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PRODUCT-DETERMINING FACTORS IN THE GRIGNARD REACTIONS OF BENZOPHENONES. THE ROLE OF THE STRUCTURE OF ALKYL GROUPS IN GRIGNARD REAGENTS

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The mechanism of the Grignard reactions of substituted benzophenones with two kinds of alkyl Grignard reagent, n-C_3H_7MgBr and i-C_3H_7MgBr, was investigated. In these reactions, both addition and reduction products were also generated. Based on the results of product analysis and stopped-flow, ESR and association measurements, it was confirmed that the product distribution was governed by several factors: the oxidizing ability of benzophenones, the association ability of Grignard reagents and the structure of alkyl groups of Grignard reagents. In particular, the strength of C—Mg and β-C—H bonds of Grignard reagents could strongly affect the product distribution.

INTRODUCTION

Since the synthetic utility of organomagnesium compounds was reported by Grignard in 1901,[1] there have been many studies on the mechanism of the Grignard reactions.[2–13] However, some essential problems still remain unresolved, including the problem of addition vs reduction for controlling the product distribution, which is important for chemical syntheses. Although several groups have approached this problem with regard to the isotope effect,[14] relative reaction rate[15] and stereochemistry,[16] a general interpretation for explaining all factors controlling the product distribution is still lacking.

Recently, we established the mechanism of the Grignard reactions of benzil,[17] benzophenone[18] and fluorenone[19] by means of product analysis and UV-visible, ESR and stopped-flow techniques. The confirmed mechanism of the Grignard reaction of benzophenone is shown in Scheme 1. In the initial stage of the reaction, intermediate monomeric and dimeric radical ion pairs were afforded in a stepwise manner. Based on the experimental findings, we discussed the problem of addition vs reduction in the Grignard reactions. In our latest paper, the reactions of monoketones with EtMgBr were investigated.[20] From a detailed product analysis under various conditions, it was found that the distribution of addition vs reduction was governed by the oxidizing ability of benzophenones and the solvent polarity, which was closely related to the degree of association of the Grignard reagents. To provide a further systematic interpretation, we report here the results of product analysis, ESR, stopped-flow and association measurements in the reactions of substituted benzophenones with two kinds of Grignard reagent, n-C_3H_7MgBr and i-C_3H_7MgBr, which have β-hydrogen atoms in their alkyl moieties. It will be confirmed explicitly that the structure of the Grignard reagents is one of the essential factors controlling the product distribution.

RESULTS

Reactions of substituted benzophenones with n-C_3H_7MgBr(2a)

First, n-propylmagnesium bromide (n-C_3H_7MgBr), having two β-hydrogen atoms in its alkyl group, was selected for the reactions with various substituted benzophenones. After n-C_3H_7MgBr (**2a**; 1.5 mmol) had been allowed to react with benzophenone (**1f**; 0.3 mmol) in tetrahydrofuran (THF; 6.5 ml) for 6 h under strictly dry and deaerated conditions, the reacting

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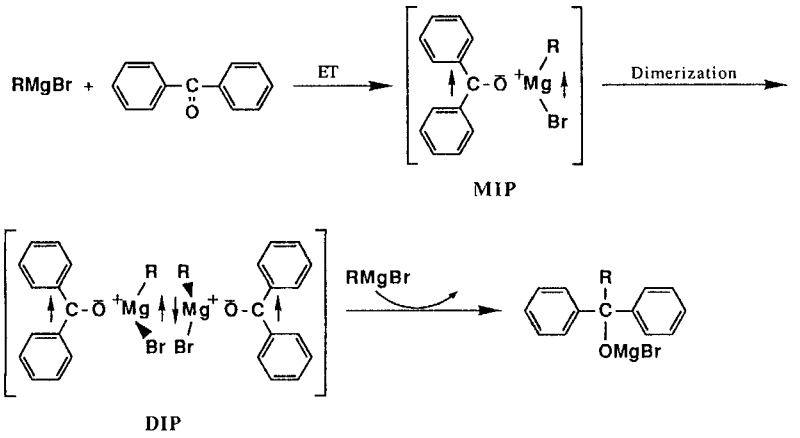
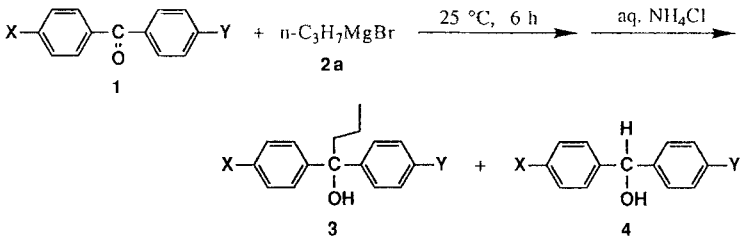


Scheme 1



Scheme 2

solution was quenched with saturated NH_4Cl solution and worked up as usual. The ^1H NMR analysis showed the presence of only two kinds of product in the reaction mixture: 1,1-diphenylbutanol (**3f**; 17%) and benzhydrol (**4f**; 83%) (so long as the reaction solution was free from transition metals, water and oxygen, no other by-products were detected in the reaction products[21]).

Each product was isolated by column chromatography on silica gel and identified by m.p., ^1H NMR, IR and mass spectrometric (MS) measurements. Compound **3f**, with an *n*-propyl group attached to the carbonyl group, was a so-called addition product (Add.), and reduced compound **4f** was a reduction product (Red.). Similarly, in the reactions of substituted benzophenones (**1a–e** and **g–i**) with **2a**, two kinds of product, Add. and Red., were generated (Scheme 2). These Grignard reactions were also carried out in diethyl ether (DEE) and 1,2-dimethoxyethane (DME). All the results are summarized in Table 1 and Figure 1. In every case, the determination of the amount of each product was based on integral values of terminal methyl proton (Add.) and methyne proton (Red.). The proton of the methyl group (Add.) appeared at 0.91 ppm as a triplet (3H, $J = 7{\cdot}3$ Hz), and that of the methyne group (Red.) appeared at 5·82 ppm as a singlet (1H). In most cases, the amount of Red. was greater than that of Add.

Figure 2 shows the plot of log(Add./Red.) values vs Hammett's σ-values. From Figures 1 and 2, it can be seen that two factors, the polarity of the solvents and the oxidizing ability of benzophenones, control the Add./Red. distribution in a systematic manner. In DEE, for example, the log(Add./Red.) values (open circles) decrease on a monotonous line with increasing σ-values. On the other hand, in THF, the log(Add./Red.) values (black circles) lie horizontally on two lines or maybe on a slight upward curve. Thus, one line involving points 5–8 has a positive ρ value and the other involving points 1·3 has a negative ρ value. In DME both the product distribution and Hammett relation seems to be in the middle of two extremes (THF and DEE). These trends agreed with the results of the reactions of EtMgBr with substituted benzophenones reported in previously.[20]

Reactions of substituted benzophenones with *i*-C_3H_7MgBr(2b)

Reactions of substituted benzophenones with isopropylmagnesium bromide (*i*-C_3H_7MgBr) were studied

Table 1. Product yields in the reaction of **1** with **2a**

Benzophenone	Solvent	Yield (%) Add. 3	Red. 4	Log(Add./Red.)
1a	THF	21·1	78·9	−0·57
(X = Y = Cl)	DME	12·7	87·3	−0·77
σ = 0·454	DEE	19·4	89·6	−0·62
1b	THF	20·9	79·1	−0·58
(X = Br, Y = H)	DME	16·7	83·3	−0·70
σ = 0·232	DEE	24·5	75·5	−0·49
1c	THF	20·3	79·7	−0·59
(X = Cl, Y = H)	DME	16·9	83·1	−0·69
σ = 0·227	DEE	24·6	75·4	−0·49
1d	THF	16·6	83·4	−0·70
(X = Y = F)	DME	21·5	78·5	−0·56
σ = 0·124	DEE	33·0	67·0	−0·31
1e	THF	17·1	82·9	−0·68
(X = F, Y = H)	DME	21·6	78·4	−0·56
σ = 0·062	DEE	34·5	65·5	−0·28
1f	THF	17·0	83·0	−0·69
(X = Y = H)	DME	20·8	79·2	−0·58
σ = 0	DEE	32·2	67·8	−0·32
1g	THF	20·4	79·6	−0·59
(X = PhO, Y = H)	DME	29·5	70·5	−0·38
σ = −0·028	DEE	51·5	48·5	−0·03
1h	THF	18·2	81·8	−0·65
(X = Me, Y = H)	DME	24·8	75·2	−0·48
σ = −0·170	DEE	45·1	54·9	−0·09
1i	THF	24·6	75·4	−0·49
(X = MeO, Y = H)	DME	41·5	58·5	−0·15
σ = −0·268	DEE	64·9	25·1	0·27

using a similar procedure to that described for the reactions with n-C_3H_7MgBr. In contrast to the case with n-C_3H_7MgBr, the product distribution was complicated with i-C_3H_7MgBr. For example, in the reaction of benzophenone (**1f**) with i-C_3H_7MgBr (**2b**), four kinds of product were isolated by silica gel column chromatography: 2-isopropylbenzophenone (**6f**), 4-isopropylbenzophenone (**7f**), 1,1-diphenyl-2-methylpropanol (**8f**) and benzhydrol (**4f**). Compounds **6f** and **7f**, in which the isopropyl group is attached to the phenyl ring of **1f**, were so-called abnormal addition products. Monosubstitution on the phenyl ring of benzophenones further complicated the situation. In the reaction of 4-bromobenzophenone (**1b**) with **2b**, for example, six kinds of product were isolated by silica gel column chromatography: 4-benzoyl-1-bromo-3-isopropylcyclohexa-1,4-diene (**5b**), 4-bromo-2-isopropylbenzophenone (**6b**), 4-bromo-2′-isopropylbenzophenone (**6′b**), 4-bromo-4′-isopropylbenzophenone (**7b**), 1-(4-bromophenyl)-1-phenyl-2-methylpropanol (**8b**) and 4-bromobenzhydrol (**4b**).

