Surface photochemistry: ¹³C enrichment by photolysis on silica gel¹

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Received February 10, 1984

This paper is dedicated to Professor Paul de Mayo on the occasion of his 60th birthday

LINDA J. JOHNSTON and S. KING WONG. Can. J. Chem. 62, 1999 (1984).

The enrichment of the ¹³C isotope by partial photolysis of dibenzyl ketone on silica gel has been demonstrated. The ¹³C enrichment is substantial and is parallel to the increase in the probability of geminate radical recombination on a silica surface as compared with that in solution. A substantial ¹³C enrichment was also observed for the rearranged starting material, 1-phenyl-4'-methylacetophenone. The single-stage isotope separation factors are different for the two ketones although both are isomers derived from the same benzyl-phenylacetyl radical pairs.

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On a démontré qu'il se produit un enrichissement de l'isotope ¹³C lors de la photolyse partielle de la dibenzylcétone sur du gel de silice. L'enrichissement en ¹³C est important et il augmente avec l'augmentation de la probabilité de recominaison du radical geminé sur la surface de la silice par opposition à la probabilité en solution. On a aussi observé un enrichissement important en ¹³C dans le produit de départ transposé, la phényl-1 méthyl-4' acétophénone. Même si les deux cétones sont des isomères dérivés de la même paire de radicaux benzyl-phénylacétyles, les facteurs de séparation isotopique pour une étape sont différents.

[Traduit par le journal]

Virtually all methods of isotope enrichment are based upon differences in mass or related properties. However, in 1971, Lawler and Evans (1) predicted that, according to the radical pair theory for magnetic polarization (2, 3), the separation of isotopes based upon differences in their magnetic moments rather than their masses should be possible. In 1976 the observation of Buchachenko *et al.* (4*a*) of ¹³C enrichment during the photolysis of dibenzyl ketone confirmed that magnetic effects could lead to isotope separation. Since then there have been a number of investigations of the influence of magnetic isotope and magnetic field effects on radical reactions (4–8).

A geminate radical pair in solution may undergo a number of processes: intersystem crossing (isc), diffusional separation, recombination to produce products or regenerate starting materials, or transformation to a new radical pair. A basic premise of the radical pair theory is the postulate that the chemical behaviour of a radical pair may be influenced by the spin of magnetic nuclei through the electron-nuclear hyperfine coupling (hfc) isc interaction. Since the hfc interaction is one of the major mechanisms for isc in radical pairs containing magnetic nuclei, the presence of such nuclei will increase the isc rate, particularly when the hfc constants are large. For example, a triplet radical pair containing a magnetic isotope with a large hfc constant (e.g., ¹³C) will undergo more rapid isc than will the same triplet pair containing a nonmagnetic isotope (^{12}C) . If isc to a singlet radical pair followed by cage recombination competes with diffusional separation and nongeminate reaction of the radicals, then the cage products are expected to be enriched in the magnetic isotope while the escape products will be impoverished.

The ¹³C enrichment which occurs during the photolysis of dibenzyl ketone, 1, (4, 6, 7) can be explained in terms of Scheme 1. Excitation followed by rapid isc produces a short-lived triplet which undergoes α cleavage to generate a triplet phenylacetyl-benzyl radical pair (9, 10). In solution this radical pair decays by either recombination to generate starting material or diffusional separation (10). Decarbonylation of the

free phenylacetyl radicals occurs and the benzyl radicals combine to yield dibenzyl. The original acyl-benzyl radical pairs containing ¹³C nuclei will undergo more rapid isc to a singlet pair than will those containing ¹²C nuclei, while more of the radicals containing ¹²C will escape from their original partners. Therefore, the cage products, regenerated **1** (and its isomer, 1-phenyl-4'-methylacetophenone, **2**, when formed (6)) will be enriched in ¹³C. The free radical products will, on the other hand, contain more ¹²C than did the original starting material.

