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Organometallic Reaction Mechanisms. XIII. Identification of the Ketyl Intermediates Formed in Reactions of Grignard Reagents with Ketones

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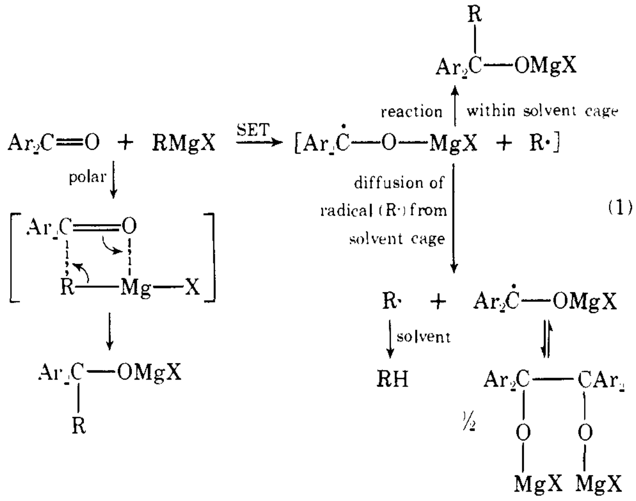
Abstract: In addition to magnesium 2-methylbenzophenone ketyl ([Ph(Ph′)$\dot{C}$O]$_2$Mg; Ph′ = 2-methylphenyl, Ph = phenyl), the bromomagnesium [BrMgO$\dot{C}$(Ph)Ph′], methylmagnesium [CH$_3$MgO$\dot{C}$(Ph)Ph′], and 1-(2-methylphenyl)-1-phenylethoxy magnesium [Ph(Ph′)(CH$_3$)COMgO$\dot{C}$(Ph)Ph′] ketyls of 2-methylbenzophenone have been prepared in diethyl ether and studied by uv and ESR spectroscopy. The ketyl produced during reaction of 2-methylbenzophenone with excess methylmagnesium bromide has been identified as the bromomagnesium ketyl of 2-methylbenzophenone associated with methylmagnesium bromide. In reactions of methylmagnesium bromide with excess 2-methylbenzophenone, the ketyl produced is the bromomagnesium ketyl of 2-methylbenzophenone associated with the 1,2-addition product [Ph(Ph′)(CH$_3$)OMgBr].

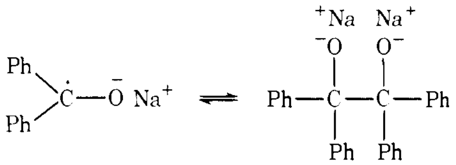
A single electron transfer (SET) mechanism, as well as a polar mechanism, has been suggested for the addition of Grignard reagents to aromatic ketones (eq 1).[1] The evidence cited in support of an electron transfer mechanism includes the detection of ketyl radical anions, or the products expected from them. In our investigation[1f-h,2] into the importance of the single electron transfer mechanism in Grignard reactions, we have chosen to study the role of ketyls in the reaction between methylmagnesium bromide and 2-methylbenzophenone in diethyl ether.



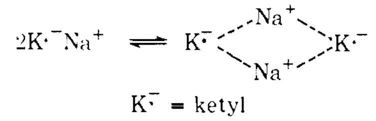
(1)

Although magnesium ketyls of benzophenone and substituted benzophenones have been observed by ESR, very little information about them is available. Spectroscopic studies of aromatic ketyl radical anions indicate that several forms of a ketyl may exist in equilibrium with each other and that these equilibria are dependent on solvent, temperature, and concentration.[3] Ketyls produced by reduction of the ketone with alkali and alkaline earth metals in all but the most polar solvents (liquid ammonia, DMF) are found to exist as ion pairs. The majority of the literature is concerned with the alkali metal ketyls, with only brief mention of the alkaline earth metal ketyls.

In hydrocarbon solvents and the less polar ethers (such as diethyl or di-*n*-butyl ether), the ketyl radical anion, sodium benzophenone ketyl, is in equilibrium with the diamagnetic pinacolate (eq 2). In more polar solvents, no pinacolate is present. The alkali metal ketyl ion pair (often referred to as monomer ketyl) may be further associated in solution to form ion quadruplets (ketyl dimers) (eq 3).



