The Competition between Cross-coupling and the Exchange Reaction in the Photoreduction of Aromatic Ketones

Torben Lund, Birger Lundgren and Henning Lund

^aInstitute of Life Science and Chemistry, Roskilde University Center, DK-4000 Denmark and ^bDepartment of Chemistry, University of Århus, Langelandsgade, DK-8000 Denmark

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Four aromatic ketones K with different reduction potentials and a series of hydrogen atom donors AH_2 with different oxidation potentials of AH^+ were irradiated in pairs and the product composition analyzed. Based on the product analysis the rate $k_{\rm ex}$ of the exchange reaction $K+AH^+\to KH^++A$, was characterized as slow, medium fast or fast, respectively, relative to the radical-radical coupling reactions of K^+ and AH^+ . The results clearly point to the value of a knowledge of the oxidation potential of the AH^+ radicals and the reduction potential of the ketones for the prediction of the outcome of the photoreduction of a ketone by an alcohol or another hydrogen atom donor.

The photoreduction of benzophenone by alcohols is one of the most well-studied photochemical reactions.^{1–5} The reaction is illustrated in most textbooks by the photoreduction of benzophenone by an alcohol, eqns. (1) and (2).^{6,7}

$$Ph_2CO \xrightarrow{h\nu} Ph_2CO^*$$
 (1)

$$\begin{split} & Ph_2CO^* + RR'CHOH \rightarrow \frac{1}{2}Ph_2C(OH) - C(OH)CPh_2 \\ & + RR'CO \end{split} \tag{2}$$

The first step results in the transfer of a hydrogen atom from the alcohol to the triplet excited state of the ketone [eqn. (3)]; this is followed by the transfer of a hydrogen atom from the substituted hydroxymethyl radical to the ground state ketone [eqn. (4)], but in only a few cases is the mechanism discussed in the textbooks.^{8,9}

$$Ph_2CO^* + RR'CHOH \rightarrow Ph_2\dot{C}(OH) + RR'\dot{C}(OH)$$
 (3)

$$Ph_2CO + RR'\dot{C}(OH) \rightarrow Ph_2\dot{C}(OH) + RR'CO$$
 (4)

A simple question might be asked. Why is the cross-coupling product, the mixed pinacol (Ph)₂C(OH)C(OH)(RR') not observed in the reaction? Even though the radicals are formed as a triplet pair some coupling could occur after spin inversion. The problem is not discussed in any textbooks and only very few papers have dealt with this problem.^{10,11}

The general scheme for the photoreduction of ketones (K) by hydrogen atom donors (AH_2) such as alcohols and alkylbenzenes is shown in Scheme 1.

$$K \xrightarrow{hv} K^*$$
 (5)

$$K^* + AH_2 \xrightarrow{k_6} KH^* + AH^*$$
 (6)

$$2 \text{ KH} \cdot \xrightarrow{k_7} \text{ K}_2 \text{H}_2 \tag{7}$$

$$KH' + AH' \xrightarrow{k_8} KHAH$$
 (8)

$$2 AH \xrightarrow{k_9} A_2 H_2 \tag{9}$$

$$2 AH' \xrightarrow{k_{10}} A + AH_2 \tag{10}$$

$$K + AH \xrightarrow{k_{ex}} KH + A \tag{11}$$

Scheme 1

In the photoreduction of benzophenone by toluene a statistical ratio (1:2:1) of bibenzyl (A₂H₂), the cross-coupling product (Ph)₂C(OH)CH₂Ph (KHAH) and benzophenone pinacol (K_2H_2) is obtained. ¹²⁻¹⁴ How can this difference in the coupling behavior of the 1-hydroxy-1methylethyl radical (Me2COH) and the benzyl radical with hydroxydiphenylmethyl radicals (Ph2COH) be explained? Furthermore, in the photoreduction of acetone by benzhydrol the mixed (Ph)₂C(OH)C(OH)(CH₃)₂ is observed, ¹⁰ whereas this product is not obtained in the photoreduction of benzophenone with 2-propanol. This indicates that the coupling reaction between a hydroxydiphenylmethyl radical

and a 1-hydroxy-1-methylethyl radical is not an inherently slow reaction but is comparable in rate to similar coupling reactions. In both photoreductions the same 1-hydroxy-1-methylethyl and hydroxydiphenylmethyl radicals are produced by the initial hydrogen abstraction process [eqn. (6)]. However, the product distribution is different in the two photoreductions.

