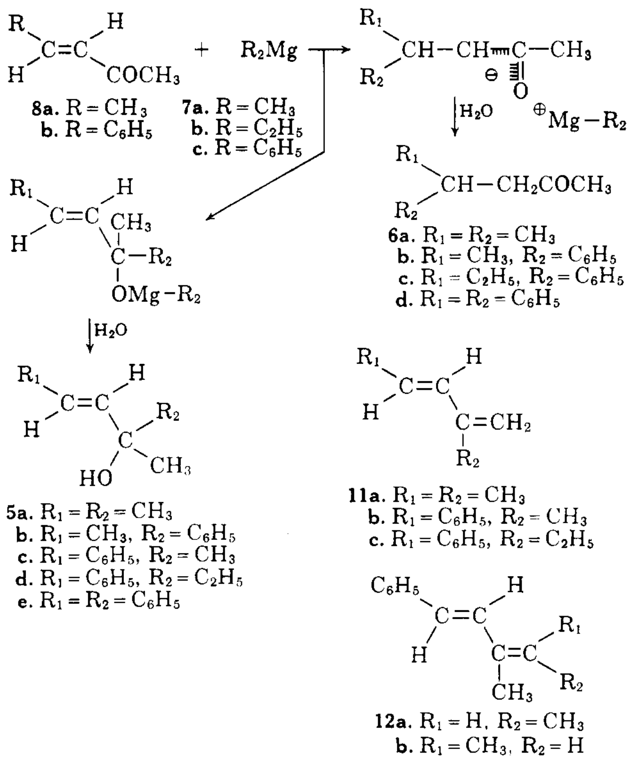


Chart I

The appearance of magnesium bromide only in the suggested transition states **9** leading to normal addition has led to the prediction[2b] that conjugate addition should be enhanced in the absence of magnesium bromide and normal addition should be enhanced by the presence of excess magnesium bromide.[24]

An experimental test (Table I) of this prediction reveals that enhancement of conjugate addition of organomagnesium compounds to α,β-unsaturated ketones in the absence of magnesium bromide is, in general, a minor effect. That the small effects observed are attributable to the absence of magnesium bromide rather than to the presence of varying amounts of impurities is indicated by a reversal of the effect when the dialkylmagnesium compounds are treated with an equimolar amount of magnesium bromide prior to reaction with the unsaturated ketone. We were unable to obtain meaningful data for reactions of the unsaturated ketones **8** with Grignard reagents containing excess magnesium bromide since the products **5** from normal addition were destroyed by the reaction conditions, presumably by dehydration of the unsaturated alcohols and subsequent polymerization of the dienes formed.

Effect of Concentration.—In spite of the general ineffectiveness of magnesium bromide in altering the

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(8)(a) H. Gilman and R. E. Brown, *J. Am. Chem. Soc.*, **52**, 1181 (1930); (b) H. Gilman and R. E. Fothergill, *ibid.*, **51**, 3149 (1929).

(9)(a) C. G. Swain, *ibid.*, **69**, 2306 (1947); (b) J. Vekemans and A. Bruylants, *Bull. soc. chim. Belges*, **68**, 541 (1959).

(10) S. J. Storfer and E. I. Becker, *J. Org. Chem.*, **27**, 1868 (1962).

(11) C. G. Swain and H. B. Boyles, *J. Am. Chem. Soc.*, **73**, 870 (1951); See also E. T. McBee, O. R. Pierce, and J. F. Higgins, *ibid.*, **75**, 1736 (1953).

(12) G. F. Wright, *ibid.*, **61**, 1152(1939).

(13) J. Miller, G. Gregoriou, and H. S. Mosher, *ibid.*, **83**, 3966, 5051 (1961).

(14) D. O. Cowan and H. S. Mosher, *J. Org. Chem.*, **27**, 1 (1962).

(15) R. E. Dessy, G. S. Handler, J. H. Wotiz, and C. A. Hollingsworth, *J. Am. Chem. Soc.*, **79**, 3476 (1957).

(16) R. E. Dessy and G. S. Handler, *ibid.*, **80**, 5824 (1958).

(17) R. E. Dessy, *J. Org. Chem.*, **25**, 2260 (1960).

(18)(a) The lack of an appreciable concentration of free carbanions in dialkylmagnesiums is indicated by the fact that triphenylmethylmagnesium compounds form colorless ether solutions (ref. 2a) and by a study of the ultraviolet spectrum of dicinamylmagnesium [R. H. DeWolfe, D. L. Hagemann, and W. G. Young, *J. Am. Chem. Soc.*, **79**, 4795 (1957)]; see also (b) J. E. Nordlander, W. G. Young, and J. D. Roberts, *ibid.*, **83**, 494 (1961); and (c) J. E. Leffler, "The Reactive Intermediates of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1956, pp. 174–220.

(19) Although W. V. Evans and R. Pearson [*J. Am. Chem. Soc.*, **64**, 2865 (1942)] have reported the presence of colloidal material in solutions of phenylmagnesium bromide, the conclusion that Grignard reagents are primarily colloidal suspensions of polymeric reagents (ref. 18c) seems to us unwarranted. Since clear, colorless solutions of dialkylmagnesium compounds may be prepared readily (see Experimental), it is clear that these materials are not colloidal. Molecular weight measurements (ref. 10) in tetrahydrofuran suggest that dialkylmagnesium compounds are partially dimeric in that solvent.

(20) N. Allentoff and G. F. Wright, *J. Org. Chem.*, **22**, 1 (1957).

(21)(a) A. Kirrmann and R. Hamelin, *Compt. rend.*, **251**, 2990 (1960); (b) R. Hamelin, *Bull. soc. chim. France*, 684, 915, 926 (1961).

(22) R. E. Lutz and W. G. Reveley, *J. Am. Chem. Soc.*, **63**, 3180 (1941).

(23) The cyclic mechanism **10** for conjugate addition has been criticized by E. R. Alexander and G. R. Coraor [*ibid.*, **73**, 2721 (1951)] on the grounds that such a process is sterically improbable for the observed conjugated addition of Grignard reagents to cyclohexenone. This question will be considered further in a subsequent paper by H. O. House and H. W. Thompson, *J. Org. Chem.*, **28**, 360 (1963).

(24)(a) This latter prediction was based upon the earlier conclusion (ref. 11a) that magnesium bromide catalyzes normal addition to ketones. This conclusion, which was derived from the diminished amounts of enolization and reduction as side reactions when excess magnesium bromide was present, has become untenable in view of repeated observations (ref. 5–7, 24b) that the rate of reaction of dialkylmagnesium compounds with ketones is *retarded* when magnesium bromide is added; (b) see H. O. House and D. D. Traficante, *J. Org. Chem.* **28**, 355 (1963).

