nmr, melting point, mixture melting point, and tlc mobility (R_f 0.36, silica gel G, ether)] as the previously prepared sample.

Isotulipinolide (24).—Tulipinolide (1, 175 mg) was suspended in 1 *N* KOH and warmed for 2 hr on a steam bath. The solution was quickly evaporated, treated with 3 ml HOAc, and evaporated, and the process repeated again. The residue was dissolved in $CHCl_3$, extracted with 5% $NaHCO_3$ and H_2O, dried (Na_2SO_4), and evaporated to leave a 50-mg residue. Chromatography of the residue over 4 g of silica gel G with $CHCl_3$–Et_2O (1:1) as eluting solvent gave 27 mg of an oil that was one spot on tlc and was formulated as desacetylisotulipinolide (**23**): $[\alpha]^{22}D$ +130° (*c* 0.054, MeOH); ir 3610, 3460, 1760, and 1660 cm^{-1}; mass spectrum *m/e* (rel intensity) M^+ 248.1417 (3.5) ($C_{15}H_{20}O_3$ calcd 248.1412), 230 (3), 108 (13), 84 (36), and 18 (100).

Acetylation of desacetylisotulipinolide (**23**, 27 mg) with Ac_2O–pyridine at room temperature for 20 hr gave a residue that after chromatography on silica gel G using $CHCl_3$–Et_2O (20:1) as eluting solvent gave 15 mg of an oil that was one spot on tlc and was formulated as isotulipinolide (**24**): $[\alpha]^{22}D$ +36 (*c* 0.056, MeOH), ir 1760, 1735, 1660, and 1250 cm^{-1}; mass spectrum *m/e* (rel intensity) M^+ 290.1507 (0.6) ($C_{17}H_{22}O_4$ calcd 290.1518), 230 (5), 107 (14), 84 (50), and 43 (100). A comparison (ir, nmr, and tlc) of this material with laurenobiolide[13] showed them to be the same.

Eupatolide Methanesulfonate (25).—A 500-mg sample of eupatolide (**11**) dissolved in 4 ml of pyridine and cooled in an ice bath was treated with 0.3 ml of CH_3SO_2Cl. After 17 hr the solution was diluted with H_2O and extracted with $CHCl_3$ and the $CHCl_3$ extract was washed with 1% HCl and H_2O. The $CHCl_3$-soluble residue was crystallized from EtOH–isopropyl ether to give 412 mg of eupatolide methanesulfonate (**25**): mp 112–113°; ir 1770, 1670, 1350, and 1175 cm^{-1}.

Anal. Calcd for $C_{16}H_{22}O_5S$: C, 58.88 H, 6.80 S, 9.81. Found: C, 58.57 H, 6.93 S, 9.68.

Treatment of Eupatolide Methanesulfonate (25) with KOH.—A 400-mg sample of **25** was stirred with 8 ml of EtOH, and 72 ml of 0.4 *N* KOH was added. After 24 hr at room temperature, the reaction solution was acidified with dilute HOAc, saturated with NaCl, and extracted with ether. The ether extract was washed with water, dried (Na_2SO_4), and evaporated to leave 243 mg of an oily residue. Chromatography of the oil was on 15 g of silica gel G with $CHCl_3$–Et_2O (1:1) as eluting agent. Early fractions gave 37 mg of deacetylisotulipinolide (**23**) identical (tlc, ir, and nmr) with the product of alkaline hydrolysis of tulipinolide (**1**). Later fractions contained eupatolide (**11**).

Reduction of Dehydroeupatolide (27).—To a solution of dehydroeupatolide[2] (100 mg) in 7 ml of *i*-PrOH at 40° was added 6 mg of $NaBH_4$. After 10 min the solution was acidified with dilute HOAc, diluted with H_2O, and extracted with ether. The ether-soluble residue (95 mg) showed three spots on tlc. Separation of these substances was accomplished on 5 g of silica gel G using $CHCl_3$–Et_2O (1:1) as solvent system. Two products were identified as eupatolide (**11**) and dihydroeupatolide (**12**), while the third from spectral evidence appeared to be 11,13-dihydrodehydroeupatolide, but deacetyltulipinolide (**26**) was not detected.

Registry No.—**1**, 24164-12-3; **2**, 24164-13-4; **3**, 35001-07-1; **4**, 35001-08-2; **5**, 35001-09-3; **6**, 24164-20-3; **7**, 24165-31-9; **8**, 35001-12-8; **9**, 35001-13-9; **10**, 35001-14-0; **12**, 35001-16-2; **13**, 35001-15-1; **14**, 35001-17-3; **15**, 35001-18-4; **16**, 35001-19-5; **17**, 35001-20-8; **18**, 35001-21-9; **19**, 35001-22-0; **22**, 35001-23-1; **23**, 35001-24-2; **24**, 35001-25-3; **25**, 35001-26-4; **28**, 35001-27-5.

