

A Comparative Product Investigation between Grignard Reactions of Benzophenone and Coupling Reactions of Electrogenerated Benzophenone Radical Anions and Alkyl Radicals in THF

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Dedicated to Professor Henning Lund on the occasion of his 70th birthday.

Lund, T., Ohlrich, D. and Borling, P., 1999. A Comparative Product Investigation between Grignard Reactions of Benzophenone and Coupling Reactions of Electrogenerated Benzophenone Radical Anions and Alkyl Radicals in THF. Acta Chem. Scand. 53: 932–937. © Acta Chemica Scandinavica 1999.

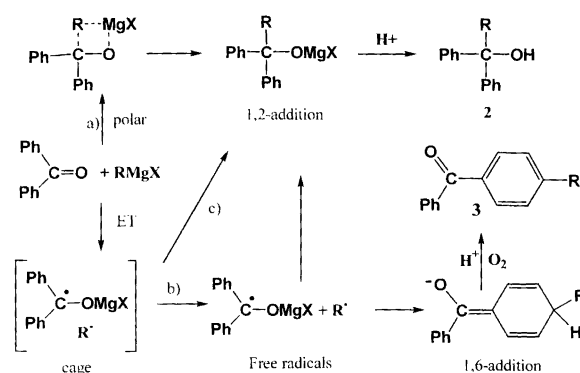
The 1,6- to 1,2-addition product ratios of the Grignard reactions of benzophenone with *t*-, *s*- and *n*-C₄H₉MgCl have been compared with the corresponding ratios obtained by the electrolysis of benzophenone in presence of *t*-, *s*- and *n*-C₄H₉S⁺(CH₃)₂, ClO₄⁻ in THF. The Grignard reaction ratios 0.81, 0.50 and 0.19, respectively, were obtained whereas the corresponding electrolysis ratios were 2.26, 1.23 and 1.61. From this comparison of product ratios it is concluded that none of the Grignard reactions of benzophenone proceeds through a complete free coupling process of benzophenone radical anions and butyl radicals. The ET character of the Grignard reactions of benzophenone with *t*-, *s*- and *n*-C₄H₉MgCl was estimated to be 65, 61 and 26%, respectively.

Over the last 30 years the polar vs. electron transfer (ET) nature of the Grignard reaction has been discussed intensively.^{1–17} It is now well established that the ET mechanism plays an important role in the Grignard reactions of easily reducible aryl ketones, such as fluorenone and benzophenone. The evidence is based on direct observation of radical intermediates by ESR and UV spectroscopy,^{10–13} measurements of kinetic isotope effects,^{5,6,13} kinetics investigations³ and Marcus-type calculations.^{3,15,16} Product distributions have also been used as important indirect 'ET-indicators'.^{3,5,8} Formation of the so-called 'abnormal' 1,4- and 1,6-addition products together with the 'normal' 1,2-addition main product has been taken as evidence for an ET mechanism.^{2,3,7}

In the reaction of *t*-C₄H₉MgBr with benzophenone in THF, 45% of the addition products are the abnormal 1,6-addition product (see Table 2) whereas CH₃MgBr reacts with benzophenone by clean 1,2-addition.² This observation may be rationalised by assuming that CH₃MgBr reacts via a 100% concerted polar addition mechanism and *t*-C₄H₉MgBr follows predominately the two-step ET pathway (route b) shown in Scheme 1.^{1,2}

Besides this polar vs. ET mechanistic scheme suggested by Blomberg¹ and Holm,^{2,3} a number of different mech-

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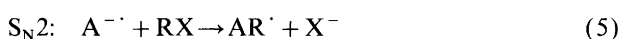
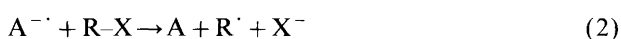
Scheme 1.

anisms have been discussed. Holm has recently proposed an inner-sphere ET mechanism in which the reaction is initiated by a concerted ET and magnesium transfer from RMgX to the ketone.^{5,6} Ashby has suggested a reaction scheme which involves an initial ET-step with formation of an ET-complex and formation of the addition products by radical coupling inside the complex.⁷ Maruyama has proposed the formation of a dimer ketyl ion radical as a key intermediate.^{11–13} As the basis of our discussion in this paper we will consider the polar

(route a) vs. ET competition mechanism (route b) shown in Scheme 1.