(2)



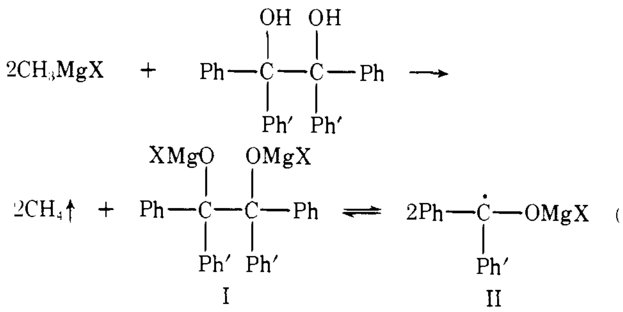
(3)

K·$^-$ = ketyl

The purpose of the present study was to prepare by unequivocal methods all of the ketyls that could possibly result from the reaction of methylmagnesium bromide with 2-methylbenzophenone. These ketyls were to be observed and characterized by ESR and uv spectroscopy so that, when the reaction of methylmagnesium bromide and 2-methylbenzophenone was observed directly by ESR and uv spectroscopy, the intermediate in the reaction could be conclusively identified. In addition it was hoped that a direct relationship between the concentration of the ketyl produced in the reaction and the amount of pinacol produced on hydrolysis could be established.

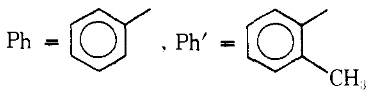
Results and Discussion

Although ketyl radical anions can be produced by reduction of the ketone with magnesium amalgam[4] or magnesium and magnesium halide,[5] the most convenient method we found involves the reaction of the corresponding pinacol with stoichiometric amounts of Grignard reagent or R_2Mg compound (eq 4).

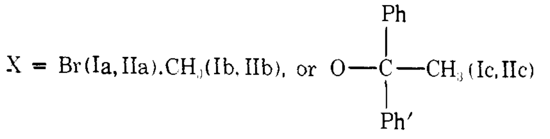


$$2CH_3MgX + Ph-\underset{Ph'}{\overset{OH}{C}}-\underset{Ph'}{\overset{OH}{C}}-Ph \longrightarrow 2CH_4\uparrow + \underset{\mathrm{I}}{Ph-\underset{Ph'}{\overset{XMgO}{C}}-\underset{Ph'}{\overset{OMgX}{C}}-Ph} \rightleftharpoons \underset{\mathrm{II}}{2Ph-\underset{Ph'}{\dot{C}}-OMgX} \quad (4)$$

where

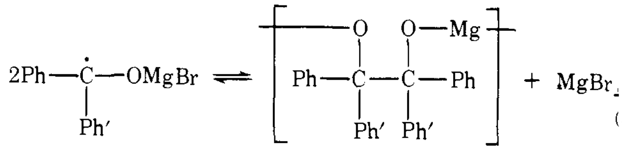


and



$$X = Br(Ia, IIa), CH_3(Ib, IIb), \text{ or } O-\underset{Ph'}{\overset{Ph}{C}}-CH_3(Ic, IIc)$$

The bromomagnesium ketyl IIa ($Ph\dot{C}(Ph')OMgBr$) which could be formed in the reaction of CH_3MgBr with 2-methylbenzophenone was prepared in ether solution according to eq 4.[6] Solutions of IIa were pink and in the visible region exhibited a λ_{max} of 512 nm and a shoulder at approximately 525-535 nm (Figure 1a). The ESR spectrum was a very broad quartet ($a_H \simeq 5$ G; line width > 2 G) similar to that of other 2-methylbenzophenone ketyl radical anions of alkali metals reported by Maruyama.[7] Calculation of the ketyl concentration by double integration of the ESR spectrum gave an extinction coefficient for λ 512 nm of 2300. When the ketyl was generated from pinacol solutions of 0.01 *M* concentration or higher, the absorbance rapidly dropped (the initial rate was roughly second order in ketyl), and a white precipitate formed usually within an hour. After hydrolysis of the precipitate, the only organic product was the pinacol. Analysis of one sample of the precipitate showed % Br = 2.2 and % Mg = 6.8, which is inconsistent with Ia (% Br = 26.6 and % Mg = 8.1). All observations suggest that the precipitate is polymeric with magnesium 2,2′-dimethylbenzopinacolate (% Mg = 5.8, % Br = 0) as a major "repeating unit"; see eq 5. Successive dilutions of a solution of ketyl IIa in a sealed apparatus under vacuum revealed that the pinacolate:ketyl ratio (Ia:IIa) was independent of concentration in the range of 6.6×10^{-5} *M* to 1.0×10^{-3} *M* pinacolate. Therefore, the degree of association does not change on conversion of pinacolate to ketyl; most likely then, ketyl IIa is dimeric (eq. 6). Such