TABLE I

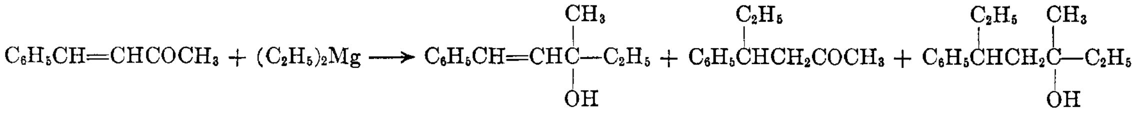
REACTION OF ORGANOMAGNESIUM COMPOUNDS WITH α,β-UNSATURATED KETONES

Organomagnesium compound[b]	% Normal addition[a]	
	$CH_3CH{=}CHCOCH_3$	$C_6H_5CH{=}CHCOCH_3$
$(CH_3)_2Mg \cdot MgBr_2$	93	94 (95)[c]
$(CH_3)_2Mg$	91	89
$(C_2H_5)_2Mg \cdot MgBr_2$	. .	20
$(C_2H_5)_2Mg$	. .	15
$(C_6H_5)_2Mg \cdot MgBr_2$	50 (53)[c]	77 (70)[c]
$(C_6H_5)_2Mg$	47	43

[a] The numbers listed, which are the average values from two or *more runs, represent the percent of alcohol* **5** *(including any* dienes **11** and **12** derived from the alcohols **5**) in the product. The values in this table are derived from reaction of two equivalents of the organomagnesium compound with one equivalent of the unsaturated ketone. [b] For the numbers not enclosed in parentheses, the formulas $R_2Mg \cdot MgBr_2$ refer to the Grignard reagent prepared in the usual manner. [c] For the numbers enclosed in parentheses, the formulas $R_2Mg \cdot MgBr_2$ refer to the reagent obtained by mixing two equivalents of the dialkylmagnesium compound with two equivalents of magnesium bromide.

TABLE II

EFFECT OF CONCENTRATION ON PRODUCT RATIO



$$C_6H_5CH{=}CHCOCH_3 + (C_2H_5)_2Mg \longrightarrow C_6H_5CH{=}CH\overset{CH_3}{\underset{OH}{C}}{-}C_2H_5 + C_6H_5\overset{C_2H_5}{C}HCH_2COCH_3 + C_6H_5\overset{C_2H_5}{C}HCH_2\overset{CH_3}{\underset{OH}{C}}{-}C_2H_5$$

8b **7c** **5d** **6c** **14**

Molarity of **8b**	Molarity of **7c**	Molarity[b] of $MgBr_2$	Conjugate addition,[a] % (of product)
0.075	0.75	. . .	86
.015	.75	. . .	86
.015	.15	. . .	88
.075	.75	0.75	67
.015	.75	.75	72
.015	.15	.15	77

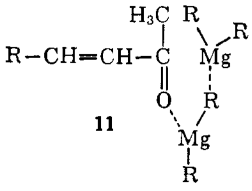
[a] The figures listed are the averages of two or more runs and include **6c** plus **14**. [b] The magnesium bromide is that present in the preparation of the Grignard reagent.

ratio of normal to conjugate addition, the fundamental idea of the popular[2b] cyclic six-membered transition state (as in **9**) can be retained if a transition state such as **11** is envisioned for normal addition, and transition state **10** is retained for conjugate addition. This idea also has been subjected to experimental test (Table II) by varying the concentrations of the reactants in order to learn whether the kinetic orders[13] in the organomagnesium compound differ for normal and conjugate addition (as would be predicted if **10** and **11** are correct). The variations in concentration were made in such a way that there was always a tenfold excess of diethylmagnesium present (assuming that only one ethyl group will react).[6,10] In this way the concentration of the organometallic remained essentially constant and we could be confident that we were studying reactions involving only the first ethyl group of the diethylmagnesium. For those reactions conducted in the absence of magnesium bromide, it is clear that neither changes in ketone concentration nor changes in the organometallic concentration alter the ratio of conjugate to normal addition. Thus, it can be concluded that the kinetic order of both reactions in the organometallic compound and in the ketone is the same.

The concentration effects observed (Table II) in the reaction when magnesium bromide is present are small but appear to be real. The observed ratios of conjugate to normal addition, namely, 2.0, 2.6, and 3.4, differ by much too small factors to be consistent with the simple kinetic expressions, k_c [ketone] $[Et_2Mg_2Br_2]^n$ and k_n [ketone] $[Et_2Mg_2Br_2]^{n+1}$ for conjugate and normal addition, respectively. The interpretation to be placed on these small changes, as well as the slight enhancement of normal addition in the presence of magnesium bromide (Table I) especially with benzalacetone (**8b**) and the phenyl Grignard reagent, is not clear.

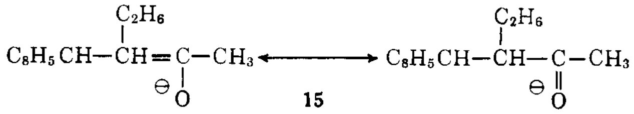
The possible effect of changes in concentration ratios[13,14] (*i.e.*, concentration of organomagnesium compound/concentration of ketone) on the proportion of conjugate to normal addition also has been examined. In two cases (**7c** + **8a**, Table IV and **7b** + **8b**, Table VII) mixing the reactants by slowly adding the organomagnesium compound to the ketone (*i.e.*, inverse addition), a procedure which ensures that the ketone will be in excess during the first half of the reaction, did not significantly alter the proportion of conjugate addition. The use of a flow system[24b] for mixing ethylmagnesium bromide with benzalacetone (**8b**) also did not significantly alter the ratio of conjugate to normal addition. The fact that the conjugate-normal addition ratio is not altered by an inverse order of mixing where the alkylmagnesium alkoxide **13** is present accompanied by unchanged ketone indicates either that the kinetic order for consumption of the ethyl group of the alkoxide **13** ($R = C_2H_5$) is the same for both normal and conjugate additions or that the intermediate alkoxide **13** ($R = C_2H_5$) deos not react with benzalacetone (**8b**) under reaction conditions employed. In this respect the competition between normal and conjugate addition reactions differs from the competition between normal addition and the side reactions, enolization, and reduction.[24b]

Of incidental interest in the reaction of ethylmagnesium derivatives with benzalacetone (**8b**), was the formation of the saturated alcohol **14**. This material became the major product when large excesses of diethylmagnesium or long reaction times were employed. However, none of this product was formed when the reactants were mixed in a flow system permitting short reaction times. This saturated alcohol apparently is formed in a relatively slow reaction between the initially formed enolate **15** and diethylmagnesium.[25] Essentially the same mixture of diastereoisomers of structure **14** was produced in the reaction with benzalacetone (**8b**) and with the saturated ketone **6c**.