Small amounts of ¹³C enrichment have been observed in 1 recovered after partial photolysis in solution (4, 6, 7); the value for α , the single-stage enrichment parameter, was ~ 1.04 in benzene (6a). Pines and co-workers (7) concluded from their investigations of temperature and solvent viscosity effects that the enrichment efficiency was strongly dependent on viscosity with maximum effects at intermediate viscosities. Turro and co-workers (6) have reported substantial increases in enrichment for photolysis of 1 in aqueous micellar solutions: α_{CO} (1) \simeq 1.35, α_{CH} (1) \simeq 1.18, and α'_{CO} (2) \simeq 1.26, where α' refers to the single stage enrichment parameter for 2 and the subscripts refer to the position of the ¹³C enrichment. The larger enrichment at the carbonyl rather than the methylene carbon was consistent with the hfc constants (6d) for ^{13}C at the various positions. The efficient ¹³C enrichment in micelles has been attributed to the restricted space in which the radical pair finds itself (6); the micelle is thought to provide a boundary which prevents the radical pair from diffusing apart and allows more time for hfc-induced isc to occur. Decarbonylation, rather than diffusion (as in solution), was proposed as the competing escape mechanism for the triplet radical pair in a micelle.

Substantial enrichment ($\alpha = 1.66$) was also reported for **1** photolysed on a surface prepared by chemically bonding a hydrocarbon layer to the surface of silica gel (11). The authors suggested that the synthetic monolayer surface was analogous to a micelle in providing an artificial "reflecting boundary" which led to an enhanced magnetic isotope effect. However, it appeared more likely that the above results were a reflection of the silica gel surface properties rather than the micelle-like properties of the synthetic monolayer surface, since a number of studies have indicated that radical mobility is restricted on

¹ Publication No. 317 from the Photochemistry Unit, Department of Chemistry, The University of Western Ontario.

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silica surfaces (12-16). For example, limited translational motion has been shown to precede recombination of a singlet radical pair generated on silica gel by the photo-Fries rearrangement (12). A greater amount of movement has been reported for both benzyl (13) and cyanopropyl (14) radical pairs on silica gel. Similarly, some surface mobility has been observed for radical pairs generated by photolysis of azocumene (15*a*) and diacyl peroxides (15*b*) on silica gel. Evidence for restriction of the mobility of adsorbed radicals has been provided by the observation of previously undetected reaction pathways in the photolysis of benzoin methyl ether on silica gel (16).

Efficient ¹³C enrichment requires that diffusional separation of the radical pair be sufficiently slow that hfc-induced isc can compete, but not so slow that the rates of isc of all radical pairs are the same, regardless of whether or not they contain ¹³C or ¹²C. The slower escape of a radical from its original geminate partner on silica gel, as compared to solution, suggested that the silica gel surface should provide a suitable environment for the observation of substantial amounts of ¹³C enrichment. The present study of ¹³C enrichment on silica gel was, therefore, undertaken with the intention of searching for conditions for optimization of ¹³C enrichment and of obtaining further information concerning the mechanism of the magnetic isotope effect in restricted environments and the diffusional motion of radicals on a surface.

Data analysis

Since the amount of enrichment depends on the extent of conversion, it is useful to express the results in terms of a single-stage isotope separation factor, α , (17) which is independent of conversion and thus allows comparison of isotope separation efficiencies for different experiments. Bernstein (17) has shown that, for competitive, first-order reactions of isotopically different species, the residual unreacted starting material becomes exponentially enriched in the slower reacting isotope. This may be applied to the competitive ${}^{12}C/{}^{13}C$ reactions in the photolysis of dibenzyl ketone, as shown by Turro *et al.* (6*a*). Since molecules containing ${}^{13}C$ proceed to products at a slower rate (i.e., more geminate recombination to regenerate starting material occurs for ${}^{13}C$ radical pairs) than do those

containing ${}^{12}C$, the residual unreacted ketone will become enriched in ${}^{13}C$.