$$2Ph-\underset{Ph'}{\dot{C}}-OMgBr \rightleftharpoons \left[Ph-\underset{Ph'}{\overset{O}{C}}-\underset{Ph'}{\overset{O-Mg}{C}}-Ph \right] + MgBr_2 \quad (5)$$

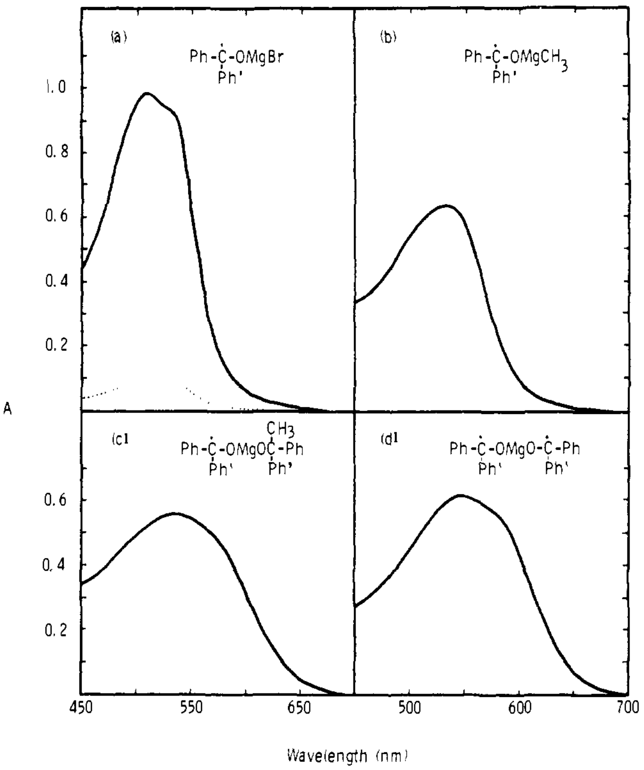
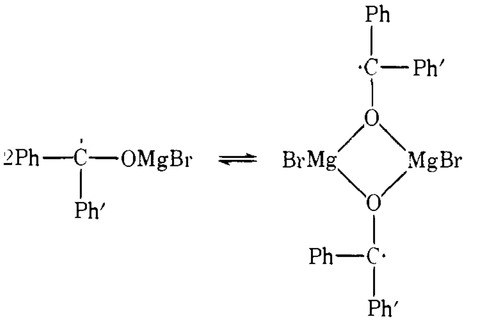


Figure 1. (a) Bromomagnesium ketyl of 2-methylbenzophenone prepared from 0.005 *M* 2,2′-dimethylbenzopinacol: (—) 1-cm path length; (. . .) 0.1-cm path length. (b) Methylmagnesium ketyl of 2-methylbenzophenone prepared from 0.005 *M* 2,2′-dimethylbenzopinacol (1-cm path length). (c) 1-(2-Methylphenyl)-1-phenylethoxymagnesium ketyl of 2-methylbenzophenone prepared from 0.0025 *M* 2,2′-dimethylbenzopinacol (0.1-cm path length). (d) Magnesium 2-methylbenzophenone ketyl prepared from 0.005 *M* 2,2′-dimethylbenzopinacol (0.1-cm path length).



$$2Ph-\underset{Ph'}{\dot{C}}-OMgBr \rightleftharpoons BrMg\underset{O}{\overset{O}{\lozenge}}MgBr \quad (6)$$

association of ketyl radical anions is not uncommon, especially in diethyl ether.[3] The equilibrium constant for the very rapidly established equilibrium $(IIa)_2 \rightleftarrows Ia$ was calculated to be 8.5.