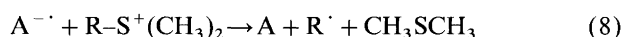
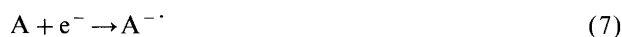
The observation of a 1,6-addition product in a Grignard reaction indicates that the ET pathway is followed to some extent. From the product distribution itself, however, it is not possible to determine how 'ET-like' or polar the reaction is. Therefore, in order to be able to determine how similar the Grignard addition product distribution would be to a product distribution of a reaction which followed a two-step ET pathway 100%, it is necessary to know the product distribution of the coupling reaction between independently generated free ketone radical anions and radicals.

Various chemical,¹⁸ electrochemical^{17,19–21} and photochemical methods^{22,23} have been used to generate free aromatic radical anions and radicals and some of these ET 'reference' coupling product mixtures have been compared with the corresponding Grignard^{17,19,23} and Wittig rearrangement products.¹⁸ Recently the ratios between 1,6- and 1,2-addition of the Grignard reactions of fluorenone were compared with the ratios obtained from the reaction of electrochemically generated fluorenone radical anions and alkyl halides, RX, in THF.¹⁷ The ratios were very similar for a series of alkyl and benzyl Grignard reagents indicating a pure ET mechanism of the Grignard reaction. The mechanism of the reaction between aromatic radical anions, A^{-•}, and alkyl halides is shown in eqns. (1)–(6).²⁴



The reaction between aromatic radical anions and alkyl halides has, however, some potential drawbacks.

The product mixtures often become complicated, especially for primary halides, by the dialkylation process [eqn. (4)]. A more fundamental problem, however, is the possibility of competition from a direct S_N2 reaction between A^{-•} and RX [eqn. (5)] which may perturb the coupling product distribution.^{20,21} Recently, Daasbjerg *et al.* introduced the reaction between electrochemically generated aromatic radical anions and sulfonium salts, R-S⁺(CH₃)₂, I⁻, as an improved method of obtaining reference coupling product distributions between free radical anions and radicals.^{20,21} The reaction mechanism is shown in eqns. (7)–(9).²⁵



Holm has proposed that the Grignard addition products obtained from the reaction between benzophenone and *t*-C₄H₉MgCl and *s*-C₄H₉MgCl are formed by a free radical coupling process.^{5,6} In order to test this proposal we have compared the ratios between the 1,6- and 1,2-addition products obtained in the reactions of benzophenone with *t*-C₄H₉⁻, *s*-C₄H₉⁻ and *n*-C₄H₉MgCl in THF with the product distribution obtained from the reaction between electrochemically generated benzophenone radical anions in THF with *t*-C₄H₉⁻, *s*-C₄H₉⁻ and *n*-C₄H₉-S⁺(CH₃)₂ salts.

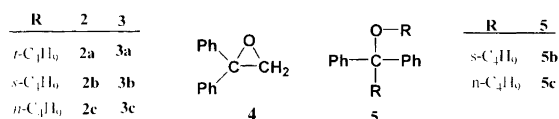
Results and discussion

The results of the product analysis of the electrolysis of benzophenone (**1**) in the presence of either alkyldimethylsulfonium salt or alkyl bromide in DMF and THF are shown in Table 1. Besides the 1,2- and 1,6-addition products **2a–c** and **3a–c** the by-products 1,1-diphenylethylene oxide (**4**) and the dialkylation products (**5b**) and (**5c**) are observed (Scheme 2). The product **4** is probably formed through a reaction between benzophenone and the ylide CH₂⁻S⁺(CH₃)R [eqn. (11)].²⁶