Each product was identified by m.p., ^{1}H NMR, IR and MS measurements. The characteristic spectral data for each product are summarized in Table 2. In the ^{1}H

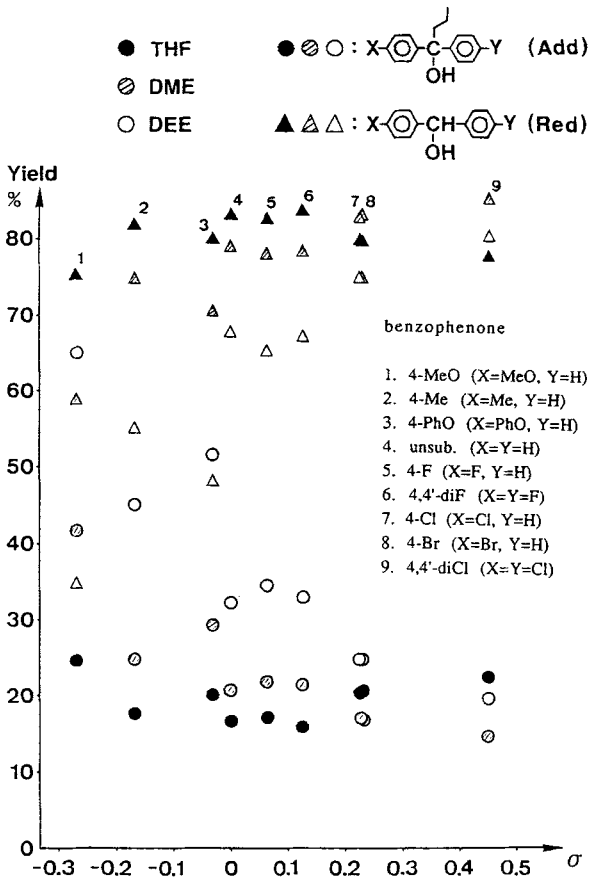
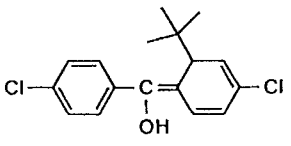


Figure 1. Product yields in the reactions of **1** with **2a** versus Hammett σ constants. [**1**] = 0·046 M; [**2a**] = 0·23 M

NMR spectra, both methyl and methyne protons of the isopropyl group of **6b**, **6b′** and **7b** appeared at 0·2–0·4 ppm downfield of those of the normal Add., **8b**. These chemical shifts are due to the ring current of the phenyl moiety toward the isopropyl group. In the reaction of substituted benzophenones with **2b**, several kinds of product were always generated (Scheme 3). The results are summarized in Table 3 and Figure 3.

The formation of *ortho* and *para* addition products is remarkable. At the same time, non-aromatized *ortho* addition products **5** were isolated in the reactions of halogenobenzophenones (**1a–e**) with **2b**. (Holm[22] reported that 1,4-addition products such as **10** were



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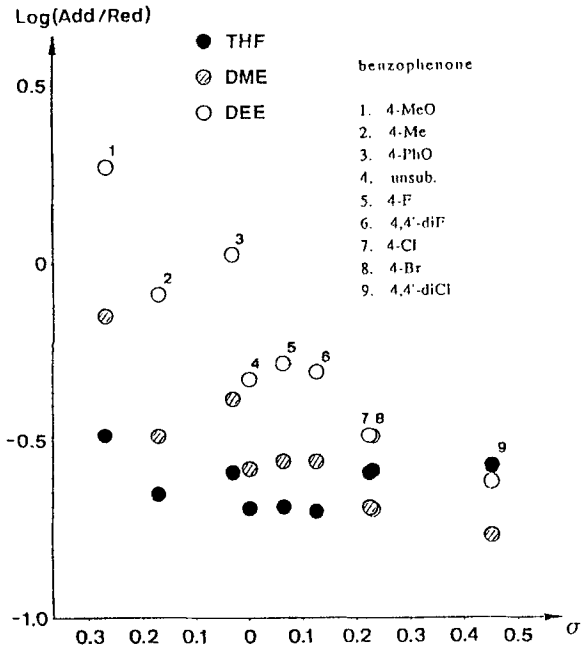


Figure 2. Logarithm of Add./Red. ratio in the reactions of **1** with **2a** versus hammett σ constants

generated in the reactions of benzophenones with *t*-BuMgBr, but the physical properties of **10** were not described at all. In our experiments, no *ortho* addition products such as **10** could be isolated). The isopropyl moiety was introduced to the electron-deficient halogen-substituted ring. The aromatized *ortho* addition products **6** were afforded in every case, and two kinds of *ortho* adduct, **6** and **6'**, were given in the reactions of monosubstituted benzophenones (for example, Fuson *et al.*[23] reported the generation of an *ortho* addition product such as **6** in the reaction of MeMgBr with benzoyldurene). In compounds **5b**, **c** and **e**, a substituted halogen atom may prevent further ring oxidative aromatization to compounds **6** (Scheme 4).

The *para* addition products **7** were always generated except for the cases of disubstituted benzophenones (**1a** and **d**). As shown in Figure 3, the amount of normal Add. was always greater than that of other products and increased with increasing σ-values in any solvent. In contrast, the amount of Red. and abnormal Add.s decreased slightly with increasing σ-values. Interestingly, the amount of Red. in the reactions with **2b** was much smaller than in those with **2a** in spite of the fact that the number of β-hydrogen atoms in the former was three times that in the latter.

Stopped-flow kinetic measurements

It is well known that a brilliant coloration due to a radical ion pair occurs in the initial stage of the Grignard reaction of benzophenone under strictly dry and deaerated conditions. In the present reactions, dramatic colorations were likewise observed. During the reaction of **1f** with **2a** in THF, a coloration was observed as follows. On mixing the reactants, a light-green colour emerged instantaneously and changed to light pink within a few seconds. The pink solution turned light yellow within 30 s. The yellow colour could be due to magnesium alkoxides, which would be transformed to the subsequent products by hydrolysis (when the reaction mixture was quenched with saturated NH_4Cl solution, the yellow colour vanished). Hence both green and pink species seem to be intermediates in this reaction. On the other hand, in the reaction of **1f** with **2f**, a deep-green colour appeared immediately and then turned deep yellow within a few seconds. In this case, the pink species was not seen.

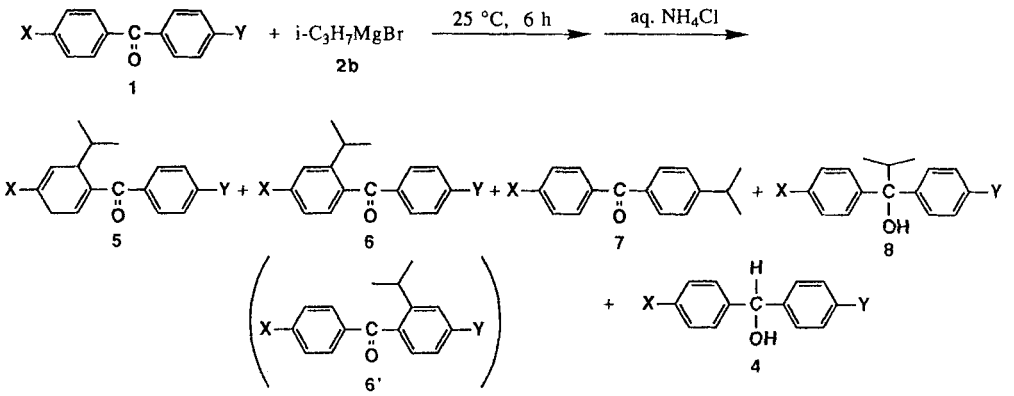
In order to establish what happened in the initial stage of the reaction, we applied a stopped-flow technique to the system. This enabled us to analyse the nature of the coloration spectroscopically. To simplify

Table 2. Spectral data for products obtained in the reaction of **1b** with **2b**

Compound	IR, ν (cm^{-1})	MS (M^+; m/z)[a]	^{1}H NMR ($CDCl_3$), δ (ppm)[b]	
			$(CH_3)_2CH$—	$(CH_3)_2CH$—
5b	1660 (C=O)	304(s)	0·83 (3H, d, J = 7·0 Hz) 1·02 (3H, d, J = 7·0 Hz)	1·96 (1H, dh, J = 3·4, 7·0 Hz)
6b	1660 (C=O)	304(s)	1·19 (6H, d, J = 6·7 Hz)	3·02 (1H, h, J = 6·7 Hz)
6'b	1660 (C=O)	304(s)	1·19 (6H, d, J = 6·7 Hz)	3·02 (1H, h, J = 6·7 Hz)
7b	1640 (C=O)	304(s)	1·30 (6H, d, J = 7·0 Hz)	3·00 (1H, h, J = 7·0 Hz)
8b	3600–3320 (OH)	306(w)	0·87 (3H, d, J = 6·7 Hz) 0·89 (3H, d, J = 6·7 Hz)	2·84 (1H, h, J = 6·7 Hz)
4b	3500–3200 (OH)	264(s)	5·64 (1H, s) (>CHOH)	

[a] s = strong peak; w = weak peak.
[b] d = doublet; h = heptet.

the situation, a large excess of the Grignard reagent (Grignard/Benzophenone = 10 : 1) was used. On mixing **1f** (0·034 M; 1 M = 1 mol dm^{-3}) with **2a** (0·34 M), an absorption band with λ_{max} at 650 nm built up within the first 50-ms delay. This band then decayed and a new absorption band with λ_{max} at 550 nm rose with an isosbestic point at 590 nm (Figure 4). Based on our previous results of stopped-flow studies on the Grignard reactions of benzophenones, the former species absorbing at 650 nm was assigned to a monomeric benzophenone radical anion ion-paired with a Grignard radical cation (a monomer radical ion pair; MIP) and



Scheme 3

Table 3. Product yields in the reactions of **1** with **2b**

Benzophenone	Solvent	Yield (%)			
		5, **6** and **6'** [a]	**7**	**8**	**4**
1a	THF	13	—	75	12
(X = Y = Cl)	DME	11	—	68	21
σ = 0·454	DEE	4	—	67	27
1b	THF	10	8	69	13
(X = Br, Y = H)	DME	10	8	63	19
σ = 0·232	DEE	4	16	54	26
1c	THF	11	9	68	12
(X = Cl, Y = H)	DME	9	8	62	21
σ = 0·227	DEE	5	16	54	26
1d	THF	11	—	65	24
(X = Y = F)	DME	10	—	50	40
σ = 0·124	DEE	11	—	55	34
1e	THF	9	12	61	18
(X = F, Y = H)	DME	9	11	46	34
σ = 0·062	DEE	5	22	46	27
1f	THF	7	16	59	18
(X = Y = H)	DME	4	15	50	31
σ = 0	DEE	4	30	39	27
1g	THF	7	12	66	15
(X = PhO, Y = H)	DME	4	16	57	23
σ = −0·028	DEE	4	26	47	23
1h	THF	6	16	60	18
(X = Me, Y = H)	DME	2	17	53	28
σ = −0·170	DEE	4	28	44	24
1i	THF	4	18	60	18
(X = MeO, Y = H)	DME	3	18	50	29
σ = −0·268	DEE	6	25	44	25

[a] Total yields of *ortho* addition products **5**, **6** and **6'**.

the latter absorbing at 550 nm was a dimeric radical anion pair (DIP). These assignments were essentially based on the comparison with the spectra of sodium benzophenone ketyl in solution.[24] Hence in the initial stage of the reaction, an electron transfer from **2a** to **1f** would give the green species MIP (λ_{max} at 650 nm), which would dimerize to afford the pink species DIP (λ_{max} at 550 nm) in a 1 : 1 ratio.