1,4 Addition of Organometallic Reagents to α,β-Unsaturated Ketones in the Presence of (−)-Sparteine

RICHARD A. KRETCHMER

Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois 60616

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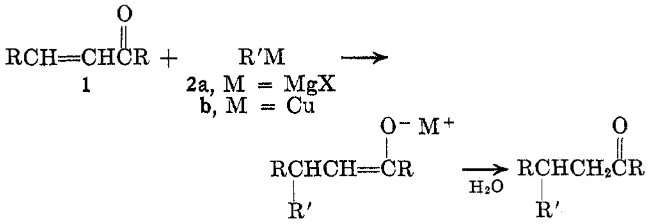
The reaction of 2-cyclohexenone, 3-penten-2-one, and 1,3-diphenyl-2-propen-1-one with a series of Grignard reagents has been studied in the presence of (−)-sparteine (4) and other additives. The resulting conjugate addition products possess an optical purity of 3-6% and represent the first examples of asymmetric 1,4 addition of achiral organometallic reagents to prochiral α,β-unsaturated ketones. Subsequent reactions of enolate anions initially produced by conjugate addition of the organometallic reagents are discussed. (−)-Sparteine is shown to reduce the reactivity of methylmagnesium iodide toward α,β-unsaturated ketones.

The ability of α,β-unsaturated ketones (**1**) to add Grignard reagents (**2a**)[1] and organocopper(I) compounds (**2b**)[2] in a 1,4 manner is well documented in

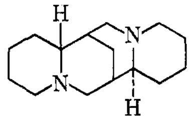


$$\mathrm{RCH{=}CH\overset{\overset{O}{\|}}{C}R} + \mathrm{R'M} \longrightarrow \mathrm{R\underset{\underset{R'}{|}}{C}HCH{=}\overset{\overset{O^-\,M^+}{|}}{C}R} \xrightarrow{H_2O} \mathrm{R\underset{\underset{R'}{|}}{C}HCH_2\overset{\overset{O}{\|}}{C}R}$$

1 2a, M = MgX
b, M = Cu

3

the literature. Recently, it has been shown that the course of this reaction can be influenced to some extent by solvent or the ligands attached to the organometallic reagent.[2b,c] In view of this, we have examined the reaction of some α,β-unsaturated ketones with Grignard reagents in the presence of (−)-sparteine (**4**). The



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results, indicated in Tables I and II, represent the first examples of asymmetric 1,4 addition of achiral organometallic reagents to prochiral α,β-unsaturated ketones.

The most apparent effect of an equimolar amount of (−)-sparteine (**4**) on an ether solution of methylmagnesium iodide is a drastic reduction of reactivity toward the enone substrates (Table I). Both 2-cyclohexenone and 1,3-diphenyl-2-propen-1-one were recovered unchanged after exposure to this reagent system for over 1 hr at room temperature. Enolization

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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) H. Gilman, R. G. Jones, and L. A. Woods, *J. Org. Chem.*, **17**, 1630 (1952); (b) H. O. House, W. L. Respess, and G. M. Whitesides, *ibid.*, **31**, 3128 (1966); (c) H. O. House and W. F. Fischer, *ibid.*, **33**, 949 (1968).