11

RMgOR′

13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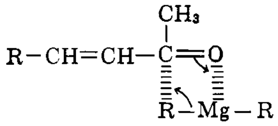
Effect of Added Cuprous Ion.—Addition of 1–5 mole % of cuprous chloride caused a very substantial increase in the proportion of conjugate addition, both with Grignard reagents as previously reported,[26] and with dialkyl- and diarylmagnesium compounds (Tables III, IV, V, and VI). In two instances addition of excess isoprene to reaction mixtures, either in the presence or absence of cuprous chloride, failed to alter significantly the proportion of conjugate addition. These observations suggest that the enhancement of conjugate addition by cuprous ion does not proceed *via* radical chain processes involving alkyl or aryl free radicals. From kinetic experiments currently in progress, we hope to establish whether the effect of cuprous ion is to catalyze conjugate addition as seems probable from the data available.

The absence of substantial effects from concentration changes or added magnesium salts suggests that the transition states for normal and conjugate addition of organomagnesium compounds to unsaturated ketones are derived from the same reactants and are similar in character. Consequently, the major obstacle to the interpretation of the mechanisms of these reactions at the present time is the uncertainty about the mechanism of normal addition. It is appropriate to note that although our data offer no evidence requiring a four-center transition state such as **16**[27] for normal addition, none of the information described in this study is incompatible with this proposal.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Experimental[28]

Preparation of the Organomagnesium Compounds.—Ethereal solutions of the Grignard reagents from methyl bromide, ethyl bromide, and bromobenzene were prepared under nitrogen in the usual way. Although the methylmagnesium bromide solutions contained excess methyl bromide, subsequent experiments with the Grignard reagent prepared from dimethylmagnesium demonstrated that the impurity had no effect. After the mixtures had been allowed to stand overnight to permit the settling of undissolved solids, the solutions were transferred to volumetric flasks which were sealed and stored in such a way that they were protected from light. To determine the concentration of the reagents, aliquots were decomposed in excess standard hydrochloric acid and back titrated with standard sodium hydroxide. The concentrations of the reagents varied over the following ranges: methyl Grignard reagent, 1.45 to 2.69 *M;* ethyl Grignard reagent, 2.20 *M;* phenyl Grignard reagent, 1.76 to 1.91 *M*. A 2.59-*M* ethereal solution of magnesium bromide was prepared by reaction of 1,2-dibromoethane with magnesium. After aliquots of the solution had been quenched in water, the bromide ion concentration was determined by titration with standard silver nitrate solution using potassium chromate as an indicator. The ethereal solutions of dimethyl-, diethyl-, and diphenylmagnesium were prepared from the organomercury compounds as previously described[29] and analyzed by the same method used for the Grignard reagents. The concentrations of the reagents varied over the following ranges: dimethylmagnesium, 0.157 to 0.866 *M;* diethylmagnesium, 0.93 *M;* diphenylmagnesium, 0.203 to 1.51 *M*. The dimethylmercury, b.p. 91–92.5° (lit.,[30] 92°), diethylmercury, b.p. 158–161° (lit.,[31] 159°), and diphenylmercury, m.p. 122.9–124.6° (lit.,[32] 121–123°), were all prepared by the general procedure of Gilman and Brown[33] or by a slightly modified procedure in which a tetrahydrofuran solution of mercuric chloride was added directly to the Grignard reagent. In all cases a sufficient volume of the organomagnesium reagent was prepared so that all runs with a given unsaturated ketone were done with the same batch of organomagnesium compound. In this way any effects resulting from the possible presence of trace impurities in the magnesium were kept constant.

Reaction of Methylmagnesium Derivatives with *trans*-3-Penten-2-one (8a).—*trans*-3-Penten-2-ol, b.p. 39.5–41° (17 mm.), $n^{27.5}_{\mathrm{D}}$ 1.4245 (lit.,[34] 116–121°, n^{20}_{D} 1.4280), acid phthalate derivative, m.p. 89.5–90° (lit.,[35] 90–90.5°), was oxidized at −5° with aqueous chromium trioxide and sulfuric acid to yield *trans*-3-penten-2-one, b.p. 110°, n^{29}_{D} 1.4314 (lit.,[36] 121–122.5°, n^{20}_{D} 1.4342), semicarbazone m.p. 140–141° (lit.,[37] 142°), containing[38] 99% of the desired unsaturated ketone. Alternatively, a sample of 3-penten-2-one, b.p. 115–118°, n^{25}_{D} 1.4352–1.4392, containing[38] 96% of the desired ketone, was isolated by fractional distillation of the product mixture from the aldol condensation of acetaldehyde with acetone.[39]

To a solution of the Grignard reagent prepared from 1.032 g. (0.043 g.-atom) of magnesium, excess methyl bromide, and 30 ml. of ether was added, dropwise and with stirring under a nitrogen atmosphere at 0°, a solution of 1.80 g. (0.021 mole) of 3-penten-2-one in 20 ml. of ether. After the mixture had been stirred for 30 min., it was washed with a cold, saturated, aqueous solution of ammonium chloride to which sufficient

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[25] (a) R. C. Fuson, T. San, and J. Diekmann, *J. Org. Chem.*, **27**, 1221 (1962); (b) In our studies the possible formation of the alcohol **14** during the isolation procedure [*cf.* R. E. Lyle and F. J. Troscianiec, *ibid.*, **24**, 333 (1959)] was excluded (see Experimental).

[26] (a) M. S. Karasch and P. O. Tawney, *J. Am. Chem. Soc.*, **63**, 2308 (1941); (b) J. Munch-Peterson and V. K. Anderson, *Acta Chem. Scand.*, **15**, 271 (1961).

[27] (a) The suggestion of Meisenheimer as discussed in ref. 2b; (b) C. G. Swain and L. Kent [*J. Am. Chem. Soc.*, **72**, 518 (1950)] have suggested a comparable mechanism for the addition of organolithium compounds to ketones; (c) R. E. Dessy and R. M. Salinger, 140th National Meeting of the American Chemical Society, Chicago, Ill., September 3–8, 1961, Abstracts of Papers, p. 9Q; (d) R. E. Dessy and F. Paulik, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September 9–14, 1962, Abstracts of Papers, p. 6Q.

[28] All melting points are corrected and all boiling points are uncorrected. The infrared spectra were determined with either a Baird, Model B, or a Perkin-Elmer, Model 21, infrared recording spectrophotometer fitted with a sodium chloride prism. The ultraviolet spectra were determined with a Cary recording spectrophotometer, Model 11MS. The microanalyses were performed by Dr. S. M. Nagy and his associates and by the Scandinavian Microanalytical Laboratory. Unless otherwise stated, magnesium sulfate was employed as the drying agent.

[29] W. Schlenk, *Ber.*, **64**, 736 (1931).

[30] C. S. Marvel and V. L. Gould, *J. Am. Chem. Soc.*, **44**, 153 (1922).