In contrast, the spectroscopic behaviour in the reaction of **1f** with **2b** was different from that with **2a**. As shown in Figure 5, an absorption band with λ_{max} at 650 nm, which emerged within 20 ms after mixing of **1f** (0·029 M) with **2b** (0·29 M), decayed uniformally without no isosbestic point. After 1 s, a weak absorption band with λ_{max} at 550 nm could be observed. As with **2a**, the species absorbing at 650 nm was assigned to an MIP and that at 550 nm to a DIP. This result indicates that the major decay processes from the green MIP would be direct conversion processes to products, although the dimerization process to DIP could not be ignored.

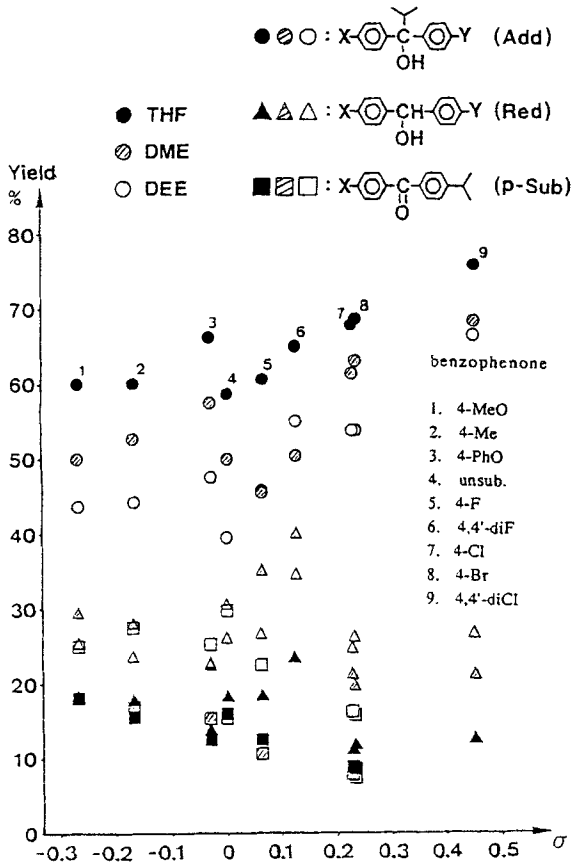
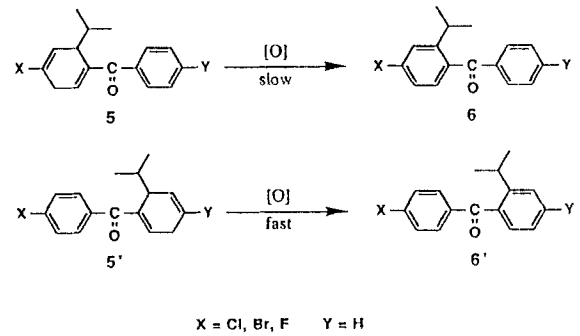


Figure 3. Product yields in the reactions of **1** with **2b** versus Hammett σ constants. [**1**] = 0·046 M; [**2b**] = 0·23 M



Scheme 4

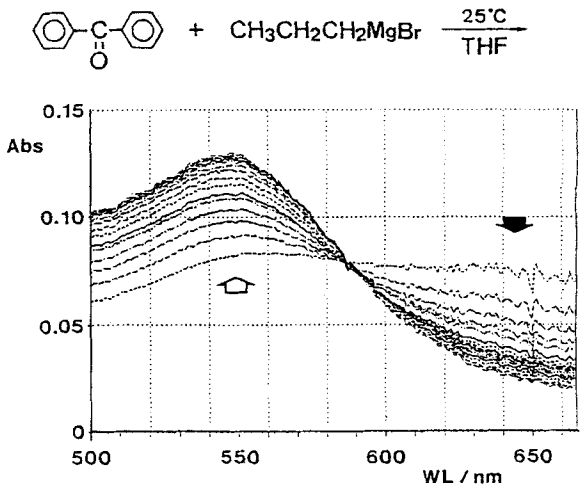


Figure 4. UV–visible spectral change during the reaction of **1f** with **2a** in THF. [**1f**] = 0·034 M; [**2a**] = 0·34 M. Reaction at 25 °C under a nitrogen atmosphere

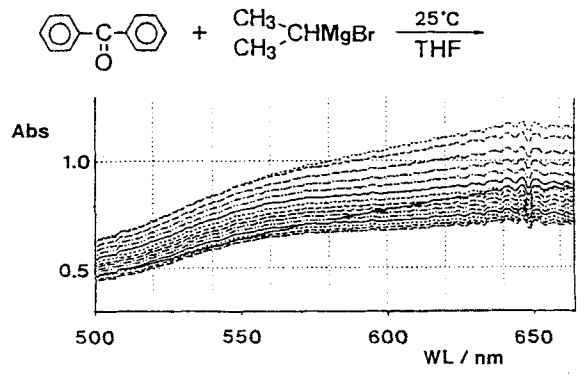


Figure 5. UV–visible spectral change during the reaction of **1f** with **2b** in THF. [**1f**] = 0·029 M; [**2b**] = 0·29 M. Reaction at 25 °C under a nitrogen atmosphere

Further, the rise and decay rate constants of the green MIP were estimated by monitoring the absorbance at 650 nm. The rise curve fitted well a single exponential curve with a pseudo-first-order rate constant (k') which was proportional to the initial concentration of the Grignard reagent (Table 4). The second-order rate constant (k) was estimated to be $4{\cdot}7 \times 10^2$ M^{-1}s^{-1} for **2a** and $1{\cdot}0 \times 10^3$ M^{-1}s^{-1} for **2b** [we have reported[18c] the rate constants of SET in some Grignard reactions of benzophenone (**1f**): k ($M^{-1}s^{-1}$) = 6 (vs PhMgBr), 11 (MeMgBr), 230 (vs *n*-BuMgBr) and 700 (vs EtMgBr)]. In the reaction of **1f** with **2a**, the decay rate constant of MIP was second order with respect to the concentration of MIP. This indicates that the dimerization process dominates the decay pathway of MIP. However, the decay curve of MIP in the reaction of **1f** with **2b** could not be analysed clearly, probably because several decay pathways from MIP could occur concurrently.

Table 4. Rate constant of formation of green MIPs in the reactions of **2** with **1f** in THF, observed at 650 nm, under a nitrogen atmosphere

[**2a**]/*M*	k' (s^{-1})	[**2b**]/*M*	k' (s^{-1})
0·08	37	0·08	118
0·17	53	0·16	180
0·34	154	0·32	343

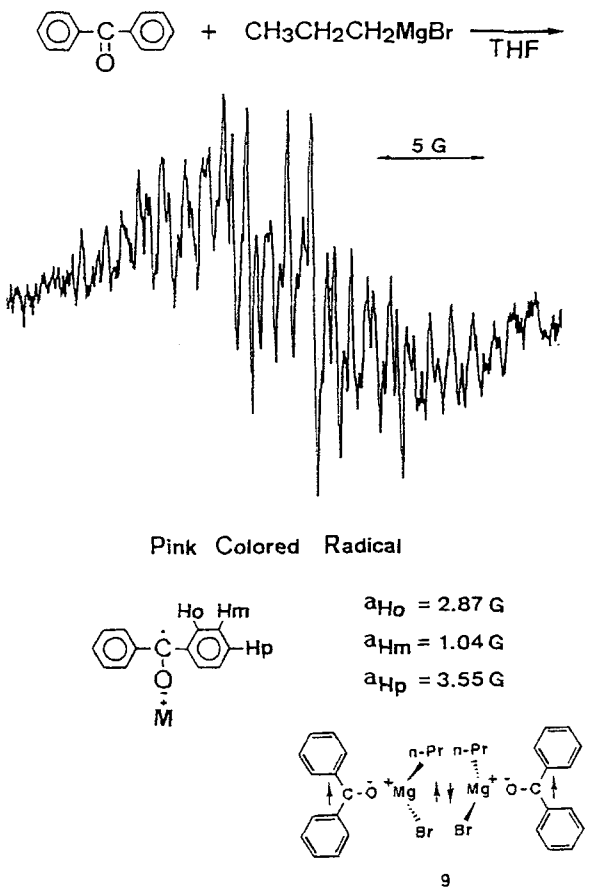


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Figure 6. ESR spectrum of the pink radical intermediate formed in the reaction of **1f** with **2a** in THF at room temperature. [**1f**] = 0·046 M; [**2a**] = 0·21 M

$$d[MIP]/dt = -d[B]/dt = k[B][G]_0 = k'[B]$$
$$k' = k[G]_0$$

where B = benzophenone and G = Grignard reagent.

ESR measurements

In order to clarify the structure of intermediate radicals, an ESR method was applied to the present reactions. As with the stopped-flow measurements, the reactions of **1f** with **2a** and **b** in THF were examined. The measurements were carried out at 25 °C under strictly dry and deaerated conditions. As mentioned above, in the reaction of **1f** with **2a**, two kinds of radical ion pair, MIP and DIP, emerged stepwise in the initial stage. Although the green species was too short-lived to be detected, a sharp and well resolved spectrum of the pink species was obtained by ESR, as shown in Figure 6. From analysis of the hyperfine structure and comparison with our previous ESR results, this radical was assigned to a dimeric benzophenone radical anion ion-paired with Grignard radical cation.[18a,b] It could be represented as the structure **9**, in which paired antiparallel arrows indicate spin-paired electrons (we have reported[18b] that the triplet spin pair of DIP in the reaction of 2-methylbenzophenone with EtMgBr was observed by ESR at 77 K). This interpretation was also supported by the preceding stopped-flow study. Under the conditions described in Figure 6, the lifetime of the pink DIP was a few minutes. On the other hand, in the reaction of **1f** with **2b**, no ESR signal was observed because the green species vanished within a few seconds even under the optimized conditions.