Table 1. Ratios between 1,6- and 1,2-addition (**3/2**) obtained in the electrolysis of benzophenone in the presence of R-S⁺(CH₃)₂, ClO₄⁻ or R-Br in DMF and THF.^a

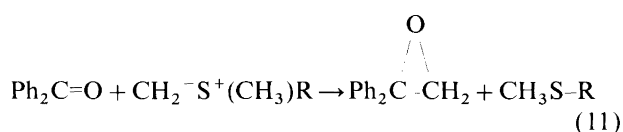
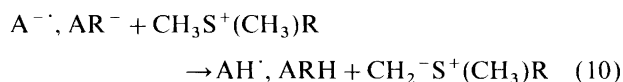
R	Solvent	R-S ⁺ (CH ₃) ₂ , ClO ₄ ⁻			R-Br		
		Yield of 2+3 (%) ^b	Yield of 4 (%) ^b	(3/2)	(3/2) ^c	Yield of 2+3 (%) ^b	Yield of 5 (%) ^b
<i>t</i> -C ₄ H ₉	DMF	62	0	1.39	0.95	84	0
<i>s</i> -C ₄ H ₉	DMF	52	19	0.73	0.35	74	11
<i>n</i> -C ₄ H ₉	DMF	29	41	0.93	0.08	44	30
<i>t</i> -C ₄ H ₉	THF	46	0	2.26	2.77	79	0
<i>t</i> -C ₄ H ₉	THF + Mg ²⁺	42	0	2.61 ^d	2.49 ^e	62	0
<i>s</i> -C ₄ H ₉	THF	17.3	25	1.23	1.24	59	7.7
<i>n</i> -C ₄ H ₉	THF	13.1	55	1.61	0.19	31	27

^aAll ratios and product yields are average values of the product analysis of 3–8 electrolyses. ^bProduct yield = 100 (mmol of product/mmol of consumed benzophenone) %. ^cThe product **5** is derived from the 1,2-addition product. The yield of **5** is therefore included in the yield of **2** in the calculation of the ratio (**3/2**). ^d[Mg²⁺] = 30 mM. ^eAverage of the ratios 2.88 and 2.11 obtained in two experiments with [Mg²⁺] = 22 mM and 20 mM, respectively.



Scheme 2.

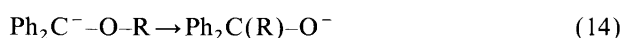
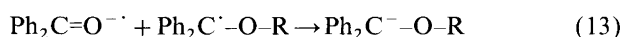
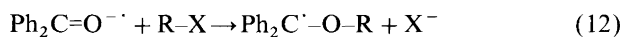
The ylide may be obtained by a proton abstraction from the sulfonium salt by a base, i.e. the benzophenone radical anion or AR⁻ [eqn. (10)].²⁷



As seen from Table 1 the yield of **4** increases from *tert*-butyl to *n*-butyldimethylsulfonium salt. This may be explained by a decrease of the rate of the ET reaction between A^{·-} and the sulfonium salt [eqn. (8)] relative to the rate of the deprotonation reaction [eqn. (10)]. The dialkylation products **5b** and **5c** are obtained by an S_N2 reaction between the initially formed 1,2-addition products with *s*- and *n*-C₄H₉Br respectively [eqn. (5)].

The ratios **3/2** shown in Table 1 are average values obtained from 3–8 electrolysis experiments with an average standard deviation of ±10%. A number of experiments were performed in order to verify that the initially formed 1,6-addition product is oxidized completely to the ketone **3** by the standard electrolysis work-up procedure described in the Experimental part. Identical ratios **3/2** were obtained by treatment of half of the final electrolysis mixture to the standard work-up procedure and the other half to either careful oxygen bubbling or treatment with the oxidizing compound 2,3-dichloro-5,6-dicyanobenzoquinone.