[31] E. Frankland and B. F. Duppa, *Ann.*, **130**, 104 (1864).

[32] H. O. Calvery, "Organic Syntheses," Coll. Vol. 1, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 228.

[33] H. Gilman and R. E. Brown, *J. Am. Chem. Soc.*, **52**, 3314 (1930).

[34] E. R. Alexander and R. W. Kluiber, *ibid.*, **73**, 4304 (1951).

[35] H. W. J. Hills, J. Kenyon, and H. Phillips, *J. Chem. Soc.*, 576 (1936).

[36] A. L. Wilds and C. Djerassi, *J. Am. Chem. Soc.*, **68**, 1715 (1946).

[37] S. Krapiwin, *Bulletin de la Society Imperiale des Naturalistes de Moscou*, 1 (1908); *Chem. Zentr.*, **81 I**, 1335 (1910).

[38] A gas chromatography column packed with 4-methyl-4-nitropimelonitrile suspended on ground firebrick was employed.

[39] The authors are indebted to the Union Carbide Chemicals Corporation for a sample of this mixture.

aqueous ammonium hydroxide had been added to bring the solution to pH 7.5 to 8. The ether layer was dried and concentrated by distillation of the ether through an 80-cm. Vigreux column. Fractional distillation of the crude residue separated 1.025 g. of a fraction, b.p. 51° (24 mm.), $n^{29.5}_{\mathrm{D}}$ 1.4240 [lit.,[40] b.p. 37° (13 mm.), n^{17}_{D} 1.4285], containing[38] 96% of the allylic alcohol **5a** as well as 0.417 g. (total yield 1.442 g. or 67%) of fractions, b.p. 47–51° (24 mm.), $n^{29.5}_{\mathrm{D}}$ 1.4189–1.4224 containing[38] the ketone **6a** as well as the alcohol **5a**. The alcohol exhibits infrared absorption[41] at 3580 cm.$^{-1}$ (unassoc. O—H), at 3340 cm.$^{-1}$ (assoc. O—H) and 970 cm.$^{-1}$ [*trans* CH=CH) with weak end absorption (ϵ 65 at 210 mμ) in the ultraviolet.[42] Reaction of a 1.5-g. (0.015 mole) sample of the alcohol **5a** with the cyanic acid generated[43] from 5 g. (0.04 mole) of cyanuric acid afforded the crude allophanate which was taken up in ether. The pure **allophanate** crystallized from ether as white needles, m.p. 116.5–118.5°, yield 0.25 g. (9%).

Anal. Calcd. for $C_8H_{14}O_3N_2$: C, 51.60; H, 7.58; N, 15.04. Found: C, 51.58; H, 7.64; N, 15.28.

An authentic sample of methyl isobutyl ketone **6a**, b.p. 116.5°, n^{26}_{D} 1.3940 (lit.,[44] b.p. 118.5°, n^{20}_{D} 1.3956), semicarbazone m.p. 132.5–133° (lit.,[45] 134°), was prepared by the hydrogenation of mesityl oxide over platinum. This sample was shown to be identical with a sample of the ketone collected[38] from the organometallic reaction by comparison of the infrared spectra of the two samples.

An authentic sample of the diene **11a**, b.p. 76° n^{27}_{D} 1.4399 (lit.,[46] b.p. 76–77°, n^{20}_{D} 1.4418) was obtained by distillation of the allylic alcohol **5a** from potassium bisulfate. The diene has infrared absorption[41] at 1610 cm.$^{-1}$ (conj. C=C), at 965 cm.$^{-1}$ (*trans* CH=CH) and at 885 cm.$^{-1}$ (C=CH$_2$) with an ultraviolet maximum[42] at 227 mμ (ϵ 17,100).

For the quantitative experiments summarized in Table III, the desired quantity of organomagnesium compound and any additives were diluted with ether and then the unsaturated ketone plus sufficient ether to make the total reaction volume 25 ml. were added. The resulting reaction mixtures were stirred under a nitrogen atmosphere at room temperature for 45 min. and then washed with an aqueous solution of ammonium chloride and ammonium hydroxide. The ethereal solutions were dried and then analyzed by gas chromatography[38] employing columns which had been calibrated with known mixtures. The percentages of normal addition in Table III are the average values obtained from two or more runs. In no case did the deviation of an individual run from the average value exceed 2%. In the runs containing cuprous chloride, the low solubility of this salt resulted in only partial solution of the cuprous chloride in the initial reaction mixture. The molarity values in Table III and subsequent tables are calculated from the quantity of cuprous chloride added to the reaction mixture. In none of the cases summarized in Table III was the diene **11a** detected in the reaction mixtures.

TABLE III

REACTIONS OF METHYLMAGNESIUM COMPOUNDS WITH *trans*-3-PENTEN-2-ONE (**8a**)

Molarity of ketone	Methyl-magnesium compound	Added substance(s)	Normal addition, % (of product)
0.29	0.29 *M* $Me_2Mg_2Br_2$	. . .	93
.16	0.16 *M* Me_2Mg	. . .	91
.39	0.38 *M* $Me_2Mg_2Br_2$	0.04 *M* CuCl	27
.19	0.19 *M* $Me_2Mg_2Br_2$	0.04 *M* CuCl 4 *M* isoprene	18
.19	0.19 *M* $Me_2Mg_2Br_2$	4 *M* isoprene	92

Reaction of Phenylmagnesium Derivatives with *trans*-3-Penten-2-one (8a).—Reaction of 50 ml. (0.095 mole) of a 1.91 *M* ethereal solution of phenylmagnesium bromide with 4.01 g. (0.048 mole) of the unsaturated ketone for 30 min. followed by the previously described isolation procedure afforded 5.462 g. (70%) of the product mixture, b.p. 67.5–130° (0.2 mm.), containing[47] biphenyl, 2-phenyl-*trans*-3-penten-2-ol (**5b**), and 4-phenyl-2-pentanone (**6b**) as well as other unidentified minor components. Chromatography of a 3.75-g. sample from this mixture on 150 g. of Woelm neutral alumina (activity III) separated 0.187 g. of biphenyl, m.p. 69.2–70.3°, 0.613 g. of the ketone **6b**, and 1.455 g. of the allylic alcohol **5b** as well as 1.301 g. of fractions containing various mixtures of these three components. The alcohol **5b**, after further purification by distillation through a short path still [$n^{26.5}_{\mathrm{D}}$ 1.5284, lit.,[48] n^{18}_{D} 1.5327], exhibits infrared absorption[41] at 3600 cm.$^{-1}$ (unassoc. O—H), at 3460 cm.$^{-1}$ (assoc. O—H) and at 975 cm.$^{-1}$ (*trans* CH=CH) with a series of low intensity (ϵ 140 to 280) maxima in the 240- to 270-mμ region of the ultraviolet.[42]

Anal. Calcd. for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.73; H, 8.65.