Association measurements

It is well known that, in solution, Grignard reagents are in a Schlenck equilibrium:

$$2RMgX \rightleftarrows R_2MgMgX_2 \rightleftarrows R_2Mg + MgX_2$$

To establish the role of the composition of associated species in the reaction, we studied the association constant of each Grignard reagent in THF and DEE using a novel apparatus designed and constructed in our laboratory.[20] The principle of this method is as follows. First, the formal concentration of a Grignard reagent can be estimated from the difference in vapour pressure

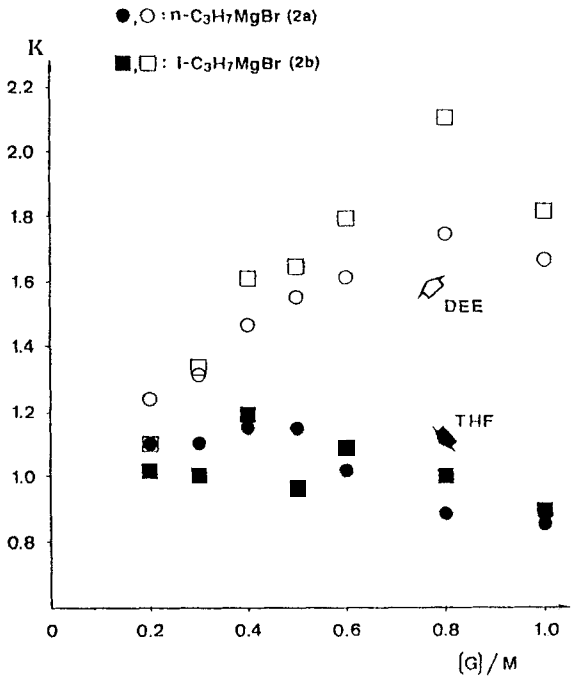


Figure 7. Association constants (K) versus concentration of the Grignard reagents

between a pure solvent and a solution of the Grignard reagent. Then, comparison of the formal concentration with the absolute concentration estimated by Gilman *et al.*'s method[25] gives an association constant. This method is excellent in that one can estimate the actual association constant of the reagent at the reaction temperature. (Previously, Ashby and co-workers[26] studied the association of Grignard reagents in solution by means of the ebullioscopic method; however, the association constant at the reaction temperature could not be obtained by their method.)

The results are depicted in Figure 7. In THF both Grignard reagents dissolve mostly as the monomer at any concentration. On the other hand, in DEE they dissolve mostly as the monomer at lower concentrations and as the dimer at higher concentrations. At the concentration (0·23 M) adopted for product analysis, both reagents exist mostly as the monomer in THF and to some extent as the dimer in DEE.

DISCUSSION

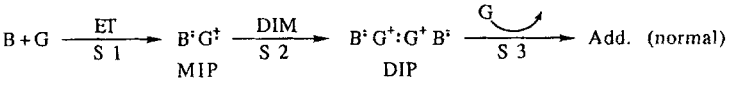
As we have reported previously,[18] the Grignard reaction of benzophenone is initiated by an electron transfer from the Grignard reagent to benzophenone, and it was clarified that monomeric and dimeric radical ion pairs were generated stepwise in the initial stage of the reaction (Scheme 1). Based on those results, in our latest paper[20] we studied the reactions of substituted benzophenones with an *n*-alkyl Grignard reagent, EtMgBr. It is well known that alkyl Grignard reagents which have β-hydrogen atoms give reduction products together with normal addition products. In some cases the amount of Red. was greater than that of Add. In this study, two factors that determine the product distribution were found: the oxidizing ability of benzophenones and the solvent polarity. The latter factor is closely related to the degree of association of the Grignard reagent. Further, the importance of an another factor, the structure of the alkyl groups of Grignard reagents, has been predicted and ascertained. Below we shall discuss the product-determining factors, giving attention especially to the structure of the alkyl groups of the Grignard reagents.

As reported previously,[20] Grignard reagents can be divided into three classes according to the strength of the C—Mg bonds:[27] (1) S-class, where the reagent has a strong C—Mg bond, but has no β-hydrogen atom; the bond energy is above 250 kcal mol^{-1}; 'MeMgBr' and 'PhMgBr' belong to this class; (2) W-class, where the reagent which has a weak C—Mg bond with a bond energy below 200 kcal mol^{-1}; '*t*-BuMgBr' belongs to this class; (3) M-class, where the reagent has a C—Mg bond energy mid-way between those of the S- and W-classes; 'EtMgBr' and '*n*-BuMgBr' belong to this class.

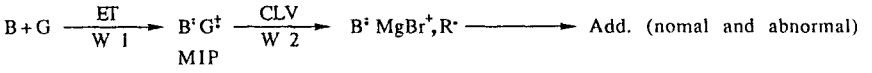
Following above classifications, the reaction pathways can be described as shown in Scheme 5. As can be seen, the product-affording pathways are different from each other. In the present reactions both '*n*-C_3H_7MgBr' and '*i*-C_3H_7MgBr' are classified as M-class judging from their C—Mg bond energies, but their reactivities differ. The reactivity of **2a** toward benzophenones is similar to that of other *n*-alkyl Grignard reagents such as EtMgBr and *n*-BuMgBr.

As shown in Figures 1 and 2, the product distribution is controlled by the oxidizing ability of the benzophenone derivatives and the solvent polarity. Although the complete explanation is not repeated here, the overall trend of the plot of log(Add./Red.) values vs σ-values in the reactions of **2a** is similar to that of EtMgBr. For example, in the reactions of substituted benzophenones with **2a** in THF, the amount of Red. is always greater than that of Add., and the plot of log(Add./Red.) vs σ shows an upward curve with a minimum near $\sigma = 0$. The product distribution would be mainly governed by M1 → M2, M1 → M4 and M1 → M5 → M6 processes (Scheme 6). (We have already indicated that the DIP would afford the normal addition product assisted by another one molecule of Grignard reagent; hence the contribution of an M7 process would be negligible although it could not be ruled out.) In Figure 2, the slope reflects the contribution of the oxidizing ability of benzophenones in the region $\sigma > 0$ and the association ability of **2a** in the region $\sigma < 0$. That is, in the reactions of benzophenones

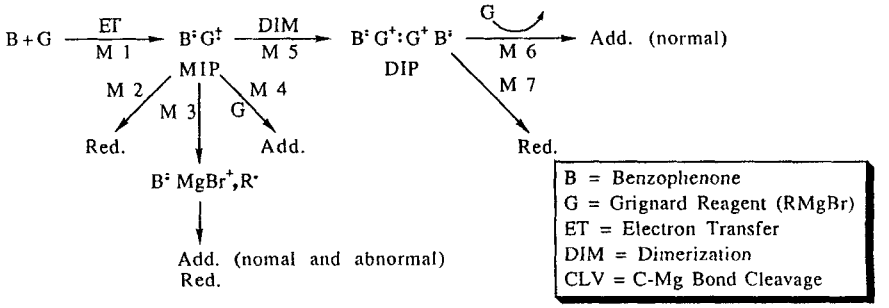
(1) S-Class



(2) W-Class

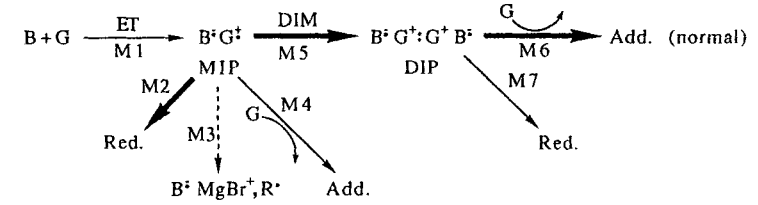


(1) M-Class

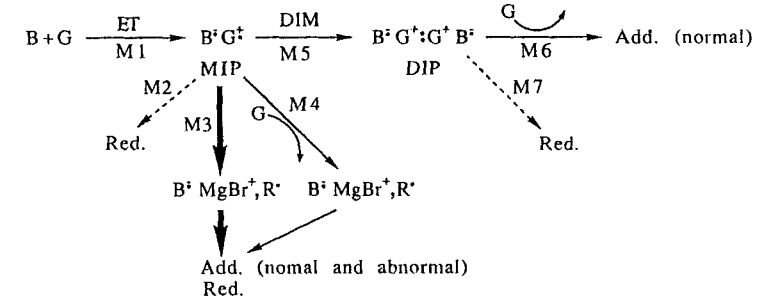


Scheme 5

(a) n-C_3H_7MgBr



(b) i-C_3H_7MgBr



Scheme 6

substituted by electron-withdrawing halogen atoms (**1a–e**) with **2a**, the M1 process is relatively faster, and the M1 → M2 and M1 → M5 → M6 processes will govern the product distribution. In these reactions, with increasing oxidizing ability of ketones, the contribution of M5 → M6 processes via DIP becomes greater because of the higher concentration of MIP in solution, giving relatively higher amounts of Add. In contrast, in the reactions of **2a** with benzophenones substituted by electron-donating groups (**1g–i**), the M1 process is relatively slow, and M1 → M4 in addition to M1 → M2 and M1 → M5 → M6 processes will govern the distribution. The M1 → M4 processes are the pathway to afford Add. via an electron transfer from the dimeric Grignard reagent to the benzophenone. As shown in Figure 7, almost all of **2a** dissolves as the monomer, but a few percent of the reagent still remains as the dimer at 0·23 M in THF. Hence, in the region $\sigma < 0$, with decreasing oxidizing ability, the contribution of the M4 process via MIP that is derived from the dimeric Grignard reagent will become greater because of the lower concentration of MIP in solution, giving relatively higher amounts of Add. (Swain and Boyles[28] and McBee *et al.* [29] reported separately that, in the Grignard reactions, addition of magnesium halides led to the generation of higher amounts of Add.) The dimeric Grignard reagent may be more electron donating than the monomeric one (in the reaction of fluorenone with MeMgBr, the rate of ET in DEE was eight times faster than that in THF).

On the other hand, in the reactions of benzophenones with **2a** in DEE, the log(Add./Red.) values decrease monotonically with increasing σ-values. The product distribution would be controlled by M1 → M2, M1 → M4 and M1 → M5 → M6 processes (Scheme 6). Since in DEE **2a** is dimeric to some extent (Figure 7), the contribution of the M4 process is relatively greater. Overall, the amount of Add. in DEE is higher than that in THF. For all σ-values, the slope of log(Add./Red.) vs σ would reflect the effect of association of the Grignard reagent. With decreasing oxidizing ability of benzophenones, the contribution of the M4 process will become greater because of the lower concentration of MIP, giving relatively higher amounts of Add.