TABLE I

1,4 ADDITION OF GRIGNARD REAGENTS TO α,β-UNSATURATED KETONES IN THE PRESENCE OF VARIOUS ADDITIVES

Run	Organometallic (mol %)[a]	Additive (mol %)	Substrate	Product	Time, hr[b]	Solvent	Yield, %[c]	Substrate recovery, %[c]
1	CH_3MgI (124)	Sparteine (124)	2-Cyclohexenone	3-Methylcyclohexanone	1	Et_2O	<1[d]	38
2	CH_3MgI (125)	Sparteine (125)	2-Cyclohexenone	3-Methylcyclohexanone	18[e]	Benzene	<1	<1[f]
3	CH_3MgI (100)	Sparteine (200) + CuCl (99)	2-Cyclohexenone	3-Methylcyclohexanone	0.5[g]	Et_2O	17	2[f]
4	C_6H_5MgBr (124)	Sparteine (221) + CuCl (110)	2-Cyclohexenone	3-Phenylcyclohexanone	1	Et_2O	17	f
5	CH_3MgI (156)	None	1,3-Diphenyl-2-propen-1-one	1,3-Diphenyl-3-methyl-1-propanone	0.5	Et_2O	39	f
6	CH_3MgI (155)	Sparteine (170)	1,3-Diphenyl-2-propen-1-one	1,3-Diphenyl-3-methyl-1-propanone	1.5	Et_2O		100
7	CH_3MgI (120)	Sparteine (120)	1,3-Diphenyl-2-propen-1-one	1,3-Diphenyl-3-methyl-1-propanone	16[e]	Benzene	45	<1[f]
8	CH_3MgI (124)	Sparteine (260) + CuI (131)	1,3-Diphenyl-2-propen-1-one	1,3-Diphenyl-3-methyl-1-propanone	1	Et_2O	7[d]	25[d,f]
9	CH_3MgI (125)	Sparteine (249) + CuCl (130)	1,3-Diphenyl-2-propen-1-one	1,3-Diphenyl-3-methyl-1-propanone	1	Et_2O	50 (64)[d]	
10	CH_3MgI (140)	Sparteine (281) + LiCl (136)	1,3-Diphenyl-2-propen-1-one	1,3-Diphenyl-3-methyl-1-propanone	1.5	Et_2O	<1	80
11	C_2H_5MgBr (124)	Sparteine (250) + CuCl (131)	3-Penten-2-one	4-Methyl-2-hexanone	0.5[g]	Et_2O	10	5[f,h]

[a] Mole per cent of Grignard reagent calculated on the basis of the amount of magnesium employed. [b] At room temperature unless otherwise indicated. [c] Isolated yield unless otherwise indicated. [d] Determined by nmr. [e] At reflux temperature. [f] Uncharacterized higher molecular weight material was formed in this reaction. [g] At ice-bath temperature. [h] 4-Methyl-3-*sec*-butyl-2,6-heptanedione was obtained in 27% yield.

TABLE II

OPTICAL ACTIVITY OF PRODUCTS RESULTING FROM 1,4 ADDITION OF ORGANOMETALLIC REAGENTS TO α,β-UNSATURATED KETONES IN THE PRESENCE OF (−)-SPARTEINE

Registry no.	Run[a]	Product	$[\alpha]^{25}\mathrm{D}$	Configuration	Optical purity, %
13368-65-5	3	3-Methylcyclohexanone[b]	+0.91[c]	R[d]	6.3[e]
34993-51-6	4	3-Phenylcyclohexanone[b]	+0.12[f]	R[g]	
20698-96-8	7	1,3-Diphenyl-3-methyl-1-propanone[h]	−0.38	R[i]	3.1[i]
	9	1,3-Diphenyl-3-methyl-1-propanone[h]	−0.61[j]	R[i]	5.0[i]
1731-00-6	11	4-Methyl-2-hexanone[b]	+0.36	S[k]	4.6[k]
34994-54-9	11	4-Methyl-3-*sec*-butyl-2,6-heptanedione	+1.04		

[a] Numbering identical with that used in Table I. [b] Purified by preparative gas chromatography on a 15 ft × 0.25 in. column packed with 10% silicon QF-1 on Chromosorb P. [c] $CHCl_3$ sclution, *c* 2.14. [d] E. J. Eisenbraun and S. M. McElvain, *J. Amer. Chem. Soc.*, **77**, 3383 (1955); R. Adams, C. M. Smith, and S. Loewe, *ibid.*, **64**, 2087 (1942). [e] Optically pure (*R*)-3-methylcyclohexanone has $[\alpha]^{25}\mathrm{D}$ +14.35° (*c* 9.674, $CHCl_3$). [f] $CHCl_3$ solution, *c* 16.30. [g] Assigned on the basis of a positive Cotton effect in ethanol. [h] Purified by preparative gas chromatography on a 5 ft × 0.25 in. column packed with 15% silicone SF-96 on Chromosorb P. [i] J. H. Brewster and M. W. Kline, *J. Amer. Chem. Soc.*, **74**, 5179 (1952). [j] CCl_4 solution. [k] C. Djerassi and L. E. Geller, *J. Amer. Chem. Soc.*, **81**, 2789 (1959).

does not appear to be responsible for this recovery of starting material, since 1,3-diphenyl-2-propen-1-one is incapable of undergoing this type of reaction. These results are not entirely surprising, however, in view of the ability of pyridine and quinoline to surpress the rate of reaction of phenylmagnesium bromide with benzophenone.[3] When ether was replaced by benzene as the solvent, reaction did take place between methylmagnesium iodide and 1,3-diphenyl-2-propen-1-one, after prolonged reflux, to give the conjugate addition product in 45% yield. An attempt to react 2-cyclohexenone with methylmagnesium iodide under these conditions afforded large quantities of nonvolatile, carbonyl-containing material, but no isolable conjugate addition product.