The other possible ketyls formed in the reaction of methylmagnesium bromide with 2-methylbenzophenone were also investigated. The methylmagnesium ketyl IIb ($Ph\dot{C}(Ph')OMgCH_3$) was prepared in ether solution by the reaction of $(CH_3)_2Mg$ with the pinacol according to eq 4. This ketyl, which could result from the reaction of $(CH_3)_2Mg$ (which exists in the Grignard solution) with 2-methylbenzophenone, exhibited a visible absorption band of

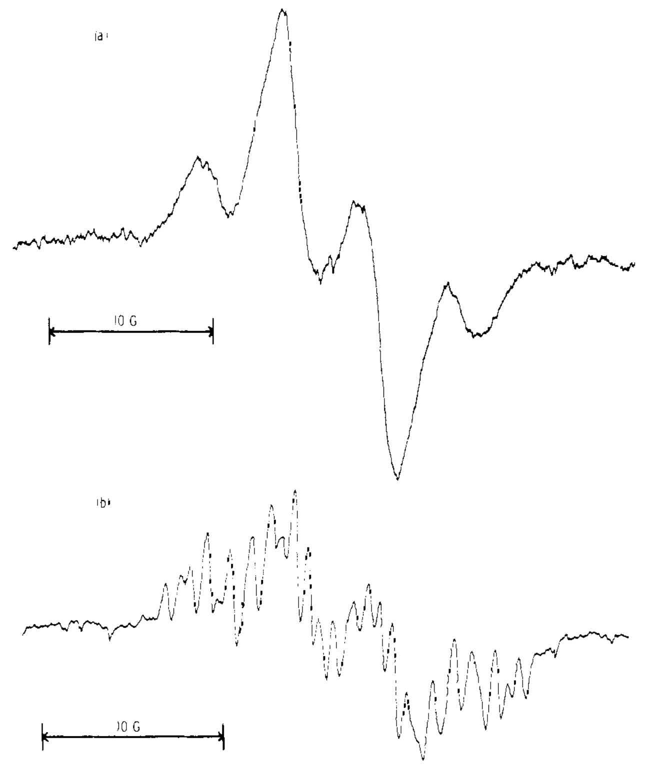
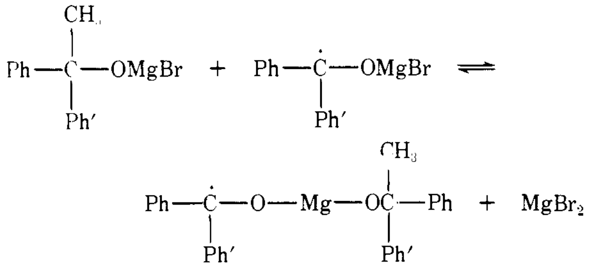


Figure 2. (a) 1-(2-Methylphenyl)-1-phenylethoxymagnesium ketyl of 2-methylbenzophenone. (b) Methylmagnesium ketyl of 2 methylbenzophenone.

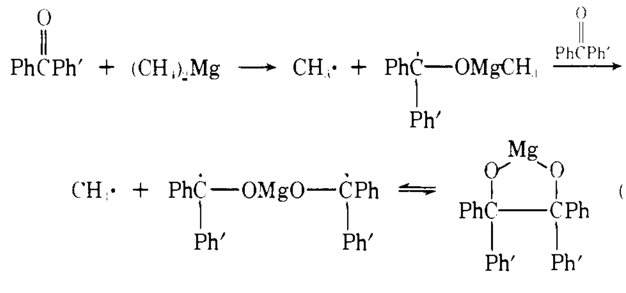
similar width to ketyl IIa; however, the λ_{max} was 537–543 nm, and no apparent shoulders were observed (Figure 1b). The extinction coefficient for the λ_{max} was calculated to be 3200. The ESR spectrum of IIb showed more hyperfine structure than any of the other ketyls studied (Figure 2). Calculation and assignment of hyperfine coupling constants for this partially resolved spectrum were not made. As in the case of IIa, a white precipitate formed in the pink solution when the original pinacol concentration was above 0.01 *M*.

The 1-(2-methylphenyl)-1-phenylethoxymagnesium ketyl (IIc) $[Ph(Ph')(CH_3)C\text{-}OMg\text{-}O\text{-}\dot{C}(Ph')Ph]$ was prepared according to eq 4 by reaction of $CH_3MgOCPh(Ph')CH_3$ with the pinacol. This ketyl could result from the reaction of CH_3MgBr with 2-methylbenzophenone by reaction of the bromomagnesium ketyl (IIa) with the normal addition product $[Ph(Ph')(CH_3)C\text{-}OMgBr]$ (eq 7). This ketyl resulted in a dark purple solution with a very broad visible absorption having λ_{max} 534–540 nm (Figure 1c). The ESR spectrum was a broad quartet ($a_H \simeq 5$ G) very similar to that of IIa.