The reactivity of **2b** was specific. In the reactions of substituted benzophenones with **2b**, abnormal *ortho* and *para* addition products were generated in addition to normal Add. and Red. In the reaction of **1** with **2b**, the radical cation of **2b** generated via an M1 process tend to produce an isopropyl radical and a magnesium cation via the C—Mg bond cleavage (Evans and coworkers[30] reported that electrochemical single-electron oxidation of a Grignard reagent in solution led to C—Mg bond cleavage). Generated 'free' isopropyl radicals would attack the benzophenone radical anion at the positions having a high spin density. Thus, abnormal *ortho* and *para* addition products are obtained because the *ortho* and *para* positions of the benzophenone radical anion have appreciable spin densities. The main products were always 'normal' addition products in any solvents. Overall the product distribution would be governed by M1 → M2, M1 → M3, M1 → M4 and M1 → M5 → M6 processes in any solvent. Among these pathways, the M1 → M5 → M6 processes would give the higher *(normal Add.)/(other products)* ratio. This may be due to the structural difference between MIP and DIP, although a more detailed explanation cannot be given. The relationship between the amount of normal Add. and σ can be explained as follows: with increasing oxidizing ability of benzophenones, the contribution of M1 → M5 → M6 processes becomes greater because of the higher concentration of MIP in solution, giving relatively higher amounts of normal Add. Further, the degree of association of Grignard reagents also determines the order of the amount of normal Add. among the solvents. As shown in Figure 7, **2b** dissolves mostly as the monomer in THF and to some extent as the dimer in DEE at 0·23 M, i.e. the contribution of the M4 process derived from dimeric **2b** in THF is smaller, but that in DEE is relatively greater. Hence the decrease of the contribution of M5 → M6 processes in DEE would result in the generation of lower amounts of normal Add.

Spectroscopic data support the above interpretation. First, the stopped-flow investigation gave information about the initial stage of the Grignard reaction. In the reaction of benzophenone with **2a** in THF, M1 → M5 processes were observed clearly. The rate constant of the electron-transfer process, M1, was estimated to be $4{\cdot}7 \times 10^2$ M^{-1}s^{-1}. On the other hand, in the reaction of benzophenone with **2b** in THF, it was found that the M1 → M2, M1 → M3 and M1 → M4 processes were dominant and the M1 → M5 processes were minor. The manner of the direct decay processes from MIP to products was clearly observed. The rate of the M1 process was estimated to be $1{\cdot}0 \times 10^3$ M^{-1}s^{-1}. Second, the ESR investigation indicated the real structure of the intermediate radical species. Although the structure of green MIP could not be observed, that of pink DIP generated in the reaction of **2a** with benzophenone was clearly detected.

Overall, it was clarified that the oxidizing ability of benzophenones, the degree of association and the structure of Grignard reagents determine the product distribution in the Grignard reactions of benzophenones. Among these, the importance of the structure of the Grignard reagents was clearly ascertained in this present study. A relative comparison of the properties of *n*-C_3H_7MgBr (**2a**) and **i**-C_3H_7MgBr (**2b**) arising from the structure of their alkyl groups is given in Table 5.

In addition to the oxidizing ability of benzophenones, the reducing ability of Grignard reagents (Holm[9a,d] reported the anodic over-voltages of several

Table 5. Comparison of the properties of **2a** and **2b**

Reagent	Reducing ability	Strength of C—Mg bond	Strength of β-C—H bond
2a	Low	Strong	Weak
2b	High	Weak	Strong

Grignard reagents) determine the rate of the electron transfer (ET) process (M1); the higher the reducing ability of the Grignard reagent, the faster is the rate of the ET.[31] The estimated rate of ET from **2a** was half of that from **2b**. The strength of the C-Mg and β-C—H bonds controls the decay processes of $2^{+\cdot}$ which is initially formed via ET from **2** and **1**. Since the normal alkyl Grignard radical cation $\mathbf{2a}^{+\cdot}$ has a strong C—Mg and weak β-C—H bonds, an unstable 'free' *n*-propyl radical is difficult to generate and the β-hydrogen of $\mathbf{2a}^{+\cdot}$ is likely to be abstracted by $\mathbf{1}^{-\cdot}$. On the other hand, the branched alkyl Grignard radical cation $\mathbf{2b}^{+\cdot}$ has a weak C—Mg and stronger β-C—H bonds. In this case, a relatively stable 'free' isopropyl radical could be generated via C—Mg bond cleavage. Of course, although the contribution of a dimerization pathway could not be ruled out, the C—Mg bond cleavage process (M3) would be the major decay pathway from $\mathbf{2b}^{+\cdot}$. Because in $\mathbf{2b}^{+\cdot}$ β-hydrogen is difficult to release, the isopropyl radical is stable enough to attack the phenyl ring of $\mathbf{1}^{-\cdot}$, resulting in the formation of the abnormal *ortho* and *para* addition products.

EXPERIMENTAL

All melting points were measured with a Yanagimoto micro-melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded with JEOL-PS-100 and JEOL-GX-400 spectrometers with TMS as an internal standard, and chemical shifts are reported as δ (ppm) values. IR spectra were measured with a JASCO IRA-1 spectrometer. Mass spectra were measured with a JEOL JMS-DX-300 mass spectrometer. Stopped-flow measurements were carried out with an Otsuka Electronic RA-401 stopped flow system with an RA-451 data processor. ESR spectra were recorded with a JEOL JES-FE1XG X-band ESR spectrometer system. Absolute amounts of radicals, *g*-values and hyperfine splitting constants were determined by comparison with 1,1-diphenyl-2-picrylhydrazyl and Mn^{2+} marker. HPLC measurements were made with a Shimadzu SPD-6A and LC-6A HPLC system. Column chromatography was performed using Wako-gel C-200 and FC-40.

Materials. 4,4′-Dichlorobenzophenone (**1a**), 4,4′-difluorobenzophenone (**1d**), benzophenone (**1f**), 4-phenoxybenzophenone (**1h**) and 4-methoxybenzophenone (**1j**) were commercially available and recrystallized twice from benzene. 4-Bromobenzophenone (**1b**), 4-chlorobenzophenone (**1c**), 4-fluorobenzophenone (**1e**) and 4-methylbenzophenone (**1i**) were prepared by Friedel–Crafts acylation and recrystallized twice from benzene.[32] Grignard reagents (**2a** and **b**) in a desired solvent were prepared from magnesium turnings (99·995% pure; Wako) and freshly distilled *n*- and iso-propyl bromide under an argon atmosphere as usual. All the commercially available solvents were distilled from reservoirs including sodium benzophenone ketyl. Absolute concentrations of the prepared Grignard reagents were determined by Gilman *et al.*'s method.[25]

Reactions. All Grignard reactions were performed in a sealed reaction vessel under strictly dry and deaerated conditions (Figure 8). Prior to sealing of parts A and B, both a solution of the Grignard reagent and saturated NH_4Cl solution were introduced into A and B by syringes and strictly deaerated. After connecting each part to the body of the reaction vessel by glass-blowing, a known amount of benzophenone was placed in part C. The vessel was then evacuated under a high vacuum, and a known amount of THF was distilled into part C. Finally, the vessel was sealed off from the vacuum line.

A representative procedure is as follows. After mixing 0·3 mmol of benzophenone with 1·5 mmol of *n*-propylmagnesium bromide (0·7 M; 2·2 ml) in THF (6.5 ml), the reacting solution was allowed to stand for 6 h at 25 °C and then quenched with saturated NH_4Cl solution under deaerated condition. The hydrolysed reaction mixture was extracted with diethyl ether and the organic phase was washed with brine and dried over anhydrous magnesium sulphate. After evaporating the solvent, the amount of each product was determined by ^{1}H NMR. If necessary, HPLC was also used. Each component was isolated by column chromatography on silica gel with hexane, hexane–benzene and hexane–diethyl ether as eluents. At least three separate experiments were performed for each reaction and the average values are listed in Tables 2 and 3.

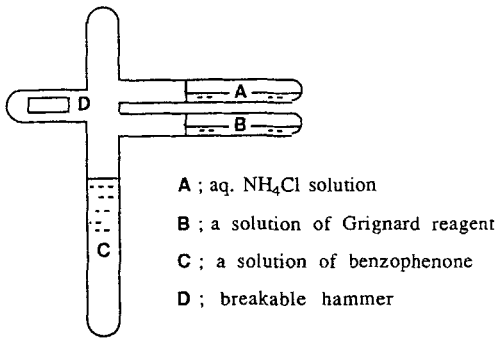


Figure 8. A sealed reaction vessel

Stopped-flow measurements. All of the instruments were dried *in vacuo* and flushed with high-purity argon gas prior to use. Samples were prepared in dry and argon-flushed vessels sealed with rubber septa. Several THF solutions of benzophenones of different concentrations were employed, but the benzophenone/Grignard reagent ratio was kept constant at 1 : 10. With syringes the reactants were transferred into reservoirs of the equipment which were kept dry with a flow of high purity nitrogen gas. In the stopped-flow kinetic measurements, the resulting curve was analysed, in every case, by inspecting both a computer curve fitting and a Guggenheim plot. Detailed conditions of the experiments are given in Figures 4 and 5 and Table 4.

ESR measurements. ESR measurements were carried out using the reaction vessel described previously.[17] After mixing a THF solution of benzophenone with the Grignard reagent under strictly dry and deareated conditions, the reaction solution was introduced into an ESR cell and measured. In the reaction of benzophenone with n-C_3H_7MgBr, the relatively long-lived pink radical species was detected clearly. On the other hand, in the reaction of benzophenone with i-C_3H_7MgBr, the green species was generated, but it was too short-lived to be detected. Detailed conditions of the experiment are given in Figure 6.

Degree of association measurements. Degree of association measurements were undertaken using an apparatus made in our laboratory as described previously.[20] All measurements were carried out at 25 °C. At least five separate experiments were performed for each measurement and the average values are given in Figure 7.

Physical properties of the products. 1,1-Bis(4-chlorophenyl)butanol (**3a**): colourless oil. MS: m/z 296, 294 (M^+). IR (NaCl): 3450 cm^{-1} (OH). ^1H NMR ($CDCl_3$): $\delta = 0{\cdot}93$ (3H, t, $J = 7{\cdot}3$ Hz), 1·26 (2H, tq, $J = 8{\cdot}2$, 7·3 Hz), 2·04 (1H, s, OH), 2·19 (2H, t, $J = 8{\cdot}2$ Hz), 7·26 (4H, d, $J = 8{\cdot}8$ Hz), 7·32 (4H, d, $J = 8{\cdot}8$ Hz).

1-(4-Bromophenyl)-1-phenylbutanol (**3b**): colourless oil. MS: m/z 306, 304 (M^+). IR (NaCl): 3450 cm^{-1} (OH). ^1H NMR ($CDCl_3$): $\delta = 0{\cdot}92$ (3H, t, $J = 7{\cdot}3$ Hz), 1·26 (2H, tq, $J = 8{\cdot}2$, 7·3 Hz), 2·09 (1H, s, OH), 2·21 (2H, t, $J = 8{\cdot}2$ Hz), 7·21 (1H, t, $J = 7{\cdot}6$ Hz), 7·27 (2H, d, $J = 8{\cdot}9$ Hz), 7·29 (2H, t, $J = 7{\cdot}3$ Hz), 7·37 (2H, d, $J = 8{\cdot}2$ Hz), 7·40 (2H, d, $J = 8{\cdot}5$ Hz).