As seen from Table 1 the coupling product ratios **3/2** between the benzophenone radical anion and the alkyl radical depends both on the solvents and the alkyl group. The **3/2** ratios in THF are approximately 1.6 times higher than in DMF. The **3/2** ratios obtained in the electrolysis of benzophenone with *n*-C₄H₉Br in DMF and THF are very small compared with the corresponding ratios with the *n*-butyldimethylsulfonium salt. A possible explanation is that the reaction between benzophenone radical anion and *n*-butyl bromide is dominated by an S_N2 process which leads to the formation of the 1,2-addition product [eqns. (12)–(14)].



The charge density is highest on the oxygen atom in the benzophenone radical anion and it may therefore be expected that the initial S_N2 attack occurs at the oxygen

atom [eqn. (12)]. After reduction of the radical to the carbanion Ph₂C⁻-O-R [eqn. (13)] the anion may undergo a Wittig rearrangement with formation of the 1,2-addition anion Ph₂C(R)-O⁻ as the major product.¹⁸ The S_N2 character of the reaction of benzophenone radical anion and *n*-BuBr in DMF and THF may be estimated to 84% and 79%, respectively, by an expression similar to eqn. (15a).²⁰ For R equal to *sec*-butyl and *tert*-butyl the ratios between the sulfonium salt and the alkyl halide methods are reasonably similar and for these two alkyl bromides, the reaction with benzophenone radical anions may be classified as a pure ET process.

Based on thermodynamic considerations, Holm has proposed that the ET process between benzophenone and RMgX is an inner-sphere process with simultaneous transfer of an electron and magnesium from RMgX to benzophenone.⁴ The initially formed benzophenone radical anion shown in Scheme 1 is therefore depicted as being complexed to a MgX⁺ ion. An Mg²⁺ or a MgX⁺ ion may perturb the spin densities of the benzophenone radical anion and thereby cause a change in the ratio **3/2**. In order to investigate the effect of the counter ion on the **3/2** ratio, a series of electrolysis were performed in THF solvents with a concentration of Mg²⁺ from 20–30 mM. As seen from Table 1, however, no effect of Mg²⁺ was observed on the **3/2** ratio.

Garst obtained a **3/2** ratio equal to 1.41 from the reaction between chemically generated lithium benzophenone radical anions (lithium ketyls) with 2,2-dimethylpentyl iodide in THF.¹⁸ The ratio is somewhat lower than our **3/2** value obtained for *tert*-butyl bromide. Garst reported some minor formation of the 1,4-addition product (5–7% relative to the 1,6-addition product).¹⁸ In our work, however, we have not been able to identify any 1,4-addition products by GC-MS.

The ratios between 1,6- and 1,2-addition of the reactions between benzophenone and *t*-, *s*- and *n*-C₄H₉MgCl (**3/2**)_G are shown in Table 2. The total yield of the addition products decreases from 100% in the reaction of *t*-C₄H₉MgCl to 38% in the reaction with *n*-C₄H₉MgCl. This is due to increased competition of a

Table 2. The ratios between the 1,6- and 1,2-addition products **3** and **2**, (**3/2**) in the reactions of benzophenone with RMgX in THF.^a

Grignard reagent	(3/2)	Yield of 2+3 (%) ^b	Yield of Ph ₂ CHOH (%)	(3/2)
<i>t</i> -C ₄ H ₉ MgCl	0.81	100	0	0.88 (THF) ^c 1.1 (DEE) ^d
<i>s</i> -C ₄ H ₉ MgCl	0.50	55	40	
<i>n</i> -C ₄ H ₉ MgCl	0.19	20	78	

^aConcentrations of benzophenone and RMgCl were 0.55 mM and 1.00 mM, respectively, in all Grignard reactions. ^bThe yield of **2+3** was calculated relative to the theoretical maximum yield. ^cFrom Ref. 7. ^dFrom Ref. 3. Ratio obtained in diethyl ether.

