by distillation through a 10-cm Vigreux column, and the pale yellow, liquid residue was fractionated *in vacuo*. The first fraction consisted of 0.486 g of colorless liquid, bp 56–58° (31–43 mm). A second 0.786-g fraction of pale yellow oil, bp 123–141° (5.0–7.0 mm), and a third 0.947-g fraction of yellow oil, bp 142–168° (0.4–5.0 mm), were also collected. The low-boiling fraction was shown to contain two components by gas chromatography.[10] The minor component, identified on the basis of its glpc retention time, consisted of recovered 3-penten-2-one. The major component (66%) was 4-methylhexan-2-one, which was obtained as a colorless liquid by preparative gas chromatography[13] (>99% pure by glpc), $[\alpha]^{25}\text{D}$ +0.36° (*c* 6.84, $CHCl_3$), and identified by spectroscopic comparison with an authentic sample.

A 0.589-g portion of the second distillation fraction was chromatographed on 30.0 g of 60–200 mesh silica gel. Fractions eluted with 2:98 and 5:95 eher–benzene contained 0.424 g of 4-methyl-3-*sec*-butylheptane-2,6-dione. Short-path distillation (2.4 mm and 117° bath) afforded the analytical sample as a colorless liquid: $[\alpha]^{25}\text{D}$ +1.04° (*c* 6.46, hexane); ir (neat) 1709 cm^{-1} (C=O); nmr (CCl_4) δ 2.04 (3 H, s, $COCH_3$) and 2.07 (3 H, s, $COCH_3$); mass spectrum (70 eV) *m/e* 198 (M^+).

Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.96; H, 11.08.

The high-boiling distillation fraction showed strong carbonyl absorption at 1709 cm^{-1} but no hydroxyl absorption in the infrared spectrum. No further attempt was made to characterize this material.

Reaction of 1,3-Diphenyl-2-propen-1-one with Methylmagnesium Iodide in the Presence of (−)-Sparteine (4) in Benzene Solution.—The following preparation is representative of the reactions carried out in benzene solution and in the presence of (−)-sparteine (4) which are summarized in Tables I and II. A solution of methylmagnesium iodide was prepared under nitrogen by dropwise addition of a solution of 4.429 g (0.031 mol) of methyl iodide in 50 ml of anhydrous ether into a flask containing 0.630 g (0.026 g-atom) of magnesium turnings over a period of 20 min at ice-bath temperature with magnetic stirring. After addition was completed, stirring was continued at room temperature for an additional 40 min, resulting in complete reaction of the magnesium. A solution of 6.105 g (0.026 mol) of (−)-sparteine (4) [distilled from CaH_2 prior to use, bp 119.0–124.0° (0.75–0.90 mm)] in 100 ml of benzene was then added. Ether was removed by distillation through a 10-cm Vigreux column in a nitrogen atmosphere. A total of 86 ml of solvent was distilled with a final distillation temperature of 80.0°. The resulting mixture was cooled to room temperature and a solution of 4.512 g (0.022 mol) of 1,3-diphenyl-2-propen-1-one, mp 58.0–58.5°, in 50 ml of benzene was added over a period of 3 min with stirring. The mixture was then heated at reflux, under nitrogen, and with stirring for 16 hr. After cooling, the mixture was decomposed with 100 ml of 3 *M* HCl. The organic layer was separated, washed once with 50 ml of 3 *M* HCl and once with 50 ml of water, and dried over anhydrous $MgSO_4$. Concentration *in vacuo* afforded 4.633 g of amber-colored oil. The principal product, 1,3-diphenyl-3-methylpropan-1-one, was isolated by preparative gas chromatography[11] as a white solid, mp 68.5–71.0°, $[\alpha]^{25}\text{D}$ −0.38° (*c* 10.78, CCl_4), and identified by spectroscopic comparison with an authentic sample. Distillation of 3.446 g of the crude product afforded 1.632 g (45%) of amber-colored oil, bp 129–136° (0.20 mm), which crystallized on seeding with the 1,3-diphenyl-3-methylpropan-1-one obtained by preparative gas chromatography, mp 70.0–72.0°. The distillation residue showed strong carbonyl absorption at 1677 cm^{-1} but no hydroxyl absorption in the infrared spectrum (measured in $CHCl_3$ solution).

Registry No.—**4**, 90-39-1; methylmagnesium iodide, 917-64-6; phenylmagnesium bromide, 100-58-3; ethylmagnesium bromide, 925-90-6; 2-cyclohexenone, 930-68-7; 1,3-diphenyl-2-propen-1-one, 91-41-7; 3-penten-2-one, 625-33-2.

Acknowledgment.—Financial support by the Petroleum Research Fund of the American Chemical Society is gratefully acknowledged.

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(10) A 15 ft × 0.25 in. column packed with 10% silicone QF-1 on Chromosorb P was employed.

(11) A 5 ft × 0.25 in. column packed with 15% silicone SF-96 on Chromosorb P was employed.