Alkyl- and arylcopper(I) compounds can be prepared by reaction of the corresponding organomagnesium halide with a copper(I) salt.[2a,4] Treatment of α,β-unsaturated ketones with these organocopper(I) reagents frequently results in predominant or exclusive 1,4 addition to the enone.[2] In view of this, 1,3-diphenyl-2-propen-1-one was allowed to react with an ether solution of methylmagnesium iodide in the presence of an equimolar amount of cuprous chloride and enough (−)-sparteine (**4**) to chelate all of the metal atoms present. Under these conditions, a 64% yield of conjugate addition product was obtained. A control experiment utilizing lithium chloride in place of cuprous chloride resulted in recovery of starting material and suggests that methylmagnesium chloride, which could be obtained by simple halogen exchange, is not responsible for the observed conjugate addition. Lack of reactivity by the Grignard–sparteine system in the absence of cuprous chloride makes it appear likely that the reactive intermediate contains copper. It

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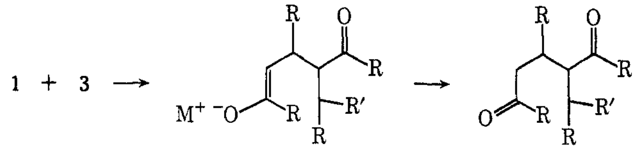
(3) (a) F. Drahowzal and H. König, *Monatsh. Chem.*, **85**, 654 (1954). (b) Bidentate ligands such as *N,N,N′,N′*-tetramethylethylenediamine have also been shown to retard the rate of reaction of dimethylmagnesium with benzophenone: H. O. House and J. E. Oliver, *J. Org. Chem.*, **33**, 929 (1968).

(4) H. Gilman and J. M. Straley, *Recl. Trav. Chim. Pays-Bas*, **55**, 821 (1936); (b) G. Costa, A. Camus, L. Gatti, and N. Marsich, *J. Organometal. Chem.*, **5**, 568 (1966).

is also noteworthy that cuprous iodide was an unsatisfactory substitute for cuprous chloride and resulted primarily in conversion of 1,3-diphenyl-2-propen-1-one to uncharacterized, high molecular weight, carbonyl-containing material. This seems to further imply that halide ion exerts some control over the intermediates reactivity and must also be included in its description.

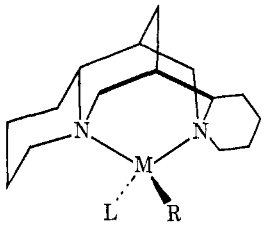
Reaction of other α,β-unsaturated ketones with the reagent systems obtained by addition of (−)-sparteine (**4**) and cuprous chloride to ether solutions of various Grignard reagents resulted in the successful production of additional conjugate addition products, although in low yield (Table I). The formation of high molecular weight, carbonyl-containing material represented the major reaction in most cases. This is unfortunate but not without precedent, and appears to be a function of the ligands present.[2c] These high molecular weight by-products appear to result from Michael addition of enolate anion **3** to a molecule of starting material **1** to give a new enolate anion **5**, which could undergo further reaction with excess enone **1** or organometallic reagent **2**. Alternatively, hydrolysis of **5** would afford 1,5-diketone **6**.[5] Thispr ocess was substantiated for the reaction of 3-penten-2-one with ethylmagnesium bromide in the presence of (−)-sparteine (**4**) and CuCl (Table I). A major product (27%) of this reaction was



5 **6**

4-methyl-3-*sec*-butyl-2,6-heptanedione (**6**, R = CH_3; R' = C_2H_5). The unenolized ketone carbonyl of **5** would not be expected to survive an ordinary Grignard reaction. In this example, however, the organometallic reagent present is presumably either largely or exclusively a copper(I) derivative. The lack of reactivity by organocopper(I) reagents toward carbonyl groups is well documented.[2b] In the event of incomplete conversion of Grignard reagent to the corresponding organocopper(I) derivative, the lack of reactivity by methylmagnesium iodide in the presence of an equimolar amount of (−)-sparteine (**4**) (Table I) makes the survival of the unenolized carbonyl group of **5** unsurprising. In this context, it should be noted that no hydroxyl-containing products were observed in the series of experiments utilizing CuCl and (−)-sparteine (**4**). It appears, therefore, that in the presence of diamine **4**, Michael reaction of the initially formed enolate anion **3** can compete effectively with conjugate addition by the organometallic reagent.