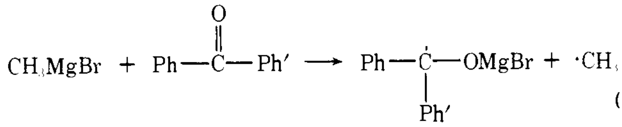
$$Ph\!-\!\overset{CH_3}{\underset{Ph'}{C}}\!-\!OMgBr + Ph\!-\!\underset{Ph'}{\dot{C}}\!-\!OMgBr \rightleftharpoons Ph\!-\!\underset{Ph'}{\dot{C}}\!-\!O\!-\!Mg\!-\!O\overset{CH_3}{\underset{Ph'}{C}}\!-\!Ph + MgBr_2 \quad (7)$$

Magnesium 2-methylbenzophenone ketyl $[Mg(O\text{-}\dot{C}(Ph')Ph)_2]$ (ketyl III) was prepared by the reaction of $(CH_3)_2Mg$ with an equimolar amount of the pinacol according to eq 4. This ketyl could be formed in the Grignard reaction of CH_3MgBr with 2-methylbenzophenone according to eq 8. Solutions of this ketyl were dark purple and had a broad absorption in the visible region similar to IIc with λ_{max} 540–545 nm (Figure 1d). The ESR spectrum was again a broad quartet ($a_H \simeq 5$ G).


(8)

A brief examination of unsubstituted benzophenone ketyls indicated that magnesium benzophenone ketyl $[Mg(O\text{-}\dot{C}Ph_2)_2]$ formed blue solutions with λ_{max} 597 nm (extinction coefficient = 9300)[8] and a slight shoulder at approximately 545 nm. The bromomagnesium benzophenone ketyl $(Ph_2\dot{C}\text{-}OMgBr)$ solutions were pink with λ_{max} 554 nm (extinction coefficient 4700) and a shoulder at approximately 526 nm. Solutions of either ketyl from benzophenone produced a white precipitate on standing.

The uv spectra and behavior of ketyls observed during the reaction of methylmagnesium bromide with 2-methylbenzophenone were dependent on the ratio of the two reactants. In reactions with excess Grignard reagent, the ketyl observed had a λ_{max} 512 nm and a shoulder at 525–535 nm (Figure 3a); the uv spectrum was essentially identical with that of the bromomagnesium ketyl IIa $[Ph(Ph')\dot{C}\text{-}OMgBr]$. Immediately on mixing the Grignard reagent and ketone, the ketyl absorbance monitored at 512 nm showed a rapid increase but then, instead of either leveling off or continuing to increase, the absorbance decreased throughout the rest of the reaction.[10] The higher the concentration of excess Grignard reagent, the faster the absorbance dropped. If methylmagnesium bromide was added to solutions of ketyl IIa $[Ph(Ph')\dot{C}\text{-}OMgBr]$ (prepared from CH_3MgBr and pinacol, eq 4), the absorbance also dropped. Apparently excess methylmagnesium bromide shifts the ketyl-pinacolate equilibrium (eq 2) more in favor of the pinacolate. When virtually colorless solutions containing the ketyl and a large excess of Grignard reagent were hydrolyzed, the deep pink color characteristic of the ketyl briefly reappeared because of the destruction of excess Grignard reagent during the hydrolysis. The decrease in the absorbance of the ketyl by excess Grignard reagent is a complication that makes a quantitative correlation between ketyl observed by uv and yield of pinacol very difficult. However, it is clear from these studies that ketyl concentration and pinacol formation are directly related. As indicated in Table I, the higher the absorbance due to the ketyl during a reaction, the more pinacol was isolated after hydrolysis. The absorbance presented in Table I was divided by the initial ketone concentration for ease of comparison with the percent yield of pinacol isolated. The values for the "% yield pinacol calculated" which are given in Table I were obtained by using the extinction coefficient (2300) and ketyl-pinacolate equilibrium constant (8.5) obtained for the bromomagnesium ketyl IIa. All of these calculated yields are below the experimental yields because of the shift in the ketyl-



$$CH_3MgBr + Ph\!-\!\overset{O}{\overset{\|}{C}}\!-\!Ph' \longrightarrow Ph\!-\!\underset{Ph'}{\dot{C}}\!-\!OMgBr + \cdot CH_3 \quad (9)$$