Notes

The Reaction of Benzalacetophenone with Methylmagnesium Iodide. A Novel Grignard Reaction

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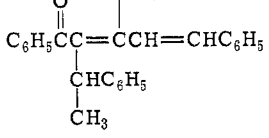
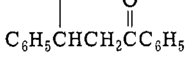
The reaction of Grignard reagents with many α,β-unsaturated ketones to give exclusive or predominant 1,4-addition products is well known.[1] It is less generally recognized, however, that, unless the Grignard reagent is used in large excess, products of high molecular weight are often formed in high yield.[2] These by-products have been regarded as arising from either ketol condensations or from diene polymerizations,[1a] but almost without exception they have not been carefully studied. The reaction of methylmagnesium bromide with benzalacetophenone (**1**) represents an isolated example where such a by-product was examined. This reaction has been reported to afford dienone **2**, in addition to β-phenylbutyrophenone (**3**), the anticipated 1,4-addition product.[2b]



$$C_6H_5\overset{\displaystyle O}{\overset{\|}{C}}\underset{\underset{\displaystyle CH_3}{\underset{|}{CHC_6H_5}}}{\underset{|}{C}}=\overset{\displaystyle C_6H_5}{\overset{|}{C}}CH=CHC_6H_5$$

2



$$C_6H_5\overset{\displaystyle CH_3}{\overset{|}{C}}HCH_2\overset{\displaystyle O}{\overset{\|}{C}}C_6H_5$$

3

We recently had occasion to examine the reaction between **1** and methylmagnesium iodide. A major product (20%) of this reaction had properties consistent with those reported for **2**, but the spectroscopic data

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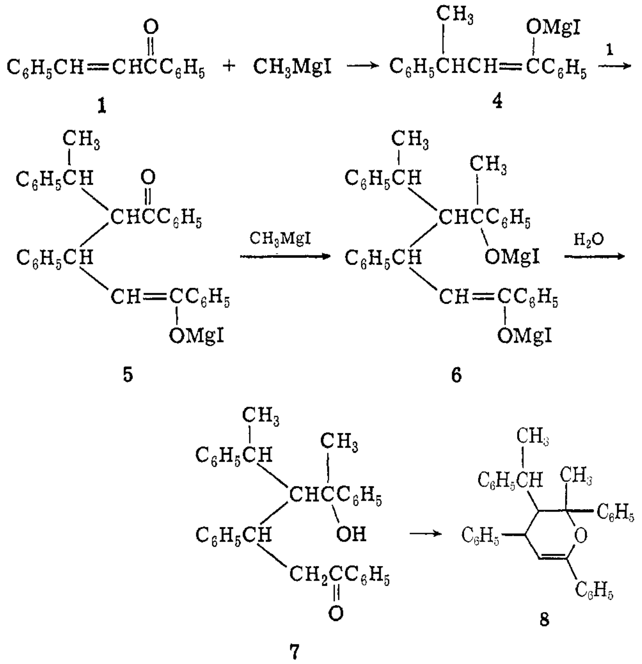
(1) (a) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, New York, N. Y., 1954, pp 196–234; (b) J. Munch-Petersen, *Bull. Soc. Chim. Fr.*, 471 (1966).

(2) (a) E. P. Kohler and W. D. Peterson, *J. Amer. Chem. Soc.*, **55**, 1073 (1933); (b) M. S. Kharasch and D. C. Sayles, *ibid.*, **64**, 2972 (1942).

were clearly incompatible with structure **2**.[3] The mass spectrum indicated a molecular weight of 430, while the nmr contained a methyl doublet at δ 1.20 and a methyl singlet at δ 1.67. In addition, the infrared spectrum failed to confirm the presence of a carbonyl group. The available data appear most consistent with the formulation of this compound as dihydropyran **8**. This compound is, presumably, formed through initial 1,4 addition of methylmagnesium iodide to benzalacetophenone (**1**) to give magnesium enolate **4** (Scheme I). Michael addition of **4** to another molecule of starting material would then afford 1,5-diketone **5**, containing one of the carbonyl groups in enolic form.[4] The unenolized carbonyl group of **5** would not be expected to survive in the presence of excess methylmagnesium iodide, and subsequent reaction should afford **6**. Hydrolysis of **6** would give hydroxy ketone **7**, which under acidic conditions would be expected to cyclize and dehydrate to give **8**.[5]

SCHEME I



The formation of **8**, under these conditions, indicates that magnesium enolate **4** is able to compete favorably with Grignard reagent for unreacted enone **1**. Utilization of a large excess of Grignard reagent in this reaction would obviously act to surpress the Michael reaction responsible for formation of **5**. It is interesting to speculate that a process similar to that of Scheme I may be responsible for the high molecular weight byproducts obtained in the Grignard reactions of other α,β-unsaturated ketones.