The parameter α is defined as the single-stage separation (17) and may be computed from the measured quantities, S, the overall separation factor, and f, the fractional conversion. These are defined for carbon isotopes in eqs. [1] and [2], where the subscripts 0 and f refer to concentrations in the initial and recovered material.

$$[1] \quad S = \frac{[{}^{12}C]_{0}[{}^{13}C]_{f}}{[{}^{12}C]_{f}[{}^{13}C]_{0}}$$
$$[2] \quad f = 1 - \frac{[{}^{12}C]_{f} + [{}^{13}C]_{f}}{[{}^{12}C]_{0} + [{}^{13}C]_{0}}$$

The magnitude of α is then obtained from eq. [3] which can, for most purposes, be approximated by eq. [5].

$$[3] \quad \log S = \frac{\alpha - 1}{\alpha} \left[\log \left(\frac{1 + SR_0}{1 + R_0} \right) - \log \left(1 - f \right) \right]$$

[4]
$$R_0 = \frac{\begin{bmatrix} 1^3 \mathbf{C} \end{bmatrix}_0}{\begin{bmatrix} 1^2 \mathbf{C} \end{bmatrix}_0}$$

$$[5] \quad \log S = \frac{\alpha - 1}{\alpha} \left[-\log \left(1 - f \right) \right]$$

In practice, α can be evaluated directly from [3] or [5] for each experiment or can be computed from the slope $((\alpha - 1)/\alpha)$ of a plot of log S versus $-\log (1 - f)$.

The above method for obtaining enrichment efficiencies cannot be used to express isotope separation efficiencies for products formed in the reaction. When dibenzyl ketone is photolysed in either micelles (6) or on silica gel (18), an isomeric product, 1-phenyl-4'-methylacetophenone, **2**, is produced. This isomer is formed by geminate recombination of the initial radical pair and is thus expected to be formed more often from ¹³C ketone molecules than from ¹²C molecules. Any isomer formed is not diluted by a large pool of unreacted, unenriched material, as is the case for regenerated dibenzyl ketone. As a result, the ¹³C enrichment, as measured by *S*, is much higher for **2** than for **1** at low conversions but increases more slowly with increasing conversion. The increase in *S* for **2** with conversion occurs because the ketone from which 2 is formed is being constantly enriched in ¹³C as the reaction progresses.

In principle, measurement of S for 2 at very low conversions for which the ¹³C enrichment for 1 is negligible can yield directly the single-stage enrichment parameter, α' , for 2. Kraeutler and Turro (6d) obtained α' by plotting log S against $-\log (1 - f)$ for 2 and extrapolating to zero conversion. The physical meaning of the plot is not clear and a considerable number of points at low conversion are required to obtain α' in this way. Therefore, a method based upon the overall separation factor, S, for 1 (i.e., the variation in ¹³C/¹²C ratios for 1 throughout the photolysis was developed for the calculation of α' for 2 in the present experiments.

The single-stage enrichment parameter α' for 2 may be defined as shown in eq. [6] where k_{13} and k_{12} are the rate constants

$$[6] \quad \alpha' = \frac{k_{13}}{k_{12}}$$

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for the formation of ${}^{13}C$ and ${}^{12}C$ 2, respectively. The rate of formation of 2 depends on the concentration of 1; integration

[7]
$$\frac{d[{}^{13}C_2]}{dt} = k_{13} [{}^{13}C_1]$$

of both sides of eq. [7], followed by a change of variable (from time to conversion, f) and substitution for [¹³C₁], as outlined in the Appendix, yields the following expression:

[8]
$$[{}^{13}C_2]_{\text{total}} = k_{13}C_0 \int_0^f \left(\frac{SR_0}{1+SR_0}\right) (1-f) df$$

A similar expression is obtained for $[^{12}C_2]_{total}$:

$$[9] \quad [{}^{12}C_2]_{\text{total}} = k_{12}C_0 \int_0^f \left(\frac{1}{1+SR_0}\right) (1-f) \, \mathrm{d}f$$

After evaluation of the integrals in eqs. [8] and [9], the relative amounts of ${}^{13}C/{}^{12}C$ for **2** may be used to evaluate k_{13}/k_{12} which, from [6], is equivalent to α' . The integration is done numerically using the known values of α and f to obtain S.