Table I. Comparison of Ketyl Absorbance and Pinacol Formation in Reactions of 2-Methylbenzophenone with Excess Methylmagnesium Bromide

$[G]/[K]$	$[FeCl_3]$, mol %[b]	$A_{max}/[K]$[c]	% pinacol[d]	
			Calcd	Found
1.04	0	0.94	0.35	2
10	0	2.0	0.74	2
100	0	5.7	2.1	3
100	0	5.8	2.1	4
10	0.005	7.3	2.7	18
10	0.05	19	7.0	48
10	0.5	56	21	68

[a] [G] = concentration of methylmagnesium bromide; [K] = concentration of 2-methylbenzophenone. [b] Mol % $FeCl_3$ relative to concentration of methylmagnesium bromide. [c] A_{max} = the maximum value of the ketyl absorbance at 512 nm during the reaction; [K] = initial concentration of 2-methylbenzophenone. [d] Calculations were carried out using A_{max} and the extinction coefficient (2300) and ketyl–pinacolate equilibrium constant (8.5) for the bromomagnesium ketyl of 2-methylbenzophenone.

pinacolate equilibrium produced by the excess methylmagnesium bromide present during the reaction. The presence of catalytic amounts of $FeCl_3$ increased the absorbance of the ketyl (and the yield of 2,2′-dimethylbenzopinacol) but did not alter the shape of the uv spectrum.

In reactions of methylmagnesium bromide with excess 2-methylbenzophenone, the absorbance of the ketyl (ketyl IV) continued to increase throughout the reaction instead of dropping as observed in reactions with excess methylmagnesium bromide. The ketyl uv spectrum exhibited a λ_{max} at 540–545 nm and a shoulder at 515–520 nm (Figure 3b) which does not correspond to any of the ketyls previously investigated (IIa, IIb, IIc, or III). However, addition of $Ph(Ph')(CH_3)COMgBr$ to a solution of IIa (in the reaction of CH_3MgBr with 2-methylbenzophenone, the addition product $Ph(Ph')(CH_3)COMgBr$ is present with the ketyl) containing no excess methylmagnesium bromide produced a very similar uv spectrum (λ_{max} 535–538 nm and shoulder at 515–520 nm (Figure 4)). Addition of 2-methylbenzophenone (at concentrations as high as 1 *M*) had no effect on the uv spectrum of IIa. Probably, in Grignard reactions with excess ketone, the ketone can tie up most of the methylmagnesium bromide, allowing the bromomagnesium ketyl formed to associate in some manner with the addition product to produce a ketyl different in structure from either the bromomagnesium ketyl IIa or the 1-(2-methylphenyl)-1-phenylethoxy ketyl (IIc). In reactions with excess methylmagnesium bromide, the ketyl may be preferentially associated with the Grignard reagent. No detectable amounts (detection limit approximately a 1% yield) of 2,2′-dimethylbenzopinacol or any other product except 1-(2-methylphenyl)-1-phenylethanol [$Ph(Ph')(CH_3)C{-}OH$] were found for reactions with excess ketone[2b] even though solutions of ketyl IIa of similar absorbance yielded readily detectable amounts of the pinacol. Possible explanations are that ketyl IV has a higher extinction coefficient than ketyl IIa and that the ketyl-pinacolate equilibrium is shifted much more in favor of the ketyl for IV than for IIa.

In the early stages of the reaction of stoichiometric amounts of methylmagnesium bromide and 2-methylbenzophenone, the ketyl behaved as in reactions with excess Grignard reagent; the λ_{max} was 512 nm, and the absorbance quickly reached a maximum and began to drop. However, as the reaction proceeded, the absorbance began to increase again, and λ_{max} was then 540 nm (ketyl IV).