The rate of the exchange reaction [eqn. (11)] is, as pointed out by Schuster, ¹⁵ very important in the determination of the product composition. Apparently the exchange reaction is fast between the 1-hydroxy-1-methylethyl radical and benzophenone and slow in the reactions of the benzyl radical with benzophenone and acetone with hydroxydiphenylmethyl radical compared with the coupling reactions. Even though the importance of the exchange reaction is well recognized ^{3-5,15} no attempts have been made to try to rationalize and explain the ob-

served variation in the exchange rates in various types of photo reduction.

The exchange reaction [eqn. (11)] has been suggested to proceed by an electron transfer (ET) from the AH. radical to K coupled with a proton transfer to K^{-1} , the result being a transfer of a hydrogen atom. The exchange rate constant k_{ex} may therefore be expected to depend on both the oxidation potential of AH and the reduction potential of the ketone. In order to test this idea four ketones (1-4) 4-methylacetophenone (1), acetophenone (2), benzophenone (3) and α, α, α -trifluoroacetophenone (4) with different reduction potentials and a series of hydrogen atom donors (A-F) 2-propanol (A), 1-phenylethanol (B), benzhydrol (C), methyl 1-phenylethyl ether (D), isopropyl methyl ether (E) and toluene (F) with different oxidation potentials were irradiated in pairs and the product composition analyzed. The oxidation potentials of several hydroxyalkyl radicals and other radicals have recently been obtained by photomodulated voltammetry. 16,17

Results and discussion

When the exchange reaction is fast, as in the case of the photoreduction of benzophenone by 2-propanol, the stoichiometric ratio between the ketone (K) and the hydrogen atom donor [the alcohol AH₂] is 2. In order to avoid depletion of K during the photolyses the reactions were performed with a 2:1 molar ratio of K and AH₂. The photolysis were performed in neat mixtures of K and AH₂ and only in the photolysis of benzhydrol (C) were minor amounts of acetonitrile added to obtain a homogeneous solution. The relative product composition of the pho-

Table 1. The product composition of the photolyses (mol %) obtained by GC-FID and HPLC.

Photolysis	start K	start AH ₂	K	AH ₂	Α	K_2H_2	KHAH	A_2H_2	Conversion (%)
1A	100	50	60	_ a	_	20	0		40 b
2A	100	50	96	_	_	2	0	_	4
3A	100	50	42	_	_	29	0	_	58
4A	100	50	0	_	_	50	0	_	100
1B	64	36	63	31	2	2.0	0.9	0.14	4.9
3B	64	36	24	0	35	20.5	0	0	62
4B	66	34	38.5	15	9	12.8	0	0	39
1C	69	31	68	9.9	0	2.8	4.38	3.7	14
2C	68	32	34	17.3	10.8	10.5	6.5	2.0	40
4C	66	34	7.5	0	25	34	0	0	100
1D	66	34	63.5	30.5	0	0.68	1.18	1.14	3.8
2D	66	34	59.4	35.5	0	0.76	1.00	0.21	3.8
3D	63	37	39	12.5	0	9.5	12.2	2.6	49
4D	64	36	33.6	33.6	5.14 °	10.7	4.21	0.73	40
1E	100	76	91	_	_	3.59	0.84	_	8
2E	100	74	95.9	_	_	1.76	0.283	_	3.8
3E	100	50	79	_	_	10.4	0	_	21
4E	100	45	75.4	_	_	12.0	0	_	24
1F	66	34	69	30	0	0.26	0.30	0.076	1.2
2F	66	34	71	27	0	0.26	1.01	0.26	2.3
3F	66	34	61.8	11.2	0	2.04	10.5	0.83	22
4F	67	33	52.9	23.8	0	4.98	5.54	1.10	23