The ketone **6b** was shown to be identical with a subsequently described sample by comparison of the gas chromatograms and the infrared spectra of the two samples.

The quantitative experiments, summarized in Table IV, were performed as in the previous case previous case utilizing gas chromatography[47] for the product analyses. In no case did the deviation of an individual run from the average values reported in Table IV exceed 2%. A blank experiment utilizing a known mixture of the alcohol **5b** and the ketone **6b** demonstrated that the isolation and analytical procedures employed did not alter the amounts of ketone and alcohol present.

TABLE IV

REACTIONS OF PHENYLMAGNESIUM COMPOUNDS WITH *trans*-3-PENTEN-2-ONE (**8a**)

Molarity of ketone	Phenylmagnesium compound	Added substance	Normal addition, % (of product)
0.19	0.19 *M* $Ph_2Mg_2Br_2$	. .	50
.95	0.95 *M* $Ph_2Mg_2Br_2$[a]	. .	55
.19	0.19 *M* $Ph_2Mg_2Br_2$[a]	. .	56
.19	0.19 *M* $Ph_2Mg_2Br_2$[b]	. .	56
.19	0.19 *M* Ph_2Mg	. .	47
.19	0.19 *M* Ph_2Mg	0.19 *M* $MgBr_2$	53
.19	0.19 *M* $Ph_2Mg_2Br_2$	0.02 *M* CuCl	11
.19	0.19 *M* Ph_2Mg	0.02 *M* CuCl	22

[a] In these runs the unsaturated ketone was added dropwise over 75 min. [b] In these runs, the organomagnesium reagent was added to the unsaturated ketone (*i.e.*, inverse addition).

Reaction of Methylmagnesium Derivatives with *trans*-4-Phenyl-3-buten-2-one (8b).—Reaction of 43 ml. (0.132 mole) of a 3.06 *M* ethereal solution of methylmagnesium bromide with a solution of 9.6 g. (0.066 mole) of the unsaturated ketone **8b** in 20 ml. of ether for 1 hr. followed by the usual isolation procedure yielded 9.5 g. (89%) of the crude, undistilled product mixture. A series of fractional crystallizations from petroleum ether at Dry Ice tempertures separated 1.06 g. (9.9%) of the pure allylic alcohol **5c** as colorless needles, m.p. 34.7–36° (lit.,[49] 36–37°). The material exhibits infrared absorption[41] at 3610 cm.$^{-1}$ (unassoc. O—H), at 3380 cm.$^{-1}$ (assoc. O—H), and at 970 cm.$^{-1}$ (*trans* CH=CH) with an ultraviolet maximum[42] at 251 mμ (ϵ 18,600). From a comparable reaction of 153 ml. (0.292

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[40] R. G. R. Bacon and E. H. Farmer, *J. Chem. Soc.*, 1065 (1937).

[41] Determined as a solution in carbon tetrachloride.

[42] Determined as a solution in 95% ethanol.

[43] H. W. Blohm and E. I. Becker, *Chem. Rev.*, **51**, 471 (1952).

[44] D. M. Cowan, G. H. Jeffery, and A. I. Vogel, *J. Chem. Soc.*, 171 (1940).

[45] H. D. Law, *ibid.*, **101**, 1016 (1912).

[46] G. S. Whitby and W. Gallay, *Can. J. Res.*, **6**, 280 (1932); *Chem. Zentr.*, **103 II**, 1425 (1932).

[47] A gas chromatography column packed with 1540 Carbowax suspended on base-washed 80–100-mesh Chromosorb was employed.

[48] V. Levy and H. Normant, *Compt. rend.*, **244**, 202 (1957).

[49] E. A. Braude and C. J. Timmons, *J. Cnem. Soc.*, 2000 (1950).

mole) of a 1.91 *M* ethereal solution of methylmagnesium bromide with 21.5 g. (0.147 mole) of the unsaturated ketone **8b** in 75 ml. of ether, distillation of the crude product afforded 18.29 g. of fractions, b.p. 59–104° (0.20 to 0.25 mm.), containing mixtures of the alcohol **5c**, the ketone **6b**, and the diene **11b**. Fractional distillation of this mixture separated 4.17 g. of the diene **11b**, b.p. 114.5–115.5° (19 mm.), which crystallized from petroleum ether at Dry Ice temperatures as colorless needles, m.p. 32.5–33° (lit.,[50] 28°). The diene has infrared absorption[41] at 1608 cm.$^{-1}$ (conj. C=C), at 965 cm.$^{-1}$ (*trans* CH=CH), and at 890 cm.$^{-1}$ ($C{=}CH_2$) with ultraviolet maxima[42] at 273 mμ (ε 28,600) and 281 mμ (ε 29,600) [lit.,[49,51] 273 mμ (ε 20,200) and 279 mμ (ε 20,200)]. After reaction of 36 ml. (0.110 mole) of a 3.06 *M* ethereal solution of methylmagnesium bromide with 20 ml. of an ethereal solution containing 8.05 g. (0.055 mole) of the ketone **8b** in the presence of 1.090 g.(0.011 mole) of cuprous chloride, distillation of the crude product afforded 4.125 g. of fractions, b.p. 115–120° (17 mm.), containing[47] from 45 to 65% of the ketone **6b**. A pure sample of the ketone **6b**, collected from a gas chromatograph,[52] exhibits infrared absorption[41] at 1720 cm.$^{-1}$ (C=O) with a series of low intensity (ε 310) maxima in the 250–270 mμ region of the ultraviolet.[42] The ketone **6b** formed a 2,4-dinitrophenylhydrazone, m.p. 74.1–75.2° (lit.,[53] 71–72°), and a semicarbazone, m.p. 131.3–132.8° (lit.,[53] 133–134°).

The quantitative studies, summarized in Table V, were performed as in previous cases utilizing gas chromatography[47] for product analyses. In no case did the deviation of an individual run from the average values reported in Table V exceed 2%.