Results and discussion

Carbon 13 enriched ketone was used as the starting material for all measurements of ¹³C enrichment resulting from photolysis of dibenzyl ketone, **1**. Analysis of the ¹³C/¹²C ratios was more accurate if enriched material was used; several preliminary experiments had indicated that there was considerable error in the mass spectral analysis if unenriched ketone was used. Dibenzyl ketone was prepared (19) from ¹³C-labelled phenylacetic acid (90% ¹³C in the carbonyl) and was mixed with an appropriate amount of natural abundance **1** to give ketone which contained 25% ¹³C in the carbonyl position. All reported α values, therefore, refer to enrichment at the carbonyl and have been corrected for the natural abundance ¹³C content at other positions.

¹³C enrichment on silica gel

Substantial ¹³C enrichment was observed in both 1 and its isomer, 2, recovered after partial photolysis of 1 on silica gel. The mass spectral results obtained for an experiment at 84.3% conversion are shown in Fig. 1: the intensity at m/e 211 relative to that at 210 was greater for recovered 1 than for the starting material. The ¹³C contents of recovered 1 and 2 were 30.4% and 35.6%, respectively, from the mass spectral intensities. These results were confirmed by nmr analysis of the two ketones. The methylene protons of both show signals that



FIG. 1. Mass spectral intensities for 1 (25% ¹³C=O) before photolysis (A) and after photolysis to 84.3% conversion (B).

are a combination of a singlet due to a ¹²C carbonyl and a doublet centred at the same chemical shift, the latter arising from the ¹³C carbonyl. Integration of the singlet and the two satellites allowed determination of the ¹³C content at the carbonyl; values determined by nmr integration agreed well with those determined mass spectrally.

The ¹³C contents in **1** and **2** recovered after photolysis on silica gel at 20°C are listed in Table 1. As expected, the ¹³C content of ketone **1** increased steadily with conversion. The calculated values for α , the single-stage enrichment factor, ranged from 1.12 to 1.18; the average was 1.14. The lower α values obtained at higher conversions may result from the overirradiation of enriched ketone caused by inhomogeneous photolysis on the silica gel surface. This explanation is substantiated by the fact that lower α values ($\alpha < 1.04$) were obtained for experiments carried out to >98% conversion. The α values of ~1.18 for the lower conversion appear, therefore, to provide a more reliable measure of the ¹³C enrichment efficiency on the silica gel surface. An α value of 1.13 was calculated from the slope of a plot of log S versus $-\log(1 - f)$ (Fig. 2) for the data in Table 1 (20°C experiments).

Comparison of the results obtained under various experimental conditions (Table 1) showed that the ¹³C enrichment was not affected by the water content of the silica gel or by the method of sample mixing. Lowering the photolysis temperature had little effect on α ; at -55° C the observed enrichments (Table 1) were similar to those obtained at 20°C, although the α values were slightly higher for dry silica gel than for undried silica.

For isomer 2 the ¹³C content was, as expected, already quite high at low conversion and did not increase very rapidly thereafter. For example, at 20°C the 33.0% ¹³C content at 29.9% conversion increased to only 35.6 at 84.3% conversion (Table 1). Values of α' were all ~1.5 for 2 recovered after photolysis of 1 at 20°C on silica gel. As for ketone 1, the enrichment for 2 at room temperature was not affected by either the dryness of the silical gel or the method of sample mixing. However, in contrast to results obtained for 1, changing the photolysis temperature from 20°C to -55° C substantially decreased the en-