^{*}Not analysed for. *Conversion %=[2*(%K2H2)+%KHAH)/%K(start)]*100%. *A=Acetophenone.

tolysis between the ketones 1-4 and the hydrogen atom donors A-F is shown in Table 1. The products were identified by GC-MS. The identification of the pinacols from GC-MS is relatively simple. The pinacols show a characteristic 'doublet' peak in GC due to the +, - and *meso* forms. Furthermore the two major fragmentation ions in the MS are due to the cleavage of the central C-C bond of the pinacol.

The product distribution is very much influenced by the rate $k_{\rm ex}$ of the exchange reaction [eqn. (11)]. If $k_{\rm ex} \sim 0$ the statistical ratio 1:2:1 between the pinacol from the ketone K (K₂H₂), the mixed pinacol (KHAH) and the pinacol (A2H2) from the alcohol AH2 is expected when it is assumed that $k_7 = k_8 = k_9$ and $k_{10} \sim 0$. The ketone A, obtained from the alcohol AH₂, is not observed under these conditions. If k_{ex} is very fast only A and K_2H_2 are observed while the cross-coupling product KHAH and the pinacol A_2H_2 are not found. When k_{ex} is comparable to the rate constants for the couplings (the intermediate case) A, K₂H₂, KHAH and A₂H₂ are formed with $[K_2H_2] > [KHAH] > [A_2H_2]$. From the composition of the product mixture of the photoreduction the exchange reaction [eqn. (11)] may therefore be classified as slow, medium fast or fast. The classification (assuming $k_{10} \sim 0$) is summarized in Table 2 and used to classify the product mixtures in Table 1 as shown in Table 3. If the rate of the disproportionation reaction [eqn. (10)] is fast compared with reactions (7)-(9) and (11) it will change the classification shown in Table 3. However, the disproportionation reaction seems important only for the 1-hydroxy-1-methylethyl radical. The 1-hydroxy-1-methylethyl radical may dimerize to pinacol or disproportionate to acetone and 2-propanol [eqn. (10) in Scheme 1]; the ratio of coupling to disproportionation has been measured to be 1:4 at room temperature. 18 The corresponding 1hydroxy-1-phenylethyl radical [PhC(OH)CH₃] and the hydroxydiphenylmethyl radical seem not to disproportionate significantly. 11,15,19

For the photoreduction of the medium-fast type in which the exchange reaction, [eqn. (11)] competes with the dimerization reactions, eqns. (7)–(9) the final product composition depends on the concentrations of KH_2 and AH_2 , the light intensity and the photolysis time. This has been shown by Schuster¹⁵ in the photoreduction of $[^2H_{10}]$ benzophenone with benzhydrol which is of the 'medium-fast' type. In the medium-fast type photoreduction of 4-methylacetophenone (1) by 1-phenylethanol (B) the time dependence of the product composition has been

Table 2. Classification of the exchange rate based on the photolysis product composition. (Product observed = Yes, not observed = No)

k _{ex}	A	K_2H_2	KAH ₂	A_2H_2	Relative amounts normally observed
Slow Medium Fast		Yes Yes Yes	Yes Yes No	Yes Yes No	$\begin{array}{c} KAH_2 \! > \! K_2 H_2 \\ K_2 H_2 \! > \! KAH_2 \! > \! A_2 H_2 \\ A \! \sim \! K_2 H_2 \end{array}$

Table 3. The relative mole product compositions of the photolyses. $(K_2H_2 = 100)$.