Table V

Reactions of Methylmagnesium Compounds with *trans*-4-Phenyl-3-buten-2-one (**8b**)

Molarity of ketone	Methylmagnesium compound	Added substance	Normal addition, % (of product)
0.59	0.54 *M* $Me_2Mg_2Br_2$	. .	94
.59	0.54 *M* $Me_2Mg_2Br_2$	0.06 *M* CuCl	72
.35	0.35 *M* Me_2Mg	. .	89
.26	0.27 *M* Me_2Mg	0.26 *M* $MgBr_2$	95

Reaction of Phenylmagnesium Derivatives with *trans*-4-Phenyl-3-buten-2-one (8b).—After reaction of 25 ml. (0.065 mole) of a 2.60 *M* ethereal solution of phenylmagnesium bromide with 30 ml. of an ethereal solution containing 4.75 g. (0.0325 mole) of the ketone **8b** for 30 min. followed by the usual isolation procedure, the crude product (8.12 g.) was chromatographed on 500 g. of Merck alumina. Crystallization of the appropriate chromatographic fraction from petroleum ether afforded 0.189 g. of biphenyl, m.p. 68.5–69.5°, 1.225 g. (17%) of 4,4-diphenyl-2-butanone (**6d**) as white plates, m.p. 47–48° (lit., 46°,[54] 47.5°[55]), and 4.325 g. (59%) of 2,4-diphenyl-3-buten-2-ol (**5e**) as white plates, m.p. 57–58° (lit.,[56] 57.2–58°), with infrared absorption[41] at 3600 cm.$^{-1}$ (unassoc. O—H), at 3450 cm.$^{-1}$ (assoc. O—H) and at 970 cm.$^{-1}$ (*trans* CH=CH) with an ultraviolet maximum[42] at 252 mμ (ε 18,700).

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.77; H, 7.39.

The ketone **6d** has infrared absorption[41] at 1715 cm.$^{-1}$ (C=O) with a series of low intensity (ε 550) maxima in the 250–270-mμ region of the ultraviolet[42] and formed a 2,4-dinitrophenylhydrazone which crystallized from ethanol as red platelets, m.p. 174–175°, yield 75%.

Anal. Calcd. for $C_{22}H_{20}N_4O_4$: C, 65.33; H, 4.99, N, 13.86. Found: C, 65.23; H, 4.85; N, 14.02.

The ketone **6d** formed a semicarbazone which crystallized from ethanol as colorless needles, m.p. 169.2–170° (lit.,[55] 171°).

For the quantitative data summarized in Table VI, the previously described reaction and isolation procedures were employed. The solvent was removed from the ethereal solution of the crude products at room temperature under reduced pressure and a 0.500-g. sample of the residual oil was diluted to 5.00 ml. with carbon tetrachloride. The optical densities of these solutions at 1715 and 970 cm.$^{-1}$ in the infrared were measured and compared with working curves prepared from known mixtures of the alcohol **5e** and the ketone **6d** to determine the percentages of these components in the mixtures. Neither biphenyl nor isoprene interfered with this analytical procedure and the absence of the starting ketone **8b**, which would have interfered, was demonstrated by the absence of absorption at 1680 cm.$^{-1}$. The deviation of individual runs from the average values reported in Table VI did not exceed 3%.

Table VI

Reactions of Phenylmagnesium Compounds with *trans*-4-phenyl-3-buten-2-one (**8b**)

Molarity of ketone	Phenylmagnesium compound	Added substance(s)	Normal addition, % (of product)
0.35	0.35 *M* $Ph_2Mg_2Br_2$	. .	77
.26	0.26 *M* $Ph_2Mg_2Br_2$	. .	71
.29	0.31 *M* Ph_2Mg	. .	43
.31	0.31 *M* Ph_2Mg	0.31 *M* $MgBr_2$	70
.33	0.33 *M* $Ph_2Mg_2Br_2$	0.014 *M* CuCl	28
.33	0.33 *M* $Ph_2Mg_2Br_2$	2 *M* isoprene	70
.33	0.33 *M* $Ph_2Mg_2Br_2$	2 *M* isoprene 0.019 *M* CuCl	30

Reaction of Ethylmagnesium Derivatives with *trans*-4-Phenyl-3-buten-2-one (8b).—After reaction of 150 ml. (0.330 mole) of a 2.20 *M* ethereal solution of ethylmagnesium bromide with 50 ml. of an ethereal solution containing 23.4 g. (0.160 mole) of the ketone **8b** for 1 hr. followed by the usual isolation procedure, a 10.25-g. portion of the crude product (28.902 g.) was chromatographed on 400 g. of Woelm neutral alumina (activity III). The fractions separated (analyzed by gas chromatography[52]) were a mixture of olefins **11c**, **12a**, and **12b** (2.139 g.), the ketone **6c** (4.777 g.), a mixture of the ketone **6c** and the alcohol **5d** (2.765 g.), and finally the alcohol **5d** (0.401 g.) corresponding to yields of 21% olefins, 58% ketone, and 8% alcohol. Distillation of the alcohol fractions afforded the pure alcohol **5d**, b.p. 119° (9 mm.) [lit.,[57] 124–125° (11 mm.)], $n^{25}D$ 1.5359, which has infrared bands[41] at 3620 cm.$^{-1}$ (unassoc. O—H), at 3470 cm.$^{-1}$ (assoc.O—H), and at 972 cm.$^{-1}$ (*trans* CH=CH) with an ultraviolet maximum[42] at 251 mμ (ε 16,900).

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.68; H, 9.32.

Distillation of the ketone fractions afforded the pure ketone **6c**, b.p. 115° (9 mm.) [lit.,[58] 130° (18 mm.)], $n^{24.6}D$ 1.5015, with infrared absorption[41] at 1718 cm.$^{-1}$ (C=O) and a series of low intensity (ε 232) maxima in the 250–270-mμ region of the ultraviolet.[42]

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.94; H, 9.32.

Gas chromatographic analysis[52] of the diene fraction indicated the presence of **11c** (20%), **12b** (30%), and **12a** (50%, components listed in order of increasing retention time). Each of the dienes was collected[52] and further purified by distillation through a short-path still. The olefin **11c**, b.p. 100–105° (14 mm.), mol. wt. 158 (mass spectrum), has infrared absorption[41] at 960 cm.$^{-1}$ (*trans* CH=CH) and 890 cm.$^{-1}$ ($C{=}CH_2$) with an ultraviolet

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(50) K. Auwers and G. Peters, *Ber.*, **43**, 3094 (1910).

(51) The previous workers (ref. 49) stated that their product was impure.

(52) A gas chromatography column packed with 20 *M* Carbowax suspended on ground firebrick was employed.

(53) M. C. Chiang, *J. Chinese Chem. Soc.*, **18**, 65 (1951); *Chem. Abstr.*, **46**, 4472 (1952).

(54) J. H. Burckhalter and S. H. Johnson, *J. Am. Chem. Soc.*, **73**, 4830 (1951).

(55) G. G. Henderson and M. A. Parker, *J. Chem. Soc.*, **71**, 676 (1897).

(56) A. C. Cope, E. L. Wick, and F. S. Fawcett, *J. Am. Chem. Soc.*, **76**, 6156 (1954).

(57) A. Klages, *Ber.*, **39**, 2587 (1906).

(58) E. P. Kohler, *Am. Chem. J.*, **38**, 511 (1907).