1-(4-Chlorophenyl)-1-phenylbutanol (**3c**): colourless oil. MS: m/z 262, 260 (M^+). IR (NaCl): 3450 cm^{-1} (OH). ^1H NMR ($CDCl_3$): $\delta = 0{\cdot}92$ (3H, t, $J = 7{\cdot}3$ Hz), 1·25 (2H, tq, $J = 8{\cdot}2$, 7·3 Hz), 2·09 (1H, s, OH), 2·22 (2H, t, $J = 8{\cdot}5$ Hz), 7·21 (1H, t, $J = 7{\cdot}3$ Hz), 7·25 (2H, d, $J = 8{\cdot}5$ Hz), 7·30 (2H, t, $J = 7{\cdot}9$ Hz), 7·33 (2H, d, $J = 8{\cdot}9$ Hz), 7·38 (2H, d, $J = 8{\cdot}2$ Hz).

1,1-Bis(4-fluorophenyl)butanol (**3d**): colourless oil. MS: m/z 262 (M^+). IR (NaCl): 3445 cm^{-1} (OH). ^1H NMR ($CDCl_3$): $\delta = 0{\cdot}21$ (3H, t, $J = 7{\cdot}3$ Hz), 1·24 (2H, tq, $J = 8{\cdot}2$, 7·3 Hz), 2·18 (2H, dd, $J = 8{\cdot}2$, 7·3 Hz), 2·23 (1H, s, OH), 6·95 (4H, t, $J = 8{\cdot}9$ Hz), 7·32 (4H, dd, $J = 5{\cdot}4$, 8·9 Hz).

1-(4-Fluorophenyl)-1-phenylbutanol (**3e**): colourless oil. MS: m/z 244 (M^+). IR (NaCl): 3435 cm^{-1} (OH). ^1H NMR ($CDCl_3$): $\delta = 0{\cdot}92$ (3H, t, $J = 7{\cdot}3$ Hz), 1·28 (2H, tq, $J = 8{\cdot}2$, 7·3 Hz), 2·12 (1H, s, OH), 2·21 (2H, t, $J = 8{\cdot}3$ Hz), 6·95 (2H, t, $J = 8{\cdot}9$ Hz), 7·21 (1H, t, $J = 7{\cdot}3$ Hz), 7·29 (2H, t, $J = 7{\cdot}3$ Hz), 7·32–7·40 (3H, m).

1,1-Diphenylbutanol (**3f**): colourless oil. MS: m/z 226 (M^+). IR (NaCl): 3440 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 0{\cdot}91$ (3H, t, $J = 7{\cdot}3$ Hz), 1·28 (2H, tq, $J = 8{\cdot}2$, 7·3 Hz), 2·10 (1H, s, OH), 2·24 (2H, t, $J = 8{\cdot}2$ Hz), 7·18 (2H, t, $J = 7{\cdot}3$ Hz), 7·27 (4H, t, $J = 7{\cdot}3$ Hz), 7·45 (4H, d, $J = 7{\cdot}6$ Hz).

1-(4-Phenoxyphenyl)-1-phenylbutanol (**3g**): colourless oil. MS: m/z 318 (M^+). IR (NaCl): 3450 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 0{\cdot}90$ (3H, t, $J = 7{\cdot}3$ Hz), 1·27 (2H, tq, $J = 8{\cdot}2$, 7·3 Hz), 2·19 (2H, t, $J = 8{\cdot}2$ Hz), 2·17 (1H, s, OH), 6·88 (2H, d, $J = 8{\cdot}8$ Hz), 6·95 (2H, d, $J = 8{\cdot}2$ Hz), 7·03 (1H, t, $J = 7{\cdot}3$ Hz), 7·17 (1H, t, $J = 7{\cdot}3$ Hz), 7·26 (4H, d, $J = 7{\cdot}3$ Hz), 7·31 (2H, d, $J = 8{\cdot}8$ Hz), 7·37 (2H, d, $J = 7{\cdot}3$ Hz).

1-Phenyl-1-(4-methylphenyl)butanol (**3h**): colourless oil. MS: m/z 240 (M^+). IR (NaCl): 3435 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 0{\cdot}89$ (3H, t, $J = 7{\cdot}3$ Hz), 1·27 (2H, tq, $J = 8{\cdot}3$, 7·3 Hz), 2·06 (1H, s, OH), 2·20 (2H, t, $J = 8{\cdot}3$ Hz), 2·27 (3H, s), 7·07 (2H, d, $J = 8{\cdot}0$ Hz), 7·17 (1H, t, $J = 7{\cdot}3$ Hz), 7·23–7·40 (4H, m), 7·36 (2H, d, $J = 7{\cdot}3$ Hz).

1-Phenyl-1-(4-methoxyphenyl)butanol (**3i**): colourless oil. MS: m/z 256 (M^+). IR (NaCl): 3425 cm^{-1} (OH). ^1H NMR ($CDCl_3$): $\delta = 0{\cdot}89$ (3H, t, $J = 7{\cdot}3$ Hz), 1·26 (2H, tq, $J = 8{\cdot}2$, 7·3 Hz), 2·18 (2H, t, $J = 8{\cdot}2$ Hz), 2·26 (1H, s, OH), 3·70 (3H, s), 6·78 (2H, d, $J = 6{\cdot}8$ Hz), 7·10–7·40 (7H, m).

4,4′-Dichlorobenzhydrol (**4a**): colourless crystals from hexane–diethyl ether; m.p. 75–77 °C. MS: m/z 254, 252 (M^+). IR (KBr): 3450 cm^{-1} (OH). ^1H NMR ($CDCl_3$): $\delta = 2{\cdot}21$ (1H, s, OH), 5·54 (1H, s), 7·23 (4H, d, $J = 8{\cdot}7$ Hz), 7·29 (4H, d, $J = 8{\cdot}6$ Hz).

4-Bromobenzhydrol (**4b**): white crystals from hexane–diethyl ether; m.p. 44–46 °C. MS: m/z 264, 262 (M^+). IR (KBr): 3450 cm^{-1} (OH). ^1H NMR ($CDCl_3$); $\delta = 2{\cdot}79$ (1H, s, OH), 5·64 (1H, s), 7·16 (2H, d, $J = 8{\cdot}5$ Hz), 7·20–7·35 (5H, m), 7·39 (2H, d, $J = 8{\cdot}5$ Hz).

4-Chlorobenzhydrol (**4c**): white crystals from hexane–diethyl ether; m.p. 36–38 °C. MS: m/z 220, 218 (M^+). IR (KBr): 3450 cm^{-1} (OH). ^1H NMR ($CDCl_3$): $\delta = 3{\cdot}01$ (1H, s, OH), 5·61 (1H, s), 7·15–7·35 (9H, m).

4,4′-Difluorobenzhydrol (**4d**): colourless oil. MS:

m/z 220 (M^+). IR (NaCl): 3450 cm^{-1} (OH). ^1H NMR ($CDCl_3$): $\delta = 2{\cdot}42$ (1H, s, OH), 5·77 (1H, s), 7·01 (4H, t, $J = 8{\cdot}8$ Hz), 7·29 (4H, dd, $J = 5{\cdot}5$, 8·8 Hz).

4-Fluorobenzhydrol (**4e**): white crystals from hexane–diethyl ether; m.p. 46–48 °C. MS: *m/z* 202 (M^+). IR (KBr): 3250 cm^{-1} (OH). ^1H NMR ($CDCl_3$); $\delta = 2{\cdot}35$ (1H, s, OH), 5·80 (1H, s), 7·00 (2H, t, $J = 8{\cdot}9$ Hz), 7·25–7·35 (7H, m).

Benzhydrol (**4f**): colourless crystals from hexane–diethyl ether; m.p. 62–64 °C. MS: *m/z* 184 (M^+). IR (KBr): 3300 cm^{-1} (OH). ^1H NMR ($CDCl_3$): $\delta = 2{\cdot}27$ (1H, s, OH), 5·82 (1H, s), 7·25 (2H, d, $J = 7{\cdot}3$ Hz), 7·30–7·40 (8H, m).

4-Phenoxybenzhydrol (**4g**): white crystals from hexane–diethyl ether; m.p. 78–80 °C. MS: *m/z* 276 (M^+). IR (KBr): 3450 cm^{-1} (OH). ^1H NMR ($CDCl_3$): $\delta = 2{\cdot}57$ (1H, s, OH), 5·82 (1H, s), 6·95 (2H, d, $J = 8{\cdot}6$ Hz), 6·99 (2H, d, $J = 7{\cdot}6$ Hz), 7·09 (1H, t, $J = 7{\cdot}3$ Hz), 7·25–7·40 (9H, m).

4-Methylbenzhydrol (**4h**): white crystals from hexane–diethyl ether; m.p. 50–52 °C. MS: *m/z* 198 (M^+). IR (KBr): 3450 cm^{-1} (OH). ^1H NMR ($CDCl_3$): $\delta = 2{\cdot}31$ (1H, s, OH), 2·33 (3H, s), 5·75 (1H, s), 7·11 (2H, d, $J = 7{\cdot}6$ Hz), 7·20–7·40 (7H, m).

4-Methoxybenzhydrol (**4i**): white crystals from hexane–diethyl ether; m.p. 62–64 °C. MS: *m/z* 214 (M^+). IR (KBr): 3450 cm^{-1} (OH). ^1H NMR ($CDCl_3$): $\delta = 2{\cdot}19$ (1H, s, OH), 3·79 (3H, s), 5·81 (1H, s), 6·86 (2H, d, $J = 8{\cdot}6$ Hz), 7·25–7·40 (7H, m).

4-(4-Chlorobenzoyl)-1-chloro-3-isopropylcyclohexa-1,4-diene (**5a**): pale yellow crystals from hexane–diethyl ether; m.p. 70–72 °C. MS: *m/z* 296, 294 (M^+). IR (KBr): 1650 cm^{-1} (C=O). ^1H NMR ($CDCl_3$): $\delta = 0{\cdot}80$ (3H, d, $J = 6{\cdot}8$ Hz), 1·01 (3H, d, $J = 6{\cdot}8$ Hz), 1·94 (1H, dhept, $J = 3{\cdot}4$, 6·8 Hz), 3·03 (1H, m), 3·24 (1H, m), 3·69 (1H, m), 5·95 (1H, dd, $J = 4{\cdot}4$, 2·0 Hz), 6·38 (1H, dd, $J = 4{\cdot}9$, 3·0 Hz), 7·42 (2H, d, $J = 8{\cdot}8$ Hz), 7·67 (2H, d, $J = 8{\cdot}8$ Hz).