Photolysis	Α	K_2H_2	KAHAH	A_2H_2	k _{ex} a
1A	_	100	0	_	Fast
2A	_	100	0	_	Fast
3A	_	100	0	_	Fast
4A	_	100	0	_	Fast
1B	100	100	46	7	Medium
3B	171	100	0	0	Fast
4B	70	100	0	0	Fast
1C	0	100	156	132	Slow
2C	103	100	62	19	Medium
4C	74	100	0	0	Fast
1D	0	100	174	168	Slow
2D	0	100	132	28	Slow
3D	0	100	128	27	Slow
4D	48	100	39	7	Medium
1E	_	100	23	_	Slow
2E	_	100	16	_	Slow
3E	_	100	0		Fast
4E	_	100	0	_	Fast
1F	0	100	115	29	Slow
2F	0	100	388	100	Slow
3F	0	100	515	41	Slow
4F	0	100	111	22	Slow

 $[^]a$ The exchange rate $k_{\rm ex}$ is classified as slow, medium or fast according to the criteria in Table 2.

followed (Table 4). In analogy to the results obtained by Schuster¹⁵ the relative concentrations of $\mathbf{2}$ (A), $\mathbf{11}$ (K_2H_2), $\mathbf{1B}$ (KHAH) and \mathbf{BB} (A_2H_2) are dependent on the photolysis time and/or the degree of photochemical conversion. After 2 h of photolysis the ratio between $\mathbf{11}$, $\mathbf{1B}$ and \mathbf{BB} was 1:0.2:0.01 and after 28 h of photolysis the ratio changed to nearly a 1:2:1. One reason for the change in the product distribution is the decrease of the concentration of the ketone K which will reduce the importance of the exchange reaction. Furthermore, some secondary photoreduction cannot be excluded in which some of the ketone (A) produced in the exchange reaction is excited and photoreduced by 1-phenylethanol with formation of A_2H_2 .

Table 4. The product composition (mol %) of the photolysis of 4-methylacetophenone (1) and 1-phenylethanol (B) as a function of the photolysis time.

Photolysis time/h	K	AH ₂	Α	K_2H_2	KAH ₂	A_2H_2	Con- version (%)
2	45.8	50.7	0.68	1.23	0.18	0.01	2.6
4	43.5	50.1	0.69	2.23	0.54	0.06	5.0
6	41.5	49.4	0.81	2.76	1.17	0.20	6.7
8	37.7	45.3	2.44	4.44	2.24	0.57	11.1
10	36.8	38.1	2.45	5.97	4.01	1.33	16.0
12	30.7	38.8	3.15	6.55	5.30	2.02	18.4
14	26.4	35.0	2.86	7.64	7.18	3.04	22.5
16	22.7	30.7	2.85	8.56	9.09	4.23	26.2
20	15.5	22.5	1.9	10.1	12.9	7.0	33.1
24	10.9	17.9	1.2	10.8	15.3	8.9	36.9
28	5.5	12.0	0.8	11.8	18.1	11.0	41.7

$$x^{1}$$
 $\xrightarrow{\text{OH}}$ $\xrightarrow{\text{OH}}$ $\xrightarrow{\text{OH}}$ $\xrightarrow{\text{CH}}$ \xrightarrow

Product	<u>x</u> 1	<u>x</u> 2_	х3	χ4	Product	γ1_	Y ²	γ3	γ4	Produ	ct Z ¹	z^2
11					1D				Ph		$\overline{\text{CH}_3}$	$\overline{\mathrm{CH}}_3$
1 B	α_{13}	$^{\text{CH}_3}$	CH_3	Н	2D	Н	CH ₃	Н	Ph	2 F	Н	CH ₃
1C	OH_3	CH_3	Ph	Н	3D	H	CF ₃	Н	Ph	3 F	Н	Ph
22	H	CH_3	OH_3	H	4D	Н	Ph	Н	Ph	4 F	Н	CF ₃
2C	Н	CH_3	Ph	Ph	DD	Н	CH_3	СН	3 Ph			3
33	Н	Ph	Ph	H	1 E	CH ₂	$_3$ $\widetilde{\mathrm{CH}_3}$	Н	CH ₃			
3 B	H	Ph	OH_3	H	2 E	Н	CH ₃	Н	CH ₃			
44	Н	CF_3	CF_3	H	3E	H	Ph	Н	CH ₃			
		Ü			4E	Н	CF_3	Н	CH ₃			