TABLE VII

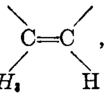
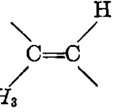
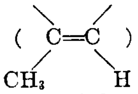
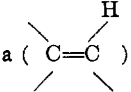
REACTIONS OF ETHYLMAGNESIUM COMPOUNDS WITH *trans*-4-PHENYL-3-BUTEN-2-ONE (**8b**)

Molarity of ketone	Ethylmagnesium compound	Product composition, %				
		Dienes **11c**, **12a**, and **12b**	Unsaturated alcohol **5b**	Ketone **6c**	Saturated alcohol **14**	Conjugate addition **6c** and **14**
0.185	0.186 *M* Et_2Mg	0	15	64	21	85
.185	0.185 *M* Et_2Mg	3	13	48	36	84[a]
.185	0.925 *M* Et_2Mg	2	11	29	58	87[b]
.075	0.75 *M* Et_2Mg	1	13	25	61	86
.015	0.75 *M* Et_2Mg	1	13	28	58	86
.015	0.15 *M* Et_2Mg	2	10	30	58	88
.22	0.11 *M* $Et_2Mg_2Br_2$	0	22	78	0	78
.22	0.22 *M* $Et_2Mg_2Br_2$	0	20	67	13	80
.157	0.157 *M* $Et_2Mg_2Br_2$	13	4	83	0	83[c]
.075	0.75 *M* $Et_2Mg_2Br_2$	31, 25, 3[d]	2, 5, 34	43, 50, 38	24, 20, 25	67
.015	0.75 *M* $Et_2Mg_2Br_2$	24, 6[d]	2, 25	47, 48	27, 21	72
.015	0.15 *M* $Et_2Mg_2Br_2$	1, 2[d]	20, 23	43, 49	36, 26	77

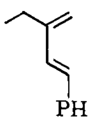
[a] In these runs, the organomagnesium compound was added to the unsaturated ketone. [b] A reaction time of 7 days was employed for these reactions. [c] In these runs the reagents were mixed in a flow system (ref. 24b) and the reaction mixture was quenched in aqueous methanol. [d] Percentage values from individual runs. Within each column the numbers are in the same order.

maximum[42] at 281 mμ (ε 27,000). The n.m.r. spectrum (60 Mc.)[41] of the sample has a multiplet centered at 2.68 τ (aromatic C—H), a pair of doublets (J = 16 c.p.s.) at 3.70 and 3.43 τ and at 3.35 and 3.08 τ (*trans* CH═CH), a partially resolved multiplet at 4.97 τ ($C = CH_2$) and a triplet centered at 8.85 τ plus a quadruplet centered at 7.67 τ (—CH_2CH_3).

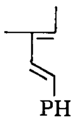
The diene **12b**, b.p. 112–118° (12 mm.), mol. wt. 158 (mass spectrum), has infrared absorption[41] at 963 cm.$^{-1}$ (*trans* CH═CH) with an ultraviolet maximum[42] at 289 mμ (ε 26,800); the n.m.r. spectrum (60 Mc.)[41] has a multiplet centered at 2.73 τ (aromatic C—H), a doublet (J = 16 c.p.s.) at 3.70 τ and 3.43 τ (*trans* CH═CH, second doublet apparently is obscured by the aromatic C—H absorption, one peak of the presumed double being discernible at 3.02 τ), a quadruplet (J ~ 6 c.p.s.) centered at 4.57 τ (olefinic proton of C═*CH*—CH_3) and a pair of peaks at 8.25 and 8.13 τ apparently resulting from a doublet (J ~ 6 c.p.s., methyl group of C═CH—CH_3) and a singlet (or unresolved multiplet) centered at 8.13 τ ($\mathit{CH}_3\text{—}\overset{|}{\text{C}}\text{═CH—CH}_3$).

The diene **12a**, b.p. 121–128° (12 mm.), n^{25}D 1.6020 [lit.,[59] b.p. 80–82° (2 mm.), n^{20}D 1.5900], mol. wt. 158 (mass spectrum), has infrared absorption[41] at 962 cm.$^{-1}$ (*trans* CH═CH) with an ultraviolet maximum[42] at 286 mμ (ε 29,500). The n.m.r. spectrum (60 Mc.)[41] of the sample has a multiplet centered at 2.77 τ (aromatic C—H), a pair of doublets (J = 16 c.p.s.) at 3.12 and 3.38 τ and at 3.55 and 3.83 τ (*trans* CH═CH), a quadruplet (J ~ 6 c.p.s.) centered at 4.40 τ (olefinic proton of C═*CH*—CH_3), and pair of bands at 8.30 and 8.20 apparently composed of a doublet (J ~ 6 c.p.s., methyl group of C═CH—CH_3) and a singlet (or unresolved multiplet) centered at 8.20 τ ($\mathit{CH}_3\text{—}\underset{}{\overset{|}{\text{C}}}\text{═CH—CH}_3$). These n.m.r. data permit the assignments of stereochemistry to the dienes **12** since the position (8.13 τ) of the methyl resonance in diene **12b**, containing the structural unit , occurs at 0.07 τ lower field than the methyl resonance (8.20 τ) of the diene **12a**, containing the structural unit .[60] The position of the olefinic proton resonance (4.57 τ) in diene **12b** () occurs at 0.17 τ higher field than the position (4.40 τ) of the corresponding peak in diene **12a** ().[61]

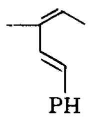
Additional evidence confirming these stereochemical assignments were obtained by mixing known quantities of each of the pure dienes **11c**, **12a**, and **12b** with a weighed quantity of anisole (employed as an internal standard) in benzene solutions. Each of the solutions was treated with approximately one equivalent of maleic anhydride, sealed under nitrogen, allowed to stand at room temperature for 3 days and then analyzed by gas chromatography.[52] No unchanged diene was detected in the solution prepared from dienes **11c** and **12a** but the ratio of diene **12b** to



11c



12a



12b

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[59] (a) A. V. Dombrovskii, *Dokl. Akad. Nauk SSSR*, **111**, 827 (1956); *Chem. Abstr.*, **51**, 9508 (1957); (b) A. V. Dombrovskii, *Zh. Obshch. Khim.*, **27**, 3041 (1957); *Chem. Abstr.*, **52**, 8087 (1958). This author did not establish the stereochemistry of his diene nor did he establish that only one isomer was present.

[60] R. B. Bates and D. M. Gale, *J. Am. Chem. Soc.*, **82**, 5749 (1960).