TABLE 1. ¹³ C enrichment	for 1	l and 2	recovered a	fter ph	otolysis of I	l on silica ge	1
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Reaction conditions"	Temperature (°C)	Conversion %	% ¹³ C at C= O^b			
			1	2	α	α
A	20	84.3	30.4	35.6	1.12	1.58
А	20	70.9	27.7	34.6	1.11	1.52
А	20	69.8	28.1	34.1	1.14	1.48
А	20	43.8	26.8	33.8	1.18	1.48
А	20	29.9	26.1	33.0	1.17	1.44
А	-55	66.8	26.9	28.2	1.09	1.14
А	-55	28.7	25.5	25.8	1.07	1.03
B, C	20	91.6	30.7	35.4	1.12	1.56
B, C	20	73.6	28.3	34.3	1.14	1.49
B	20	27.4	25.4	c	1.08	
В	-55	74.0	28.9	30.1	1.22	1.20
В	-55	50.2	27.3	28.1	1.18	1.12

"A: silica gel used without drying; B: silica gel dried at 200°C; C: sample rotated in an ultrasonic bath to aid in sample mixing.

^b The reported % ¹³C values are approximately ± 0.9 (3%); these yield α values of approximately ± 0.03 .

Yields of 2 insufficient for isolation and analysis.



FIG. 2. Log S versus $-\log(1-f)$ for 1 recovered after photolysis at 20°C on dried (\bigcirc) and undried (\bigcirc) silica gel.

richment efficiency for 2 ($\alpha' \sim 1.1$ at -55° C).

The above results indicate that, as predicted, photolysis of **1** on dry silica gel does yield substantial ¹³C enrichments in recovered ketones **1** and **2**. The observed α values for **1** are larger than those in solution ($\alpha \sim 1.04$ (6*a*)) but enrichment occurs less efficiently on the surface than it does in a micellar environment ($\alpha \sim 1.3$ (6) and the present work reported below). The α' values for **2** on the surface are, however, larger than those in micelles.

¹³C enrichment on other surfaces

Ketone 1 was photolysed on several other types of surfaces to determine their effect upon ¹³C enrichment. The results are summarized in Table 2. First, 1 recovered after photolysis on a smaller particle size (6 μ m rather than 0.2–0.5 mm) silica gel showed an enrichment ($\alpha \sim 1.13$) similar to that already observed. Second, photolysis of 1 on neutral alumina also gave a similar α value (~ 1.1); however, the situation on alumina may

TABLE 2. ¹³C enrichment for 1 and 2 recovered after photolysis of 1 on various surfaces at 20°C

	Conversion	% ¹³ C at C==0			
Surface	(%)	1	2	α	α'
6 μm silica gel	67.1	27.6	а	1.13	
Silica gel + decanol"	43.6	27.0	33.0	1.20	1.42
Silica gel + decanol ^c	74.9	27.7	34.2	1.11	1.50
Silica gel + decanol ^{c, d}	54.1	27.1	27.9	1.15	1.12
Alumina	27.3	25.4	и	1.08	
Alumina	22.6	25.6	a	1.12	

"Compound 2 not detected by gc (<0.2%).

 $^{h}4.77 \times 10^{-4}$ mol 1/g silica gel; 7.8 × 10⁻⁴ mol decanol/g.

 1.03×10^{-4} mol 1/g silica gel; 7.5×10^{-4} mol decanol/g.

"−55°C.

be more complex than that on silica gel since the product recovery as dibenzyl was only $\sim 20\%$ for the former. Isomer 2 was not detected among the reaction products when 1 was photolysed on either 6-µm silica or on alumina. This suggests that a particular surface site may be instrumental in permitting the formation of 2 during the photolysis on silica gel.

Third, 1 was photolysed on silica gel on which decanol had been coadsorbed at \sim 55% monolayer coverage, based upon calculated molecular areas. The values obtained for both α and α' at 20°C and at -55°C were not appreciably different from those for silica gel in the absence of decanol. Comparison of the present results for silica gel and silica gel plus decanol with those of Epling and Florio (11) suggest that it is the silica gel surface, not the bound hydrocarbon layer, which is responsible for the enhanced ¹³C enrichment efficiency. It seems unlikely that the hydrocarbon layer makes the surface "micelle-like" as has been suggested (11). Radicals on a hydrocarbon layer would be expected to be more mobile than those attached directly to silica gel and would be less likely to produce ¹³C enriched material via the geminate recombination pathway. Although a higher α value was obtained in the previous study (11), it should be noted that this reflects the total enrichment at all carbons and is, consequently, expected to be higher than the present α values for carbonyl enrichment.