Fig. 2.

The photoreduction in which the exchange reaction is slow ('slow type') is predicted from Scheme 1 to be more simple than the medium type in the dependence of the product composition on photolysis time. The ratio between the pinacols are expected to be constant during the photolysis. This is demonstrated (see Table 5) in the photoreduction of 4-methylacetophenone (1) by benzhydrol (C).

The radicals AH· derived from the alcohol hydrogen atom donors A, B and C are oxidized in the exchange reaction [eqn. (11)] to the corresponding ketones, 4-methylacetophenone, acetophenone and benzophenone, respectively. In the photolysis of trifluoroacetophenone (4) with the methyl ether D, acetophenone and minor amounts of [(PhC(CF₃)(OCH₃)]₂ were obtained. This may be formed by an exchange reaction in which a methyl radical is formally transferred to the acetophenone [eqn. (12)]; the mechanism is possibly analogous to that of the exchange reaction [eqn. (11)] in which a hydrogen atom is formally transferred.

The structure of the product, the methylated pinacol [(PhC(CF₃)(OCH₃)]₂ (5), was identified by independent synthesis by treatment of trifluoroacetophenone pinacol with diazomethane. In the photolysis 3E and 4E of benzophenone and trifluoroacetophenone in isopropyl me-

Table 5. The product composition (mol %) of the photolysis of 4-methylacetophenone (1) and benzhydrol (C) as a function of the photolysis time.

Photolysis time/h	κ	AH ₂	Α	K ₂ H ₂	KAH ₂	A_2H_2	Con- version (%)
1.5	61.4	29.0	0	1.80	1.64	1.33	9.5
3.0	59.2	25.5	0	2.71	2.81	2.15	15.3
4.5	59.5	24.3	0	2.82	3.00	2.28	16.2
8.5	54.0	22.66	0	4.27	4.34	3.04	23.3
10.5	53.0	22.40	0	4.60	4.68	3.33	25.2
12.5	52.8	22.63	0	2.29	4.61	3.38	20.6

thyl ether no cross-coupling products KHAH or $(CH_3)_2C(OCH_3)$ - $(CH_3O)C(CH_3)_2(=A_2H_2)$ are observed, and the exchange reaction of the photolysis is therefore characterized as fast. Acetone (=A) is observed by ¹³C NMR spectroscopy in the photolysis of **3E** and **4E**; however no methylated pinacol ether similar to that described above for ether **D** was detected. It has been suggested²⁰ that the ether radical derived from **E** may fragment according to eqn. (13).

$$CH_3O-\dot{C}(CH_3)_2 \rightarrow \dot{C}H_3 + CH_3COCH_3$$
 (13)

If this fragmentation is much faster than the dimerization reactions it might explain the lack of cross-coupling products. This might mean that the exchange reaction is not involved in the formation of acetone and that the characterization of the exchange reaction in **3E** and **4E** as fast may therefore be misleading.

The photoreduction of the ketones 1-4 with toluene is of the slow exchange type. However, the ratio between K_2H_2 , KHAH and A_2H_2 is not the expected 1:2:1 ratio (Table 2). This deviation from the statistical 1:2:1 ratio may be due to the somewhat different coupling rate constants k_7 , k_8 and k_9 .