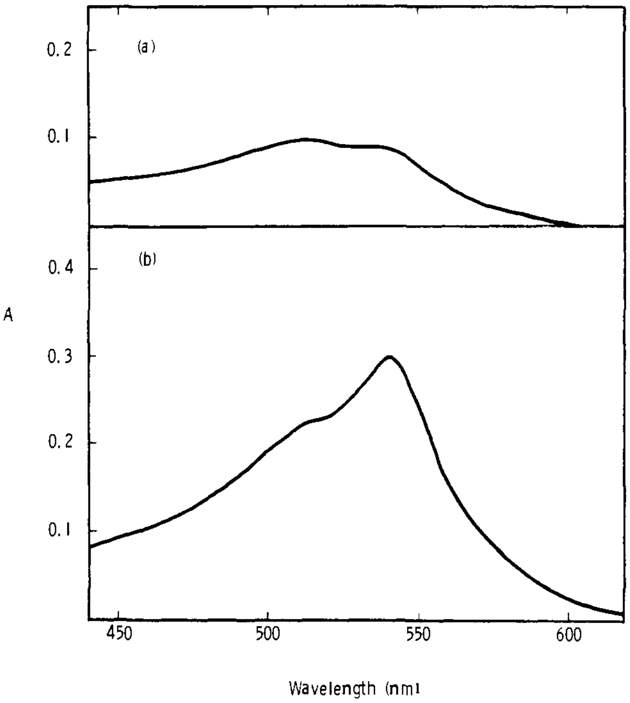


Figure 3. (a) The ketyl produced in the reaction of 2-methylbenzophenone (0.08 *M*) with methylmagnesium bromide (0.083 *M*). (b) The ketyl produced in the reaction of 2-methylbenzophenone (0.10 *M*) with methylmagnesium bromide (0.01 *M*).

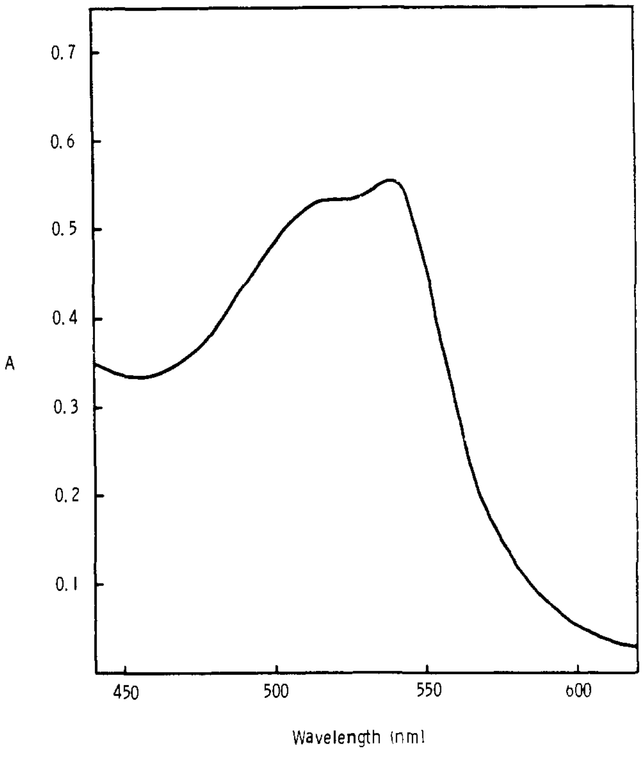


Figure 4. The bromomagnesium ketyl of 2-methylbenzophenone (total ketyl dimer and pinacolate concentration = 0.003 *M*) in the presence of 1-(2-methylphenyl)-1-phenylethoxymagnesium bromide (0.06 *M*).

Thus, clearly the bromomagnesium ketyl of 2-methylbenzophenone is directly related to the formation of 2,2′-dimethylbenzopinacol in the reaction of methylmagnesium bromide and 2-methylbenzophenone. Most likely the ketyl is formed directly in the reaction (it is also possible, but not as likely, that the pinacolate is produced first and dissociates to give the ketyl observed). The detailed structure of the ketyl, and therefore its uv spectrum, depends on the reaction conditions. In the presence of excess Grignard reagent, the ketyl is the bromomagnesium ketyl IIa, most likely in a dimeric form and further associated with the Grignard reagent. On the other hand, in reactions with excess ketone, the bromomagnesium ketyl is associated with the reaction product [Ph(Ph′)(CH$_3$)COMgBr]. The association of the ketyl with the product changes the uv-visible spectrum of the ketyl from one with λ_{max} 512 nm (Figure 3a) to the one with λ_{max} 540–545 nm (Figure 3b).