\overline{N}	Conversion	α	α'
0.34"	98.0	1.19	1.73
0.43"	34.7	1.28	1.20
0.43 ^a	39.2	1.19	1.23
1.17^{b}	94.4	1.24	1.67
1.24"	54.7	1.37	1.20

"[Surfactant] = 0.16 M.

"[Surfactant] = 0.08 M.

¹³C enrichment in micelles

For comparison with earlier work in micelles (6) and for correlation with our work on cage recombination (13), ^{13}C enriched dibenzyl ketone was photolysed in aqueous potassium dodecanoate. Our previous experimental results on the photolysis of an unsymmetrically substituted dibenzyl ketone in micelles showed that there is a strong dependence of geminate formation of dibenzyl on the average number of molecules per micelle \overline{N} (13). The probability of geminate combination decreases from 92% to 51% when \overline{N} is changed from 0.35 to 0.85. The present work was, therefore, designed to investigate the effect of variations in \overline{N} on the ¹³C enrichment efficiency. It might be expected that the ¹³C enrichment efficiency would decrease with an increase of \overline{N} since the rapid escape of radicals from their geminate partners is thought to be responsible for the low α values in solution. The results shown in Table 3 indicate that α and α' values for the recovered ketones are not particularly sensitive to \overline{N} . The high α' values at high conversion could be due to photolysis of 2 and its further enrichment by recombination to regenerate itself; the lower yields of 2 obtained at >80% conversion support this hypothesis. The observed enrichments are comparable to those reported by Turro and co-workers in other micelle systems (6).

The insensitivity of ¹³C enrichment to changes in \overline{N} was unexpected. In fact there may be a slight trend opposite to the expected one of more free radical combination products when \overline{N} is increased. It seems obvious now that the behaviour of the benzyl-benzyl radical pair is not directly correlated to that of the benzyl-phenylacetyl radical pair, which is the reaction intermediate responsible for the magnetic isotope enrichments of 1 and 2. For instance, one expects that the average initial interradical separation for the two radical pairs will be different; this separation is crucial for both radical escape by diffusion and for ¹³C enrichment by recombination.

Further discussions

Consideration of α values for 1 on a variety of surfaces and in micelles indicates that both environments are effective in enhancing the ¹³C enrichment. Since restrictions on the diffusion of the initial radical pair appear to be important in the enrichment process, the results suggest that the silica gel surface provides a slightly less restricted environment than does a micelle. The dibenzyl ratios obtained upon photolysis of unsymmetrical dibenzyl ketones also indicate more restriction of radical motion by micelles than by the silica surface. However, the differences are much greater in the latter case. This is reasonable if the lifetimes of the radical pairs are considered. The acyl-benzyl radical pair involved in the ¹³C enrichment process has a shorter lifetime than the benzyl radical pair and the surface will be much more effective in localizing this shorter-lived radical pair. On the other hand, since radical exit from a micelle is relatively slow $(10^5-10^6 \text{ s}^{-1} (20))$, the micelles can effectively localize both radical pairs until recombination occurs.

Substantially higher enrichments were observed for isomer 2 than for 1 at 20°C on silica gel. Different efficiencies had also been observed for the two ketones in micelles (6). Both 1 and 2 are derived from the same initial radical pair and one would expect α and α' values to be the same. The differences in enrichment must be a reflection of differences in the rates of processes leading to each ketone. While the initial state of the primary radical pair must be identical, the final states leading to products 1 and 2 must be different. The developing singlet character and the geometric positions of the radicals within the radical pair before coupling are the deciding factors. The present theories of CIDNP have only considered radicals as hard spheres without structures. Apparently the structure of the individual components of the radical pair and their relative positions can affect the ¹³C enrichment efficiency, and rotation should also be considered.