[61] S. L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p. 121.

anisole in the third reaction mixture remained unchanged. In the cisoid conformations (accompanying formulas) required for Diels–Alder reaction only the diene **12b** would be expected to be unreactive.[62]

A mixture of 74.1 mg. (0.451 mmole) of the diene **12a**, 44.2 mg. (0.451 mmole) of maleic anhydride, 1.5 mg. of 2,5-di-*t*-butylhydroquinone and 0.25 ml. of benzene was allowed to stand at room temperature under nitrogen for 3 days and then concentrated and diluted with hexane. Crystallization of the precipitated solid from benzene–hexane mixtures afforded 34 mg. (29%) of the crude crystalline adduct which was recrystallized several times to separate 2 mg. (1.7%) of the pure adduct as colorless prisms, m.p. 141.5–142.7° dec. (lit.,[59] 142.5°) with infrared absorption[63] at 1850 and 1775 cm.$^{-1}$ (C═O of anhydride in five-membered ring) and a series of weak ultraviolet maxima[64] ($\epsilon < 600$) in the region 250–270 mμ.

A mixture of the diastereoisomers of the saturated alcohol **14** was collected from appropriate reaction mixtures (Table VIII) by gas chromatography.[52] The material, containing a 74–26% mixture of the two diastereoisomers,[65] was shown to be identical with the subsequently described sample by comparison of the spectra and gas chromatograms[65] of the two samples.

To a cold solution of 10 ml. (22 mmoles) of a 2.2 *M* ethereal solution of ethylmagnesium bromide and 10 ml. of ether was added, with stirring under nitrogen, 1.350 g. (7.66 mmoles) of 4-phenyl-2-hexanone (**6c**). After the mixture had been stirred for 45 min. and the crude product isolated in the previously described manner, distillation afforded 1.415 g. (89.7%) of a 76–24% mixture of the diastereoisomers of **3-methyl-5-phenyl-3-heptanol** (**14**), b.p. 142° (21 mm.), n^{25}D 1.4995. The material has infrared absorption[41] at 3600 and 3490 cm.$^{-1}$ (unassoc. and assoc. O—H) with a series of low intensity ($\epsilon < 250$) in the region 240–270 mμ of the ultraviolet.[42]

Anal. Calcd. for $C_{14}H_{22}O$: C, 81.90; H, 10.31. Found: C, 81.61; H, 10.61.

Authentic samples of 4-phenyl-2-butanone, b.p. 102–105° (6 mm.), n^{25}D 1.5126 [lit.,[66] b.p. 115° (13 mm.), $n^{21.7}$D 1.511], 2,4-dinitrophenylhydrazone m.p. 128.1–128.8° (lit.,[67] 128.5–129°), 1-phenyl-1-penten-3-ol, b.p. 125–127° (8 mm.), $n^{24.5}$D 1.5579 [lit.,[68] b.p. 123° (7.5 mm.), n^{31}D 1.5550], and *trans*-1-phenyl-1,3-butadiene, b.p. 79–81° (10 mm.), n^{25}D 1.6013 [lit.,[69] b.p. 83° (11 mm.), n^{25}D 1.6089] were prepared and shown[52] to be absent in all the product mixtures obtained from ethylmagnesium derivatives and the ketone **8b**.

The quantitative data, summarized in Table VII, were obtained as previously described utilizing gas chromatography[42] for product analyses. Unless otherwise noted, the percentages in Table VII are average values from two or more runs. In no case where average values are reported did the maximum deviation from the average value exceed 4%.

For the runs reported in Table VII, a known weight of anisole was added to each sample prior to analysis. From a knowledge of the area under the anisole peak in each case and appropriate calibration mixtures, the per cent yields for the products indicated in Table VII were calculated. In no case was the yield of the combined products indicated less than 90%. In two cases where substantial amounts of the saturated alcohol **14** were formed, the reaction mixtures were decomposed both by adding the reaction mixtures to saturated, aqueous ammonium chloride and by adding saturated, aqueous ammonium chloride to the reaction mixtures. Since the former procedure did not decrease the amount of alcohol **14** produced, we conclude that this product is formed in the original reaction mixture before any water has been added.

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(62) D. Craig, J. J. Shipman, and R. B. Fowler, *J. Am. Chem. Soc.*, **83**, 2885 (1961).

(63) Determined as a solution in chloroform.

(64) Determined as a solution in ether.

(65) The analysis was obtained with a 200-ft., Ucon-50 capillary column heated to 140°. We are indebted to Drs. H. E. Johnson and E. Rick of the Union Carbide Chemicals Corporation for this analysis.

(66) A. Klages, *Ber.*, **37**, 2301 (1904).

(67) G. D. Johnson, *J. Am. Chem. Soc.*, **73**, 5888 (1951).

(68) I. E. Muskat and M. Herrman, *ibid.*, **53**, 252 (1931).

(69) O. Grummitt and F. J. Christoph, *ibid.*, **73**, 3479 (1951).

The Chemistry of Carbanions. III. The Reaction of Organomagnesium Compounds with Saturated Ketones[1a]

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Both the product compositions and the rates of reaction have been studied for 3-pentanone and diisopropyl ketone with diethylmagnesium, ethylmagnesium bromide, and the ethylmagnesium alkoxides **6**. From these and other studies, we conclude that magnesium bromide does not catalyze addition of the ethylmagnesium reagents to the carbonyl functions but does suppress the tendency of ethylmagnesium alkoxides and/or magnesium dialkoxides to give by-products resulting from enolization and reduction.

In continuing our study of the reactions of organomagnesium compounds,[2] it was of interest to examine the behavior of simple ketones **5** with various organomagnesium compounds including the Grignard reagent **1**, a dialkylmagnesium compound **2**, and the product (possibly an alkylmagnesium alkoxide **3** or its dimer **4**) obtained by reaction of one molar equivalent of a dialkylmagnesium compound with one molar equivalent of a ketone. The reactions studied are summarized in Chart I.

We first examined reactions where the reactants were mixed by adding the ketone **5** to an excess of the organomagnesium compound (normal addition procedure where the organometallic is always in excess) and by adding the organomagnesium derivative to the ketone (inverse addition procedure where the ketone is in excess during at least the first half of the reaction). In the absence of magnesium bromide, the results (Tables I and II) are in agreement with the earlier suggestion of Mosher and co-workers[3,4] that a dialkylmagnesium compound reacts with a ketone to give primarily an addition product **7**, whereas the intermediate (possibly **3** or **4**) formed after consumption of the first alkyl group reacts with a ketone to give substantial amounts of enolization (as in **5**) and reduction (as in **9**) products as well as the addition product **7**. However, the differing product ratios obtained in the two steps of this reaction are greatly reduced when a molar equivalent of magnesium bromide is present in the reaction mixture. This observation is in accord with

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(2) H. O. House, D. D. Traficante, and R. A. Evans, *J. Org. Chem.*, **28**, 348 (1963).

(3) J. Miller, G. Gregoriou, and H. S. Mosher, *J. Am. Chem. Soc.*, **83**, 3966, 5051 (1961).

(4)(a) D. O. Cowan and H. S. Mosher, *J. Org. Chem.*, **27**, 1 (1962); (b) D. Cowan and H. S. Mosher, *ibid.*, in press.