Experimental Section

Materials. Diethyl ether was purified and freed of oxygen by drying over sodium wire followed by distillation from LiAlH$_4$ under nitrogen followed by distillation from sodium benzophenone ketyl under nitrogen. 2,2′-Dimethylbenzopinacol was prepared according to the procedure of Gomberg and Bachmann[5] from the reaction of 2-methylbenzophenone with magnesium and iodine. Methylmagnesium bromide was prepared as previously described.[1f] 2-Methylbenzophenone (Eastman) was distilled under vacuum and stored in a foil-wrapped container under nitrogen. Anhydrous ferric chloride (Fisher Sublimed) was used without further purification.

Apparatus and Procedure. Preparation and transfer of solutions were carried out under nitrogen in a glove box equipped with a recirculating system described elsewhere.[11] The ESR spectra were recorded on a Magnion ESR spectrometer Model MVR-12X. The ketyl solutions, under nitrogen, were contained in ESR cells equipped with 1-mm Teflon stopcocks. Ketyl concentrations were determined by comparison of the ketyl ESR signal area (obtained by manual double integration of the derivative spectrum[12]) with that from a standard solution of 2,2,5,5-tetramethylpyrolidine-3-carboxamide-1-oxyl. Extinction coefficients calculated from these ketyl concentrations were reproducible within ±5%.

A Cary 14 spectrophotometer was used to record uv-visible spectra. Visible spectra of the reactions of 2-methylbenzophenone and methylmagnesium bromide were obtained in the following manner. A solution (at least 2 ml) of one of the reactants, usually the Grignard reagent, was added in the glove box to a 1-cm path length quartz cell equipped with a 1-mm Teflon stopcock. After the cell was placed in the Cary 14 spectrometer and the baseline absorbance determined, the stopcock was opened and the other reactant rapidly injected. Usually the cell was shaken to ensure mixing and then the spectrum recorded. In some cases, the second reactant was injected into the cell with the spectrometer already recording. For this procedure, the room was darkened and the cell compartment covered with a black cloth. Ketyl spectra were recorded either using a procedure similar to the above or by preparing the ketyl solution in the glove box and transferring it to a uv cell.

The study of the effect of concentration on the ketyl–pinacolate equilibrium was carried out in an apparatus containing two 50-ml bulbs connected by a Y tube, a graduated side arm (capable of containing 45 ml of solution) ending in a 1-cm path length quartz uv cell, and a 2-mm glass high vacuum stopcock topped by a ground glass joint for attachment to a vacuum line. Immediately below the stopcock was an O-ring joint so that the stopcock could be removed for ease in introducing reactants into the apparatus. The apparatus was flash flamed several times under vacuum and then filled with nitrogen. In the glove box, a solution of 2,2′-dimethylbenzopinacol was placed in one bulb, a solution of methylmagnesium bromide in the other, and the apparatus reassembled. After the solutions had been degassed by three cycles of freeze-pump-thaw on the vacuum line, the stopcock was closed, the apparatus removed from the vacuum line, and the reactants were mixed. A small amount (2.5–3 ml) of the ketyl solution was transferred into the uv cell and its uv spectrum recorded. Then successive portions of ether were distilled into the side arm from the reaction bulbs with a uv spectrum recorded after each dilution.

Products were analyzed by either ^{1}H NMR or GLC or both after hydrolysis with saturated aqueous ammonium chloride. The hydrolyzed samples were extracted with Et$_2$O and dried over MgSO$_4$, and the solvent was removed. They were then dissolved in CDCl$_3$ along with a known amount of tetramethylbutane as internal standard, and the ^{1}H NMR spectrum was obtained on a Varian A-60 spectrometer. After ^{1}H NMR analysis, the solvent was again removed and the sample redissolved in Et$_2$O along with a known amount of 1-tetradecanol as internal standard. GLC analyses were performed on an F & M 700 flame ionization chromatograph using 3 ft × 0.25 in. glass column packed with 10% Carbowax 20M on Chromosorb W (80–100 mesh; AW; DMCS). Although 2,2′-dimethylbenzopinacol decomposed to give a mixture of 2-methylbenzophenone and 2-methylbenzhydrol under these conditions, calibrated runs at various concentrations allowed the pinacol to be analyzed satisfactorily.

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References and Notes

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