The different temperature dependence of α and α' may be understood within this context. While α values for 1 are much less sensitive to temperature variations, α' values for 2 decreased considerably at lower temperature on silica gel. Turro has also obtained different temperature dependences for α and α' in micelles (6). The precise nature of the structure of the radical pair and its dynamics of motion as related to the electron-nuclear hfc induced intersystem crossing is at present unclear. More detailed studies of the ¹³C enrichment of 1 and 2 are required for better understanding.

Experimental

Apparatus

Proton nmr spectra were recorded on either a Varian T-60 (60 MHz) or an XL-100 (100 MHz) spectrometer. Gas chromatography – mass spectrometry was done on a Varian 1400 gas chromatograph interfaced with a Varian MAT 311 A mass spectrometer and data system. Gas chromatography was done on a Varian 2400 instrument equipped with a flame ionization detector, a temperature programmer, and a 5 ft \times 1/4 in. glass column packed with 10% SE 30 on Chromosorb W. Operating conditions were as follows: carrier gas. helium, 40 mL/min; injector, 225°C; column, 170°C; detector, 250°C. Irradiations were carried out with either a 1000-W XBO high pressure xenon lamp in a Photochemical Research Associates lamp housing or a 450-W Hanovia medium pressure mercury lamp.

Materials

Silical gel (35-70 mesh, Merck, cat. no. 7733) was used as received or dried as outlined below. Silica gel, 6-µm particle size, was used as received. Alumina, neutral (Fisher, Brockmann Activity 1) was dried for 12 h at 200°C, 0.1 Torr (1 Torr = 133.3 Pa), and was stored in a desiccator until used. Methylene chloride (Fisher spectrograde) was refluxed over P2O5 and distilled directly before use for adsorption of compounds onto dry silica gel, but was used as received for adsorption of compounds onto undried silica or other surfaces. Water for micelle solutions was triply distilled (second distillation from potassium permanganate). All other solvents were reagent grade and were used as received. Decanol was distilled before use. Potassium dodecanoate was prepared form dodecanoic acid and potassium hydroxide and purified by recrystallization from methanol. Dibenzyl ketone (ICN Pharmaceutical) was recrystallized from ether (at -78° C) or petroleum ether (40-60°C), mp 30.5-32°C. ¹³C labelled dibenzyl ketone was prepared by the method of Coan and Becker (19) from phenylacetic acid (90%¹³C=O, Merck, Sharp and Dohme), and was purified by bulb-to-bulb distillation followed by crystallization from $40-60^{\circ}$ C petroleum ether, mp $32.5-33.5^{\circ}$ C.

Photolysis of 1 on silica gel

Dibenzyl ketone was adsorbed on silica gel $(4.77 \times 10^{-4} \text{ mol/g})$ from a methylene chloride solution. When the ketone was to be adsorbed on silica gel dried at 200°C at ≤ 1 Torr for ≥ 5 h, the previously described method and apparatus were used (18). For samples on silica gel which had not been predried, a methylene chloride solution of 1 was added to a preweighed silica sample in a round bottom flask. After solvent removal by evacuation, the sample was transferred to an irradiation cell and evacuated for ~ 15 min at 1 Torr. All samples were then degassed to 10⁻⁵ Torr by 3 or more freezethaw cycles at liquid nitrogen temperatures. Dry, deoxygenated nitrogen was then added to the sample tube before it was sealed. The samples were rotated and irradiated with a 1000-W xenon lamp. The light was focused on one end of a 16-mm quartz light pipe and the sample was rotated under the other end. During irradiation the samples were cooled with either cold running water (20°C) or by immersion in a methanol – Dry Ice bath $(-78^{\circ}C)$.