4-Benzoyl-1-bromo-3-isopropylcyclohexa-1,4-diene (**5b**): colourless oil. MS: *m/z* 306, 304 (M^+). IR (NaCl): 1660 cm^{-1} (C=O). ^1H NMR ($CDCl_3$): $\delta = 0{\cdot}83$ (3H, d, $J = 7{\cdot}0$ Hz), 1·02 (3H, d, $J = 7{\cdot}0$ Hz), 1·96 (1H, dhept, $J = 3{\cdot}4$, 7·0 Hz), 3·13 (1H, m), 3·35 (1H, m), 3·68 (1H, m), 6·19 (1H, dd, $J = 4{\cdot}5$, 1·8 Hz), 6·35 (1H, dd, $J = 4{\cdot}1$, 3·1 Hz), 7·45 (2H, t, $J = 7{\cdot}6$ Hz), 7·55 (1H, t, $J = 7{\cdot}6$ Hz), 7·73 (2H, d, $J = 7{\cdot}3$ Hz).

4-Benzoyl-1-chloro-3-isopropylcyclohexa-1,4-diene (**5c**): colourless oil. MS: *m/z* 262, 260 (M^+). IR (NaCl): 1650 cm^{-1} (C=O). ^1H NMR ($CDCl_3$): $\delta = 0{\cdot}81$ (3H, d, $J = 6{\cdot}7$ Hz), 1·00 (3H, d, $J = 6{\cdot}7$ Hz), 1·94 (1H, dhept, $J = 3{\cdot}4$, 6·7 Hz), 3·03 (1H, m), 3·25 (1H, m), 3·74 (1H, m), 5·97 (1H, m), 6·42 (1H, m), 7·43 (2H, t, $J = 7{\cdot}6$ Hz), 7·55 (1H, t, $J = 7{\cdot}6$ Hz), 7·73 (2H, d, $J = 7{\cdot}3$ Hz).

4-(4-Fluorobenzoyl)-1-fluoro-3-isopropylcyclohexa-1,4-diene (**5d**): colourless oil. MS: *m/z* 262 (M^+). IR (NaCl): 1650 cm^{-1} (C=O). ^1H NMR ($CDCl_3$): $\delta = 0{\cdot}80$ (3H, d, $J = 6{\cdot}7$ Hz), 0·98 (3H, d, $J = 6{\cdot}7$ Hz), 1·92 (1H, dhept, $J = 3{\cdot}0$, 6·7 Hz), 2·97 (1H, m), 3·07 (1H, m), 3·73 (1H, m), 5·34 (1H, m), 6·35 (1H, dt, $J = 7{\cdot}0$, 3·0 Hz), 7·13 (2H, t, $J = 8{\cdot}8$ Hz), 7·78 (2H, dd, $J = 5{\cdot}5$, 8·8 Hz).

4-Benzoyl-1-fluoro-3-isopropylcyclohexa-1,4-diene (**5e**): colourless oil. MS: *m/z* 244 (M^+). IR (NaCl): 1650 cm^{-1} (C=O). ^1H NMR ($CDCl_3$): $\delta = 0{\cdot}82$ (3H, d, $J = 7{\cdot}0$ Hz), 1·02 (3H, d, $J = 7{\cdot}0$ Hz), 1·97 (1H, dhept, $J = 3{\cdot}4$, 7·0 Hz), 2·95 (1H, m), 3·17 (1H, m), 3·72 (1H, m), 5·35 (1H, m), 6·40 (1H, m), 7·45 (2H, t, $J = 7{\cdot}6$ Hz), 7·55 (1H, t, $J = 7{\cdot}0$ Hz), 7·73 (2H, d, $J = 7{\cdot}3$ Hz).

4,4′-Dichloro-2-isopropylbenzophenone (**6a**): colourless oil. MS: *m/z* 294, 292 (M^+). IR (NaCl): 1660 cm^{-1} (C=O). ^1H NMR ($CDCl_3$): $\delta = 1{\cdot}19$ (6H, d, $J = 6{\cdot}7$ Hz), 3·02 (1H, hept, $J = 6{\cdot}7$ Hz), 7·15 (1H, d, $J = 8{\cdot}2$ Hz), 7·23 (1H, dd, $J = 8{\cdot}2$, 2·0 Hz), 7·41 (1H, d, $J = 2{\cdot}0$ Hz), 7·44 (2H, d, $J = 8{\cdot}5$ Hz), 7·73 (2H, d, $J = 8{\cdot}5$ Hz).

4-Bromo-2-isopropylbenzophenone (**6b**): colourless oil. MS: *m/z* 304, 302 (M^+). IR (NaCl): 1660 cm^{-1} (C=O). ^1H NMR ($CDCl_3$): $\delta = 1{\cdot}19$ (6H, d, $J = 6{\cdot}7$ Hz), 3·02 (1H, hept, $J = 6{\cdot}7$ Hz), 7·10 (1H, d, $J = 8{\cdot}6$ Hz), 7·38 (1H, dd, $J = 8{\cdot}6$, 2·0 Hz), 7·44–7·62 (4H, m), 7·79 (2H, d, $J = 8{\cdot}8$ Hz).

4-Bromo-2′-isopropylbenzophenone (**6′b**): colourless oil. MS: *m/z* 304, 302 (M^+). IR (NaCl): 1660 cm^{-1} (C=O). ^1H NMR ($CDCl_3$): $\delta = 1{\cdot}19$ (6H, d, $J = 6{\cdot}7$ Hz), 3·02 (1H, hept, $J = 6{\cdot}7$ Hz), 7·16–7·25 (2H, m), 7·43–7·63 (4H, m), 7·68 (2H, d, $J = 8{\cdot}9$ Hz).

4-Chloro-2-isopropylbenzophenone (**6c**): colourless oil. MS: *m/z* 260, 258 (M^+). IR (NaCl): 1660 cm^{-1} (C=O). ^1H NMR ($CDCl_3$): $\delta = 1{\cdot}19$ (6H, d, $J = 6{\cdot}7$ Hz), 3·06 (1H, hept, $J = 6{\cdot}7$ Hz), 7·17 (1H, d, $J = 8{\cdot}6$ Hz), 7·23 (1H, dd, $J = 8{\cdot}6$, 2·0 Hz), 7·41 (1H, d, $J = 2{\cdot}0$ Hz), 7·46 (2H, t, $J = 7{\cdot}6$ Hz), 7·60 (1H, t, $J = 7{\cdot}3$ Hz), 7·79 (2H, d, $J = 7{\cdot}6$ Hz).

4-Chloro-2′-isopropylbenzophenone (**6′c**): colourless oil. MS: *m/z* 260, 258 (M^+). IR (NaCl): 1660 cm^{-1} (C=O). ^1H NMR ($CDCl_3$): $\delta = 1{\cdot}19$ (6H, d, $J = 6{\cdot}7$ Hz), 3·06 (1H, hept, $J = 6{\cdot}7$ Hz), 7·20–7·48 (6H, m), 7·75 (2H, d, $J = 8{\cdot}8$ Hz).

4,4′-Difluoro-2-isopropylbenzophenone (**6d**): colourless oil. MS: *m/z* 260 (M^+). IR (NaCl): 1655 cm^{-1} (C=O). ^1H NMR ($CDCl_3$): $\delta = 1{\cdot}19$ (6H, d, $J = 6{\cdot}7$ Hz), 3·08 (1H, hept, $J = 6{\cdot}7$ Hz), 6·93 (1H, dt, $J = 2{\cdot}4$, 8·2 Hz), 7·14 (3H, m), 7·21 (1H, dd, $J = 6{\cdot}0$, 8·2 Hz), 7·82 (2H, dd, $J = 5{\cdot}5$, 8·8 Hz).

4-Fluoro-2-isopropylbenzophenone (**6e**): colourless oil. MS: *m/z* 242 (M^+). IR (NaCl): 1660 cm^{-1} (C=O). ^1H NMR ($CDCl_3$): $\delta = 1{\cdot}19$ (6H, d, $J = 6{\cdot}7$ Hz), 3·12 (1H, dhept, $J = 1{\cdot}8$, 6·7 Hz), 6·90–7·45 (3H, m), 7·46 (2H, t, $J = 7{\cdot}4$ Hz), 7·59 (1H, t, $J = 7{\cdot}4$ Hz), 7·79 (2H, d, $J = 8{\cdot}7$ Hz).

4-Fluoro-2′-isopropylbenzophenone (**6′e**): colourless oil. MS: *m/z* 242 (M^+). IR (NaCl): 1660 cm^{-1} (C=O).

^{1}H NMR ($CDCl_3$): δ = 1·19 (6H, d, J = 6·7 Hz), 3·01 (1H, hept, J = 6·7 Hz), 6·90–7·45 (6H, m), 7·84 (2H, dd, J = 5·5, 8·9 Hz).

2-Isopropylbenzophenone (**6f**): colourless oil. MS: m/z 224 (M^+). IR (NaCl): 1660 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$): δ = 1·19 (6H, d, J = 7·0 Hz), 3·04 (1H, hept, J = 7·0 Hz), 7·22 (2H, m), 7·45 (4H, m), 7·58 (1H, t, J = 7·3 Hz), 7·82 (2H, d, J = 7·0 Hz).

4-Phenoxy-2-isopropylbenzophenone (**6g**): colourless oil. MS: m/z 316 (M^+). IR (NaCl): 1660 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$); δ = 1·20 (6H, d, J = 7·0 Hz), 3·03 (1H, hept, J = 7·0 Hz), 6·98 (2H, d, J = 7·9 Hz), 7·05–7·85 (11H, m).

4-Phenoxy-2′-isopropylbenzophenone (**6′g**): colourless oil. MS: m/z 316 (M^+). IR (NaCl): 1660 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$): δ = 1·17 (6H, d, J = 6·7 Hz), 3·16 (1H, hept, J = 6·7 Hz), 7·05–7·85 (13H, m).

4-Methyl-2-isopropylbenzophenone (**6h**): colourless oil. MS: m/z 238 (M^+). IR (NaCl): 1660 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$): δ = 1·19 (6H, d, J = 7·0 Hz), 2·40 (3H, s), 3·03 (1H, hept, J = 7·0 Hz), 7·04 (1H, d, J = 7·6 Hz), 7·13 (1H, d, J = 7·6 Hz), 7·42–7·48 (3H, m), 7·57 (1H, t, J = 7·6 Hz), 7·81 (2H, d, J = 8·4 Hz).

4-Methyl-2′-isopropylbenzophenone (**6′h**): colourless oil. MS: m/z 238 (M^+). IR (NaCl): 1660 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$): δ = 1·19 (6H, d, J = 7·0 Hz), 2·39 (3H, s), 3·01 (1H, hept, J = 7·0 Hz), 7·18–7·46 (6H, m), 7·71 (2H, d, J = 8·4 Hz).