-hydride transfer reaction from the Grignard reagent to benzophenone with formation of benzhydrol.³

A comparison of the 1,6- to 1,2-addition ratios between the Grignard reactions and the electrochemically generated ratios $(3/2)_{ET}$ is shown in Table 3. It is seen that the ratios of the Grignard reactions with *t*- and *s*-C₄H₉MgCl are approximately half of the values expected for a free benzophenone radical anion radical coupling process and the ratio $(3/2)_G$ of *n*-C₄H₉MgCl is eight times lower than $(3/2)_{ET}$. It may therefore be concluded that none of the Grignard reactions of benzophenone proceeds through a complete free radical coupling mechanism.

If we assume the simple concerted polar addition vs. a two-step ET competition mechanism of the Grignard reaction as depicted in Scheme 1 (routes a and b) it is possible to obtain the relative percentage proportions of the two mechanisms from the ratios $(3/2)_G$ and $(3/2)_{ET}$ [eqns. (15a) and (15b)].

% polar mechanism = p

$$= 100 [1 - (3/2)_G / (3/2)_{ET}] / [1 + (3/2)_G] \quad (15a)$$

% ET two-step mechanism = $100 - p$ (15b)

The reactions of *t*-C₄H₉ and *s*-C₄H₉MgCl proceed via a dominant ET mechanism, >60%, whereas the importance of the ET process is decreased to 26% and 0% in the reactions of *n*-C₄H₉MgCl and CH₃MgCl, respectively. It can be seen from Table 3 that the % ET character of the Grignard reactions decreases with increasing value of the redox potential of the R[•]/R⁻ couple $E_{R^{\bullet}/R^-}^{\circ}$. While experimentally obtained reversible redox potentials of RMgX compounds are unknown, it might be expected that the relative potential differences between $E_{RMgX^{\bullet+}/RMgX}^{\circ}$ will parallel the differences between the $E_{R^{\bullet}/R^-}^{\circ}$ values. From the $E_{R^{\bullet}/R^-}^{\circ}$ values it may therefore be predicted that the three butylmagnesium chlorides are much better ET donors than CH₃MgBr in agreement with the product analysis shown in Table 2.

The reduction potential of fluorenone ($E^{\circ} = -1.25$ V vs. SCE) is 0.5 V more positive than the reduction potential of benzophenone and fluorenone is therefore a much better electron acceptor than benzophenone. The % ET character of the Grignard reactions between fluorenone and the three butylmagnesium chlorides are therefore expected to be higher than the corresponding

numbers obtained for benzophenone. The above extrapolation of the benzophenone results to fluorenone is in agreement with recent results which suggested that the reaction of fluorenone with the three butyl Grignard reagents proceeds by a 100% free radical coupling mechanism.¹⁷ The $E_{R^{\bullet}/R^-}^{\circ}$ of the *n*-butyl radical is 0.43 V more negative than the corresponding value of the methyl radical.^{28,29} The driving force of the ET process between CH₃MgCl and fluorenone may therefore be estimated to be approximately the same as the driving force of the corresponding reaction between *n*-C₄H₉MgCl and benzophenone. The latter reaction proceeds with some ET character (26%) and by rough extrapolation it may be proposed that the former reaction of fluorenone with CH₃MgCl also reacts with some involvement of an ET process.

In the discussion above we have interpreted the smaller $(3/2)_G$ values relative to $(3/2)_{ET}$ as a consequence of the competition between a two-step ET free radical coupling reaction and a concerted polar addition process as shown in Scheme 1 (routes a and b). The differences between the ratios may, however, also be explained by an in-cage coupling process indicated as route c in Scheme 1. In this process the initially generated benzophenone radical anions and alkyl radicals have some spin pairing in the cage which will lead to the 1,2-addition product. The product analysis is not able to distinguish between the two mechanistic alternatives. However, if it is assumed that the Grignard process of benzophenone may be described as a competition between a one-step ET in-cage coupling process and an out-of-cage coupling process of free radicals (routes b and c) the % in-cage and % out-of-cage coupling may be estimated according to eqn. (15) similarly to the % polar and % ET calculations.