The adsorbed materials were removed from the silica gel by extraction with 100 mL of diethyl ether. The ether solution was concentrated and analyzed by gc after the addition of a known amount of eicosane as an internal standard. Calibration curves were constructed for 1, 2, and 3; the average of three or more injections was used for each determination. Dibenzyl always accounted for $\ge 90\%$ of the photolysed ketone. Yields of 2 were typically from 2-4%.

For samples containing coadsorbed decanol, the decanol was adsorbed first, followed by 1. The samples were prepared as described above using undried silica gel.

Photolysis of 1 in micelles

An appropriate amount of 1 was added to a solution of potassium dodecanoate in triply distilled water and the mixture was sonicated for 1-2 h to dissolve the ketone completely. The solution was then transferred to an irradiation vessel and degassed by purging with nitrogen for 30 min. All samples were stirred and irradiated through Pyrex with a 450-W Hanovia medium pressure mercury lamp. After photolysis, the sample was diluted to <0.02 *M* (i.e., below the cmc) and was extracted three times with ether. The formation of emulsions during the extraction procedure was minimized by the addition of sodium chloride to the aqueous phase. The combined ether layers were washed once with 10% Na₂CO₃ and once with water and were dried over anhydrous MgSO₄. The extract was concentrated and analyzed by gc as previously described. Dibenzyl accounted for ~90% of the photolysed ketone. Yields of 2 were from 6–10% for most experiments but decreased to 1-2% at >90% conversion.

¹³C analyses

1 and 2 were separated from the photolysis mixtures by preparative chromatography on silica gel plates using 10% ethyl acetate in petroleum ether as eluent. The ¹³C content in the recovered ketones was then determined by gc/ms. A Varian 1400 gas chromatograph interfaced with a Varian MAT311A mass spectrometer and a Varian data system was used. A standard sample of 1 (25% ¹³C==O) was always analyzed before samples of recovered 1 were run. Comparison of the ¹³C calculated for the standard with that determined mass spectrally allowed correction of the data for instrumental variations. For 1 the relative intensities of the molecular ion peaks at m/e 210 and 211 were used. Since 2 gave a very weak molecular ion, the ¹³C content was determined from the mass fragment peaks at m/e 119 and 120. The mass spectral intensities for both ketones were corrected for the natural abundance distributions of ¹³C at other than the carbonyl, ²H, and ¹⁷O. Separation factors, S, were then calculated from the corrected intensities and used to evaluate α and α' values.

Acknowledgements

We thank the Natural Sciencies and Engineering Research Council of Canada for financial support. We are very grateful for Professor Paul de Mayo's initiation and constant encouragement of the project.

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Appendix

Integration of [7] yields [10], which may be rewritten as

[10]
$$[{}^{13}C_2]_{total} = k_{13} \int_0^t [{}^{13}C_1] dt$$

[11] after the appropriate change of variable from time to conversion, f. The [¹³C₁] at a particular conversion, f, may be

$$[11] \quad [{}^{13}C_2]_{\text{total}} = k_{13} \int_0^f [{}^{13}C_1] \, \mathrm{d}f$$

expressed as shown in [12] where C_0 is the initial total [1] and the fraction ${}^{13}C_1$ is determined as shown below:

$$[12] [{}^{13}C_1]_f = (fraction {}^{13}C_1)_f (1 - f)C_0$$

$$[13] (fraction {}^{13}C_1)_f = \frac{{}^{13}C_f}{{}^{13}C_f + {}^{12}C_f}$$

$$[14] = \frac{SR_0}{1 + SR_0}$$

$$[15] \quad [{}^{13}C_1]_f = \frac{SR_0}{1+SR_0} (1-f)C_0$$

substitution of [15] in [11] yields

$$[16] \quad [{}^{13}C_2]_{\text{total}} = k_{13} \int_0^j \frac{SR_0}{1 + SR_0} (1 - f)C_0 \, \mathrm{d}f$$

A similar set of operations gives $[{}^{12}C_2]_{total}$ as expressed in eq. [9].

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