4-Methoxy-2′-isopropylbenzophenone (**6′i**): colourless oil. MS: m/z 254 (M^+). IR (NaCl): 1650 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$): δ = 1·19 (6H, d, J = 7·0 Hz), 3·01 (1H, hept, J = 7·0 Hz), 3·87 (3H, s), 6·92 (2H, d, J = 8·9 Hz), 7·10–7·50 (4H, m), 7·89 (2H, d, J = 8·9 Hz).

4-Bromo-4′-isopropylbenzophenone (**7b**): white crystals from hexane–diethyl ether; m.p. 56–58 °C. MS: m/z 304, 302 (M^+). IR (KBr): 1640 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$): δ = 1·30 (6H, d, J = 7·0 Hz), 3·00 (1H, hept, J = 7·0 Hz), 7·34 (2H, d, J = 8·2 Hz), 7·62 (2H, d, J = 6·7 Hz), 7·67 (2H, d, J = 6·7 Hz), 7·72 (2H, d, J = 8·2 Hz).

4-Chloro-4′-isopropylbenzophenone (**7c**): white crystals from hexane; m.p. 48–50 °C. MS: m/z 260, 258 (M^+). IR (KBr): 1640 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$): δ = 1·30 (6H, d, J = 7·0 Hz), 2·99 (1H, hept, J = 7·0 Hz), 7·34 (2H, d, J = 8·2 Hz), 7·45 (2H, d, J = 8·5 Hz), 7·72 (2H, d, J = 8·2 Hz), 7·75 (2H, d, J = 8·6 Hz).

4-Fluoro-4′-isopropylbenzophenone (**7e**): white crystals from hexane–diethyl ether; m.p. 38–40 °C. MS: m/z 242 (M^+). IR (KBr): 1640 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$): δ = 1·29 (6H, d, J = 7·0 Hz), 3·00 (1H, hept, J = 7·0 Hz), 7·15 (2H, t, J = 8·9 Hz), 7·34 (2H, d, J = 8·2 Hz), 7·72 (2H, d, J = 8·2 Hz), 7·84 (2H, dd, J = 5·5, 8·9 Hz).

4-Isopropylbenzophenone (**7f**): colourless oil. MS: m/z 224 (M^+). IR (NaCl): 1645 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$): δ = 1·29 (6H, d, J = 7·0 Hz), 2·98 (1H, hept, J = 7·0 Hz), 7·32 (2H, d, J = 8·2 Hz), 7·45 (2H, t, J = 7·3 Hz), 7·56 (1H, t, J = 7·3 Hz), 7·75 (2H, d, J = 8·2 Hz), 7·79 (2H, d, J = 7·0 Hz).

4-Phenoxy-4′-isopropylbenzophenone (**7g**): colourless oil. MS: m/z 316 (M^+). IR (NaCl): 1640 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$): δ = 1·29 (6H, d, J = 7·0 Hz), 2·98 (1H, hept, J = 7·0 Hz), 7·02 (2H, d, J = 8·9 Hz), 7·08 (2H, d, J = 8·9 Hz), 7·18 (1H, t, J = 7·3 Hz), 7·32 (2H, d, J = 7·9 Hz), 7·38 (2H, t, J = 7·3 Hz), 7·73 (2H, d, J = 8·6 Hz), 7·81 (2H, d, J = 8·9 Hz).

4′-Methyl-4-isopropylbenzophenone (**7h**): colourless oil. MS: m/z 238 (M^+). IR (NaCl): 1655 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$): δ = 1·29 (6H, d, J = 7·0 Hz), 2·44 (3H, s), 2·99 (1H, hept, J = 7·0 Hz), 7·27 (2H, d, J = 7·6 Hz), 7·32 (2H, d, J = 7·9 Hz), 7·71 (2H, d, J = 7·6 Hz), 7·73 (2H, d, J = 7·9 Hz).

4-Methoxy-4′-isopropylbenzophenone (**7i**): colourless oil. MS: m/z 254 (M^+). IR (NaCl): 1655 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$): δ = 1·29 (6H, d, J = 7·0 Hz), 2·98 (1H, hept, J = 7·0 Hz), 3·86 (3H, s), 6·94 (2H, d, J = 8·9 Hz), 7·31 (2H, d, J = 8·4 Hz), 7·71 (2H, d, J = 8·4 Hz), 7·82 (2H, d, J = 8·9 Hz).

1,1-Bis(4-chlorophenyl)-2-methylpropanol (**8a**): colourless crystals from hexane–diethyl ether; m.p. 113–115 °C. MS: m/z 294 (M^+). IR (KBr): 3450 cm^{-1} (OH). ^{1}H NMR ($CDCl_3$): δ = 0·85 (6H, d, J = 6·7 Hz), 2·06 (1H, s, OH), 2·79 (1H, hept, J = 6·7 Hz), 7·24 (4H, d, J = 8·7 Hz), 7·39 (4H, d, J = 8·7 Hz).

1-(4-Bromophenyl)-2-methyl-1-phenylpropanol (**8b**): colourless oil. MS: m/z 306, 304 (M^+). IR (NaCl: 3460 cm^{-1} (OH). ^{1}H NMR ($CDCl_3$): δ = 0·87 (3H, d, J = 6·7 Hz), 0·89 (3H, d, J = 6·7 Hz), 2·02 (1H, s, OH), 2·84 (1H, hept, J = 6·7 Hz), 7·18 (1H, t, J = 7·3 Hz), 7·29 (2H, t, J = 7·3 Hz), 7·36 (2H, d, J = 8·9 Hz), 7·40 (2H, d, J = 8·9 Hz), 7·46 (2H, d, J = 7·3 Hz).

1-(4-Chlorophenyl)-2-methyl-1-phenylpropanol (**8c**): colourless oil. MS: m/z 262, 260 (M^+). IR (NaCl): 3450 cm^{-1} (OH). ^{1}H NMR ($CDCl_3$): δ = 0·86 (3H, d, J = 6·7 Hz), 0·89 (3H, d, J = 6·7 Hz), 2·04 (1H, s, OH), 2·84 (1H, hept, J = 6·7 Hz), 7·17 (1H, t, J = 7·3 Hz), 7·23 (2H, d, J = 8·8 Hz), 7·28 (2H, d, J = 7·3 Hz), 7·42 (2H, d, J = 8·8 Hz), 7·46 (2H, d, J = 7·3 Hz).

1,1-Bis(4-fluorophenyl)-2-methylpropanol (**8d**): colourless crystals from hexane–diethyl ether; m.p. 58–60 °C. MS: m/z 262 (M^+). IR (KBr): 3450 cm^{-1} (OH). ^{1}H NMR ($CDCl_3$): δ = 0·87 (6H, d, J = 6·7 Hz), 2·02 (1H, s, OH), 2·80 (1H, hept, J = 6·7 Hz), 6·96 (4H, t, J = 8·8 Hz), 7·42 (4H, dd, J = 5·5, 8·8 Hz).

1-(4-Fluorophenyl)-2-methyl-1-phenylpropanol (**8e**): colourless oil. MS: m/z 244 (M^+). IR (NaCl): 3450 cm^{-1} (OH). ^{1}H NMR ($CDCl_3$): δ = 0·87 (3H, d, J = 6·7 Hz), 0·88 (3H, d, J = 6·7 Hz), 2·03 (1H, s,

OH), 2·85 (1H, hept, $J = 6·7$ Hz), 6·95 (2H, t, $J = 8·8$ Hz), 7·19 (1H, t, $J = 7·3$ Hz), 7·30 (2H, t, $J = 7·3$ Hz), 7·40–7·55 (4H, m).

2-Methyl-1,1-diphenylpropanol (**8f**): colourless oil. MS: m/z 226 (M^+). IR (NaCl): 3450 cm^{-1} (OH). ^1H NMR ($CDCl_3$): $\delta = 0·88$ (6H, d, $J = 6·7$ Hz), 2·10 (1H, s, OH), 2·88 (1H, hept, $J = 6·7$ Hz), 7·15 (2H, t, $J = 7·3$ Hz), 7·27 (4H, t, $J = 7·3$ Hz), 7·49 (4H, d, $J = 7·3$ Hz).

2-Methyl-1-(4-phenoxyphenyl)-1-phenylpropanol (**8g**): colourless oil. MS: m/z 318 (M^+). IR (NaCl): 3440 cm^{-1} (OH). ^1H NMR ($CDCl_3$): $\delta = 0·88$ (3H, d, $J = 6·7$ Hz), 0·91 (3H, d, $J = 6·7$ Hz), 2·01 (1H, s, OH), 2·85 (1H, hept, $J = 6·7$ Hz), 6·91 (2H, d, $J = 8·9$ Hz), 6·97 (2H, d, $J = 7·6$ Hz), 7·07 (1H, t, $J = 7·3$ Hz), 7·18 (1H, t, $J = 7·3$ Hz), 7·30 (4H, tt, $J = 7·3$, 7·6 Hz), 7·44 (2H, d, $J = 8·9$ Hz), 7·49 (2H, d, $J = 7·3$ Hz).

2-Methyl-1-(4-methylphenyl)-1-phenylpropanol (**8h**): colourless oil. MS: m/z 240 (M^+). IR (NaCl): 3450 cm^{-1} (OH). ^1H NMR ($CDCl_3$): $\delta = 0·87$ (3H, d, $J = 6·7$ Hz), 0·90 (3H, d, $J = 6·7$ Hz), 2·00 (1H, s, OH), 2·29 (3H, s), 2·86 (1H, hept, $J = 6·7$ Hz), 7·09 (2H, d, $J = 7·8$ Hz), 7·15 (1H, t, $J = 7·6$ Hz), 7·27 (2H, t, $J = 7·6$ Hz), 7·37 (2H, d, $J = 8·2$ Hz), 7·48 (2H, d, $J = 8·2$ Hz).

1-(4-Methoxyphenyl)-2-methyl-1-phenylpropanol (**8i**): colourless oil. MS: m/z 256 (M^+). IR (NaCl): 3440 cm^{-1} (OH). ^1H NMR ($CDCl_3$): $\delta = 0·87$ (3H, d, $J = 6·7$ Hz), 0·90 (3H, d, $J = 6·7$ Hz), 1·97 (1H, s, OH), 2·84 (1H, hept, $J = 6·7$ Hz), 3·76 (3H, s), 6·82 (2H, d, $J = 9·2$ Hz), 7·16 (1H, t, $J = 7·3$ Hz), 7·28 (2H, t, $J = 7·3$ Hz), 7·40 (2H, d, $J = 9·2$ Hz), 7·46 (2H, d, $J = 7·3$ Hz).

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