Conclusions

The 1,6- to 1,2-addition product ratios of the Grignard reactions of benzophenone with *tert*-, *sec*-, and *n*-butylmagnesium chloride are smaller than the ratios obtained by a coupling process between electrochemically generated benzophenone radicals and butyl radicals. It may therefore be concluded that none of the Grignard reactions of benzophenone proceeds through a completely free radical coupling mechanism. For the first time it has

Table 3. Comparison of the ratios between the 1,6- and 1,2-addition products **3** and **2** of the electrolysis of benzophenone ($E^{\circ} = -1.71$ V vs. SCE) and RS⁺(CH₃)₂ClO₄⁻ in THF, $(3/2)_{ET}$, with the corresponding ratios of the reactions of benzophenone with RMgCl, $(3/2)_G$.

R	$E_{R^{\bullet}/R^-}^{\circ}/V$ vs. SCE	Electrolysis THF R-S ⁺ (CH ₃) ₂ $(3/2)_{ET}$	Grignard THF RMgX $(3/2)_G$	Polar mechanism (%) ^c	ET mechanism (%) ^e
<i>t</i> -C ₄ H ₉	-1.77 ^a	2.26	0.81	35	65
<i>s</i> -C ₄ H ₉	-1.72 ^a	1.23	0.50	39	61
<i>n</i> -C ₄ H ₉	-1.62 ^a	1.61	0.19	74	26
CH ₃	-1.19 ^b	0.77 ^c	0 ^d	100	0

^aFrom Ref. 28. ^bFrom Ref. 29. ^cFrom Ref. 18. ^dFrom Ref. 2. ^eCalculated from eqn. (15a,b).

been possible to quantify the competition between the concerted polar addition and the ET mechanism of the Grignard reaction of benzophenone. The ET character of the reactions of benzophenone with *tert*-, *sec*-, and *n*-butylmagnesium chloride were estimated to be 65, 61 and 26%, respectively.

Experimental

Materials. Benzophenone, *t*-, *s*- and *n*-C₄H₉Br, sure-seal bottles of *t*-, *s*- and *n*-C₄H₉MgCl (1.0 M in THF), iodomethane, 2-iodo-2-methylpropane and dimethyl sulfide were obtained from Aldrich. Both *sec*- and *n*-butyl methyl sulfide were obtained from Lancaster. *N,N*-Dimethylformamide (DMF) was obtained from Fluka. HPLC grade tetrahydrofuran (THF) was distilled over benzophenone radical anion and stored under argon in a Schlenk flask. The supporting electrolyte, tetrabutylammonium tetrafluoroborate (TBABF₄) was recrystallized from a mixture of hexane–ethyl acetate and dried at 50 °C overnight under reduced pressure.

***tert*-Butyldimethylsulfonium iodide.** The sulfonium salt was synthesised according to the method of Huges and Ingold³⁰ by mixing dimethyl sulfide (10 g, 0.16 mol) with *tert*-butyl iodide (30 g, 0.16 mol) in nitromethane. After 3 days the crystals were isolated by vacuum-filtration. ¹H NMR (DMSO): δ 1.46 (s, 9 H), 2.81 (s, 6 H). ¹³C NMR (DMSO): δ 19.80, 24.41, 53.7.

***sec*-Butyldimethylsulfonium iodide.** Iodomethane (6.99 g, 0.05 mol) and *sec*-butyl methyl sulfide (5.01 g, 0.05 M) were mixed and stirred for 12 h.³¹ The precipitate was isolated by vacuum filtration and washed with diethyl ether. ¹H NMR (DMSO): δ 0.98 (t, 3 H), 1.37 (d, 3 H, *J*=6.9 Hz), 1.69 (m, 1 H, *J*=6.0, 7.5 and 20.0 Hz), 1.83 (m, 1 H, *J*=7.3 Hz), 2.85 (s, 3 H), 2.91 (s, 3 H), 3.60 (m, 1 H, *J*=6.7 Hz). ¹³C NMR (DMSO): δ 10.50, 13.22, 20.38, 22.19, 24.04, 50.96.