In the rate-determining step the excited triplet state of the ketone ${}^{3}K$ abstracts a hydrogen atom from the donor AH_{2} [eqn. (2)] with formation of a triplet radical pair KH and AH in a solvent cage. As the radicals are formed as a triplet pair a spin flip must take place to give a singlet pair before coupling occurs. It has been shown that the rate of the spin inversion is generally slow compared with the diffusion out of the solvent cage. The radical coupling therefore predominantly takes place in solution; the spin flipping has, however, been reported to be faster than diffusion in some cases. 10

As shown in Table 2 the product composition of the photoreduction process varies with both the ketone and the hydrogen atom donor. The main reason for this variation is the different values of the rate $k_{\rm ex}$ of the exchange reaction [eqn. (11)]; the variations in the rate of the coupling reactions are comparatively small. Therefore from an analysis of the different product compositions of the photolysis it is possible to estimate the relative values of $k_{\rm ex}$. In the photolysis series of benzhydrol (C) with the ketones 1, 2 and 4 $k_{\rm ex}$ increases from slow to medium to fast. In the reactions with acetophenone (2) the exchange rate decreases from fast to medium to slow when the hydrogen atom donor is changed from A to C to D.

Several mechanisms for the exchange reaction have been proposed. Demeter²¹ obtained $k_{\rm ex} = 3.6 \ 10^5 \ {\rm M}^{-1}$ s⁻¹ for the exchange reaction between the dimethylketyl radical and benzophenone and suggested a hydrogen abstraction mechanism according to Scheme 2.

$$\begin{split} Me_2\dot{C}OH + Ph_2CO &\rightleftarrows Me_2\dot{C}-O-H\cdots O = CPh_2\\ \downarrow \\ Me_2CO + Ph_2\dot{C}OH &\rightleftarrows Me_2C = O\cdots H-O-\dot{C}Ph_2 \end{split}$$

Scheme 2.

Naguib *et al.*¹¹ suggested that the exchange reaction may occur by simultaneous, spatially separated, electron and proton transfer in a hydrogen-bonded complex as visualized in Scheme 3.

Recently Wayner et al. 16,17 has obtained oxidation potentials for a number of benzyl and hydroxyalkyl radicals by photomodulation voltammetry. The oxidation potentials of 1-phenylethanol and benzhydrol has not been measured; a rough estimation of the potentials has been made by subtraction 0.5 V from the values of the corresponding methyl ethers. The difference between the oxidation potentials of methanol and ethanol and their corresponding methyl ethers is 0.5 V.17 These oxidation potentials together with the reduction potentials of the ketones 1-4 and the relative rates of k_{ex} obtained from the product analysis of the photolysis are given in Table 6. The data in Table 6 show that $k_{\rm ex}$ for a given hydrogen atom donor is increased when the reduction potential of the ketone becomes more positive. The same trend (an increase in $k_{\rm ex}$) is observed for a given ketone when the oxidation potential of the hydrogen atom donor becomes more negative. Table 6 explains why the exchange reaction between acetone and the hydroxydiphenylmethyl radical is slow as mentioned in the introduction. This is due to the fact that the reduction potential for acetone is very negative (~ -3.0 V).

Scheme 3

The overall result of the exchange reaction [eqn. (11)] is a transfer of a hydrogen atom from AH to K; the connection of the rate of the exchange reaction and the difference between the reduction potential of the ketone K (E_{κ}°) and the oxidation potential of the hydroxyalkyl radical (E_{AH}°) might indicate that an electron transfer (ET) step is involved. Such an ET step is, however, endergonic in all the cases investigated, but combined with a proton transfer from AH + (a protonated ketone) to the anion radical of the ketone K-. some of the reactions become exergonic. A calculation of the ΔG_{H^+} of such a protonation step is not possible without a knowledge of the p K_A -values of AH $^+$ and KH \cdot under the experimental conditions; they are not known but a difference in pK_A of 15-20 units between a protonated ketone and a proton at a hydroxy group of a hydroxyalkyl radical seems not unreasonable; this corresponds to ΔG_{H^+} of -0.9 to -1.2 eV.