Without exception, the conjugate addition products obtained by reaction in the presence of (−)-sparteine (**4**) possessed a low degree of optical activity (Table II). These results require that the optically active diamine **4** be considered in a description of the organometallic intermediate. The asymmetric synthesis can be rationalized most simply as proceeding through the intermediacy of an organometallic–sparteine complex such as **7**, where M may be either magnesium or copper[6] and L represents a ligand such as chloride ion. This model is also consistent with the



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ability of (−)-sparteine (**4**) to reduce the reactivity of methylmagnesium iodide in the absence of added CuCl (Table I). The diamine ring system, folded about the magnesium atom, would be expected to interfere sterically with approach by the enone substrate. Although the mechanism involved in the conjugate addition of organometallic reagents is not well understood, the results reported here are consistent with a transfer of the alkyl or aryl group from the metal to the β carbon of the enone **1** through a transition state which contains (−)-sparteine (**4**) coordinated to the metal atom. Correlation of the absolute configuration[8] of (−)-sparteine (**4**) with that of the resulting conjugate addition products has not been attempted in view of the low optical yields and lack of definitive mechanistic information.

Experimental Section[9]

Reaction of 3-Penten-2-one with Ethylmagnesium Bromide in the Presence of (−)-Sparteine (4) and Cuprous Chloride.—The following preparation is representative of the general procedure utilized for the reactions carried out in ether solution and summarized in Tables I and II. A solution of ethylmagnesium bromide was prepared under nitrogen by dropwise addition of a solution of 4.850 g (0.045 mol) of ethyl bromide in 75 ml of anhydrous ether into a flask containing 0.8986 g (0.037 g-atom) of magnesium turnings over a period of 30 min with mechanical stirring at ice-bath temperature. Stirring was continued at room temperature for an additional 30 min after addition was complete, resulting in complete reaction of the magnesium. The Grignard solution was then cooled at ice-bath temperature, and a solution of 17.426 g (0.074 mol) of (−)-sparteine (4) [distilled from CaH_2 prior to use, bp 112.0–116.5° (0.45 mm)] in 60 ml of anhydrous ether was added, resulting in formation of a white precipitate. Next, 3.860 g (0.039 mol) of cuprous chloride was added and the mixture was stirred for 15 min to give a yellow precipitate. To this was added a solution of 2.505 g (0.030 mol) of 3-penten-2-one in 75 ml of anhydrous ether dropwise over a period of 20 min with stirring. Stirring was continued at ice-bath temperature for 30 min after addition was complete. The resulting mixture was decomposed with 150 ml of 3 *M* HCl. The ether layer was separated, washed three times with 50-ml portions of 3 *M* HCl and once with 50 ml of saturated brine, and dried over anhydrous $MgSO_4$. Solvent was removed from the ether extract

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[5] E. P. Kohler and W. D. Peterson, *J. Amer. Chem. Soc.*, **55**, 1073 (1933).

[6] Organocopper(I) reagents produced by treatment of cuprous salts with Grignard reagents are of uncertain structure and may be complex compounds containing both copper and magnesium.[4b,7] If this is the case, (−)-sparteine (**4**) could be coordinated with either or both metal atoms of the reagent.

[7] N.-T. Luong-Thi and H. Riviere, *Tetrahedron Lett.*, 587 (1971).

[8] S. Okuda and K. Tsuda, *Chem. Ind. (London)*, 1115 (1961).

[9] Melting points are uncorrected. The infrared spectra were determined with a Beckman IR-8 infrared 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. Optical rotations were measured with an O. C. Rudolph and Sons, Inc., Model 200 photoelectric polarimeter equipped with a Model 340 oscillating polarizer. The optical rotatory dispersion curve for (+)-3-phenylcyclohexanone was determined with a Cary Model 60 spectropolarimeter. Microanalyses were performed by M-H-W Laboratories, Garden City, Mich.

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), $[\alpha]^{25}D$ +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: $[\alpha]^{25}D$ +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°, $[\alpha]^{25}D$ −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

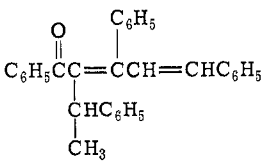
The Reaction of Benzalacetophenone with Methylmagnesium Iodide. A Novel Grignard Reaction

RICHARD A. KRETCHMER

Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois 60616

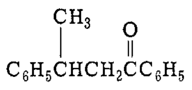
Received March 10, 1972

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]



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

2



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

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).