Experimental Section[6]

Reaction of Methylmagnesium Iodide with Benzalacetophenone.—A solution of methylmagnesium iodide was prepared under nitrogen by dropwise addition of a solution of 4.136 g (0.0291 mol) of methyl iodide in 50 ml of anhydrous ether into a flask containing 0.590 g (0.0243 g-atom) of magnesium turnings over a period of 18 min, at ice-bath temperature, and with magnetic stirring. After addition was completed, stirring was continued at room temperature for 30 min, resulting in complete reaction of the magnesium. The Grignard solution was cooled at ice-bath temperature, and a solution of 3.251 g (0.0156 mol) of benzalacetophenone (**1**), mp 58–58.5°, in 90 ml of anhydrous ether was added dropwise, with stirring, over a period of 24 min. The resulting mixture was stirred at room temperature for 30 min and then decomposed with 100 ml of 3 *M* HCl. The ether layer was washed twice with 50-ml portions of 3 *M* HCl and once with 50 ml of saturated NaCl, and dried over anhydrous $MgSO_4$. Concentration *in vacuo* afforded an amber-colored oil which was chromatographed on a 40-g column of 60–200 mesh silica gel. Fractions eluted with hexane and with 1:19 benzene–hexane were crystallized from ether to give 0.677 g (20%) of **8** as small white needles, mp 176.0–177.5°. Recrystallization from ether afforded the analytical sample: mp 178.0–179.0° (lit.[2b] mp 176°); ir (KBr) 1658 (m, C=C), 760 (s, aromatic CH), 745 (s, aromatic CH), and 697 cm^{-1} (s, aromatic CH); nmr (CCl_4) δ 1.20 (3, H, d, J = 7 Hz, $CHCH_3$), 1.67 (3, H, s, CH_3), 2.33–3.00 (2 H, complex m, aliphatic CH), 4.41 (1 H, q, $J_{ab} = 6.8$, $J_{bc} = 2.2$ Hz, $CH_aCH_bArCH_c{=}C$), 5.74 (1 H, br, $W_{1/2} = 4$ Hz, ArCHCH=C), and 6.0–8.0 (20 H, aromatic CH); mass spectrum (70 eV) *m/e* (rel intensity) 430 (M^+, 12), 325 (65), 222 (27), 221 (35), 208 (14), 207 (76), 206 (78), 205 (81), 105 (100), 91 (29), and 77 (5).

Anal. Calcd for $C_{32}H_{30}O$: C, 89.26; H, 7.02. Found: C, 89.58; H, 7.17.

Fractions eluted with 1:9 and 1:1 benzene–hexane contained 1.634 g of solid, which afforded 0.981 g (28%) of pure β-phenylbutyrophenone after crystallization from aqueous ethanol and from hexane, mp 73.5–75.0° (lit.[7] mp 74°).

Registry No.—**1**, 94-41-7; **2**, 34959-76-7; methylmagnesium iodide, 917-64-6.

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(3) Kharasch and Sayles reported the independent synthesis of **2** in quantitative yield by reaction of benzalacetophenone with β-phenylbutyrophenone in the presence of pyridine.[2b] We have been unable to duplicate this preparation.

(4) The Michael reaction of a magnesium enolate with benzalacetophenone has previously been reported.[2a]

(5) *Cf.* M. Julia and A. Rouault, *Bull. Soc. Chim. Fr.*, 1833 (1959).

(6) Melting points are uncorrected. The infrared spectra were determined with a Beckman IR-8 spectrophotometer. Nmr spectra were recorded with a Varian A-60 spectrometer using tetramethylsilane as an internal standard. The mass spectra were obtained with a Varian MAT CH7 mass spectrometer. Microanalyses were performed by M-H-W Laboratories, Garden City, Mich.

(7) M. A. Spielman and C. W. Mortenson, *J. Amer. Chem. Soc.*, **61**, 666 (1939).

Silver(II) Oxide as a Reagent. Reactions with Aromatic Amines and Miscellaneous Related Compounds

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Lee and Clarke have effected the oxidation of aliphatic amines, alcohols, aldehydes, and aromatic hydrocarbons[1,2] by means of the complexes of silver(II) oxide.[3] Syper[4] utilized the same reagent in acidic media to oxidize alcohols and aromatic hydrocarbons, while Corey, Gillman, and Ganem[5] employed it in neutral or slightly basic media for the stereospecific con-

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(1) J. B. Lee and T. G. Clarke, *Tetrahedron Lett.*, 415 (1967).

(2) T. G. Clarke, N. A. Hampson, J. B. Lee, J. R. Morley, and B. Scanlon, *ibid.*, 5685 (1968).

(3) R. N. Hammer and J. Kleinberg, *Inorg. Syn.*, **4**, 12, (1953).

(4) L. Syper, *ibid.*, 4193 (1967).

(5) E. J. Corey, N. W. Gillman, and B. E. Ganem, *J. Amer. Chem. Soc.*, **90**, 5616 (1968).