The rate of a concerted electron/proton transfer would depend, besides on $\Delta G = F(E_{AH}^{\circ} - E_{K}^{\circ}) + \Delta G_{H}^{\circ}$, on the reorganization energy λ connected with the electron transfer. The λ values of this type of reaction are not known, but as the exchange reactions are of a similar type, the λ values will probably not differ much. The main variation in the rate of the ET step is therefore due to the differences in ΔG . In order to have the reaction running at a rate which can compete with other reactions, ΔG has to be negative by a certain value, which depends on λ .

The uncertainties of the pK_A - and λ -values make calculations too uncertain at present to quote any values and to decide between a concerted ET/proton transfer¹¹ vs. hydrogen-atom transfer²¹ but the results clearly point to the value of a knowledge of the oxidation potential of the hydroxyalkyl radicals and the reduction potential of the ketones for the prediction of the outcome of a photoreduction of a ketone by an alcohol or another hydrogen atom donor.

Experimental

Materials. The ketones 1–4 and the alcohols A–C, toluene (**F**) and benzophenone pinacol were obtained from Aldrich. The ether **D** was synthesized by refluxing 1-bromo-1-phenylethane (Aldrich) (3.7 g and AgNO₃ (3.74 g) in 30 ml of methanol for 3 h. **D** was purified by distillation b.p. = 77° C (53 mmHg). The ether **E** was prepared by treatment of sodium 2-propanolate with CH₃I.

The pinacols of acetophenone (22), p-methylacetophenone (11) and trifluoroacetophenone (44) were prepared by electrosynthesis in order to obtain the response factors of these pinacols. The ketone was reduced in an H-cell at -1.6 V vs. (Ag/AgI, I⁻ = 0.1 M) at a Hg pool electrode in a 250 ml deaerated 80:20 ethanol-water solution containing 0.5 M CH₃COOK. After 1 F mol⁻¹ had been passed the cathode solution was evaporated and the crude product was recrystallised from hexane.

Table 6. Correlation of the relative rate of the exchange reaction $k_{\rm ex}$ as a function of the reduction potentials of the ketones and the oxidation potentials of the AH:

$$K + AH \xrightarrow{k_{ex}} KH + A$$

V/SCE	(– 1.11) ^b A	(-1.0) ^c B	(-1.0) ^d C	(-0.45) ^b D	(-0.45) ^b E	(+0.7) ^d F
(-2.19) 1	Fast	Medium	Slow	Slow	Slow	Slow
(-2.14) 2	Fast	X	Medium	Slow	Slow	Slow
(-1.71) 3	Fast	Fast	Χ	Slow	Fast	Slow
(-1.29) 4	Fast	Fast	Fast	Medium	Fast	Slow

^a Half-cell reaction: $AH^+ + e^- = AH^+$. ^b Wayner *et al.* (ref. 17). ^c Estimation based on data in ref. 17 (see the text). ^d Wayner *et al.* (ref. 16).

The methylated pinacol **5**, $[(PhC(CF_3)(OCH_3)]_2$, was prepared by the addition of an excess of diazomethane to a solution of trifluoroacetophenone pinacol **44** (100 mg) in CH_2Cl_2 at 0°C. After the addition of diazomethane 20 ml of HBF_4 ether complex (Aldrich) were transferred to the solution. **5**: MS: (m/z, %): 190 (14), 189 (100), 175 (10), 170 (4), 127 (7), 119 (7), 105 (28), 91 (4), 77 (13), 69 (6).

Apparatus. Products were identified by GC-MS carried out on a Hewlett Packard 5890 A gas chromatograph equipped with a 5971A MSD. An HP1 12 m, 0.25 mm internal diameter non-polar GC-column was used, injection temperature 250°C, helium flow 1.0 ml min⁻¹, temperature program 70°C for 2 min to 300°C, rate 10°C min⁻¹.