***n*-Butyldimethylsulfonium iodide.** The iodide was synthesised similarly to the *sec*-butyldimethylsulfonium iodide by substituting *sec*-butyl methyl sulfide with *n*-butyl methyl sulfide. ¹H NMR (DMSO): δ 0.93 (t, 3 H, *J*=7.4 Hz); 1.40 (m, 2 H, *J*=7.4 Hz), 1.69 (m, 2 H, 6.8 Hz), 2.86 (s, 6 H), 3.26 (t, 2 H, *J*=7.5 Hz). ¹³C NMR (DMSO): δ 13.4, 21.17, 24.28, 25.10, 41.84.

***tert*-Butyldimethylsulfonium and *n*-butyldimethylsulfonium perchlorate.** *tert*-Butyl or *n*-butylsulfonium iodide were dissolved in the minimum volume of water. A saturated solution of NaClO₄ was added and the precipitate was isolated by vacuum filtration and dried in a desiccator.

***sec*-Butyldimethylsulfonium perchlorate.** In our hands it was not possible to isolate the perchlorate salt in the way as described above for the *tert*-butyl and *n*-butylsulfonium perchlorates. The following procedure was used

instead. THF (3 ml), *sec*-butylsulfonium iodide (175 mg, 0.80 mmol) and NaClO₄ (500 mg, 4.08 mmol) were mixed in a glass tube and the mixture was shaken vigorously. By this procedure the iodide was exchanged with perchlorate and the *sec*-butylsulfonium ion dissolved as the perchlorate. The solution was added directly to the electrolysis cell.

Apparatus. GC–FID and GC–MS analysis were performed with a Hewlett-Packard 5890 gas chromatograph on a 25 m 0.25 internal diameter HP-5 column combined with a FID detector or a 5971 A MSD. The injection temperature was 250 °C, helium flow 1 ml min⁻¹ and oven temperature program 100 °C for 2 min to 300 °C at 10 °C min⁻¹. The ¹H and ¹³C NMR were recorded with a Bruker 250 MHz spectrometer.

Procedure: Electrolysis of benzophenone. Benzophenone (100 mg, 0.55 mM) was reduced in an H-cell at a platinum wire at –1.3 V vs. (Ag/AgI, I⁻=0.1 M) in a deaerated 30 ml solution of either DMF–0.1 M TBABF₄ or THF–0.3 M TBABF₄. A graphite electrode was used as the anode. To the cathode compartment was added either sulfonium salt, R–S⁺(CH₃)₂, ClO₄⁻ (175 mg, 0.80 mM) or alkyl bromide, R–Br (200 μl, 1.16 mM). After the consumption of 60–75 Coulomb (1.13–1.41 F mol⁻¹) 2–3 drops of acetic acid and tetradecane (50 μl) as an internal standard were added and the orange solution became colourless. The solution was poured into 100 ml of water and extracted in a separatory funnel with 75 ml of diethyl ether. The ether layer was separated and washed with another 100 ml portion of water and then dried over MgSO₄. The filtered solution was analysed by GC–MS and GC–FID. The following molar GC–FID response factors were obtained relative to tetradecane: 0.90 (**1**), 1.00 (**3a**) and 0.95 for 1,1-diphenylethanol (**2d**). The response factors of **2a–c** and **3b–c** were assumed to be equal to the response factors of **2d** and **3a**, respectively.

Electrolysis of benzophenone in THF containing Mg²⁺. **Generation of Mg²⁺.** A magnesium rod was oxidized in an H-cell under constant current conditions (20–30 mA) in 30 ml of a deaerated solution of THF–0.3 M TBABF₄. The magnesium rod was used as the anode and a platinum wire as the cathode. To the cathodic compartment was added 1 ml of bromoethane. After the consumption of 119–177 Coulomb corresponding to the formation of 0.61–0.92 mmol of Mg²⁺, [Mg²⁺]=20–30 mM, the current was stopped and the magnesium rod removed, rinsed with acetone, dried and weighed. The weight loss of the rod was close to the calculated value based on the consumed number of coulombs. The magnesium rod was then replaced by a platinum wire and the cell was pre-reduced under potentiostatic conditions at –1.3 V. After the consumption of 20–40 Coulomb, the current decreased to zero. Benzophenone (100 mg, 0.55 mM) and *t*-C₄H₉Br (500 μl) or *t*-

$C_4H_9S^+(CH_3)_2 ClO_4^-$ were added and the electrolysis was carried out at -1.3 V vs. (Ag/AgI, $I^- = 0.1$). After the consumption of 70 Coulomb, 2–3 drops of acetic acid and tetradecane (50 μ l) were added. The cathode solution was extracted with water–diethyl ether as described above.

Grignard reactions. Dry THF (2 ml) was transferred under argon to a glass tube equipped with a small magnet and sealed with a rubber septum. The tube was constantly flushed with a slow flow of argon. Grignard reagent (1 ml, 1.0 M solution in THF equivalent to 1.0 mmol of RMgCl) was transferred under argon from the Aldrich Sure-Seal bottle to the reaction tube by standard syringe techniques. A solution of benzophenone in THF (3 ml of a 0.18 M stock solution, equivalent to 0.55 mmol) was transferred under argon to the reaction tube. After 10 min of magnetic stirring 3 ml of a saturated solution of NH_4Cl and 1 drop of acetic acid were added and the reaction mixture was bubbled with oxygen for 20 min. Tetradecane (50 μ l) was added as an internal standard and the reaction mixture was poured into water and extracted with 10–15 ml of diethyl ether. The separated ether layer was shaken with another portion of water and analysed by GC–MS and GC–FID.

Identification of products. *2,2-Dimethyl-1,1-diphenylpropan-1-ol (2a)*. MS [m/z , %]: 184 (26), 183 (100), 181 (10), 165 (11), 106 (12), 105 (100), 78 (11), 77 (92), 51 (12).

4-tert-Butylbenzophenone (3a). MS [m/z , %]: 238 (51), 224 (23), 223 (100), 161 (16), 118 (12), 115 (16), 91 (12), 77 (70), 51 (13). In agreement with a previously reported spectrum.³²

2-Methyl-1,1-diphenylbutan-1-ol (2b). MS [m/z , %]: 240 (0.1), 184 (23), 183 (100), 181 (7), 165 (7), 106 (8), 105 (98), 78 (8), 77 (66), 51 (11).

4-sec-Butylbenzophenone (3b). MS [m/z , %]: 238 (67), 210 (22), 209 (100), 165 (13), 162 (13), 105 (78), 104 (17), 77 (74), 51 (14).

1,1-Diphenylpentan-1-ol (2c). MS [m/z , %]: 222 (0.4), 184 (13), 183 (100), 165 (3), 105 (56), 91 (3) 78 (3), 77 (27). In agreement with a previously reported spectrum.³³

4-n-Butylbenzophenone (3c). MS [m/z , %]: 238 (32), 181 (15), 167 (18), 165 (10), 162 (11), 161 (100), 105 (28), 91 (10), 77 (23). In agreement with a previously reported spectrum.³⁴

1,1-Diphenyloxirane (4). The product was synthesised in high yield (75%) by electrolysis of benzophenone with trimethylsulfonium iodide in DMF and by the reaction of dimethylsulfonium methylide and benzophenone in dimethyl sulfoxide.³⁵ 1H NMR ($CDCl_3$): δ 3.28 (s, 2 H), 7.33 (m, 10 H). ^{13}C NMR ($CDCl_3$): δ 56.8, 61.8, 127.9, 128.1, 128.9, 139.5. MS [m/z , %]: 196 (5), 168 (14), 167 (100), 166 (30), 165 (60), 152 (25). The 1H and ^{13}C NMR spectra are in agreement with previously reported spectra. The MS spectrum is, however, somewhat different.³⁶

(1,1-Diphenylpentyl) butyl ether (5). MS [m/z , %]: 296 (10), 239 (7), 224 (29), 223 (100), 180 (14), 179 (14), 178 (16), 167 (25), 165 (28), 163 (28), 161 (17), 105 (27).

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Received January 18, 1999.