Benzophenone pinacol decomposed to benzophenone on the injector block. Photolysis mixtures containing benzophenone pinacol was therefore analysed, besides by GC, by HPLC, performed on a RP-18 Nuclosil column with 20% water-80% methanol as the eluent. The detection wavelength was 230 nm.

Photolysis. All photolyses were run on samples in Pyrex tubes which had been degassed by several freeze—thaw cycles. The tube was irradiated by a focused light beam from a Oriel 500 W Hg lamp installed in a Oriel light house. The light passed through a water filter and a Scott 305 nm cut-off filter. In a typical photolysis 2 mmol of ketone were mixed with 1 mmol of the hydrogen atom donor. No solvents were used. However, in order to have a homogeneous solution in the photolysis with benzhydrol (C) 0.5 ml of acetonitrile was added. The samples were irradiated from 1–8 h.

Identification of products. MS: (m/z, %): 11: 209 (5), 137 (4), 136 (40), 135 (100), 134 (4), 121 (15), 119 (11), 91 (15), 65 (6), 43 (100). 1B: 136 (19), 135 (86), 122 (16), 121 (20), 119 (7), 105 (7), 91 (10), 77 (8), 65 (4), 43 (100). 1C: 184 (30), 183 (40), 165 (5), 136 (12), 135 (100), 119 (6), 105 (50), 91 (8), 77 (28), 43 (39). 22: 123 (5), 122 (55), 121 (86), 120 (4), 107 (10), 105 (16), 78 (8), 77 (18), 51 (8), 43 (100). 2C = 3B: 184 (33), 183 (100), 165 (7), 121 (30), 106 (8), 105 (84), 78 (7), 77 (43), 51 (7), 43 (32). 33:

Decomposes to benzophenone in the GC injector. 44: 176 (42), 175 (99), 156 (15), 127 (17), 106 (9), 105 (100), 78 (10), 77 (34), 69 (14), 51 (10). **1D**: 137 (2), 136 (29), 135 (100), 121 (3), 119 (3), 105 (5), 103 (2), 91 (6), 77 (5), 43 (29). **2D**: 136 (9), 135 (100), 105 (6), 103 (2), 91 (3), 78 (2), 77 (7), 51 (2), 43 (10), 32 (2). **3D**: 183 (12), 165 (2), 136 (12), 135 (100), 103 (2), 78 (2), 77 (18), 51 (3), 43 (13). **4D**: 136 (19), 135 (100), 105 (23), 103 (6), 91 (3), 78 (6), 77 (23), 69 (3), 51 (5), 43 (33). **DD**: 135 (15), 122 (70), 121 (100), 120 (6), 107 (12), 105 (26), 78 (13), 77 (20), 51 (8), 43 (71). **1E**: 135 (18), 119 (4), 105 (2), 91 (7), 77 (2), 74 (4), 73 (100), 65 (3), 43 (28), 41 (2). **2E**: 194 (2), 135 (2), 122 (8), 121 (100), 105 (88), 91 (5), 78 (3), 77 (9), 51 (83), 43 (42), 41 (2). **1F**: 194 (2), 122 (6), 121 (100), 105 (10), 92 (10), 91 (15), 77 (11), 65 (6), 63 (3), 51 (4), 43 (41). **2F**: 122 (7), 121 (100), 105 (6), 92 (12), 91 (17), 77 (10), 65 (7), 51 (4), 43 (56). **3F**: 256 (5), 184 (16), 183 (100), 165 (4), 106 (6), 105 (79), 91 (9), 77 (40), 65 (4), 51 (6). **4F**: 175 (42), 127 (7), 105 (56), 93 (7), 92 (100), 91 (68), 77 (18), 69 (7), 65 (13), 51 (7).

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