

## PROBES FOR THE MICELLAR CAGE EFFECT. THE MAGNETIC $^{13}\text{C}$ -ISOTOPE EFFECT AND A NEW CAGE PRODUCT IN THE PHOTOLYSIS OF DIBENZYL KETONE

Bernhard KRAEUTLER\* and Nicholas J. TURRO

*Chemistry Department, Columbia University, New York New York 10027, USA*

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An isotopic enrichment factor,  $\alpha$ , is employed as a novel probe to study the effect of solute and of detergent concentration on micellar parameters. The formation of a new cage product is also found to follow monotonically the concentration of micelles in aqueous detergent solutions. It is shown by these probes that the average occupancy of the micelles by the solute does not significantly alter the dynamic micellar behavior with respect to reactions that occur in the micelle cage.

### 1. Introduction

Magnetic effects on chemical reaction rates have only recently come to the attention of the chemist. The discovery of the phenomenon of chemically induced dynamic nuclear polarization (CIDNP) [1,2] provides a theoretical and phenomenological basis for analyzing such effects. Tremendous nuclear polarizations (deviations from the thermalized Boltzmann distribution) may be observed when thermally or photochemically induced radical reactions are carried out in the probe of an NMR spectrometer. These polarization effects have found an elegant and powerful explanation in the radical pair theory of CIDNP [3,4] and emphasize the importance of the interaction between nuclear magnetic moments and electron magnetic moments in radical pair reactions. These seemingly insignificant energetic contributions of the hyperfine couplings (hfc's) can perturb strongly a symmetry property of the radical pairs: The electronic spin states (singlet or triplet) of geminate radical pairs can be switched during very short time scales ( $10^{-8}$  s!) — sufficiently fast to influence their pair reactivity even during their fleeting existence in a common solvent "cage".

The generally rapid loss of spin correlation in radical

pairs in homogeneous solutions, a consequence of the diffusive separation [5–7] is detrimental to the observation of a sizeable kinetic magnetic (or spin) isotope effect in radical reactions. Inhibition of such diffusive escapes is achieved in aqueous detergent solutions by entrapment of reactive species in the reaction zone in micellar aggregates. For example, above the "critical micelle concentration" (cmc) the existence of micelles provides the experimentalist with the ability to sequester radical pairs in micellar "super cages" [8,9].

### 2. Isotopic separation in the photolysis of dibenzyl ketone

The photoinduced decarbonylation of dibenzyl ketones has recently been demonstrated to be dramatically influenced by the "reduced dimensionality" [10] of the reaction space available for the radical pairs in micelles. High selectivity for geminate radical recombinations [10] and a dramatic enrichment of  $^{13}\text{C}$  in the carbonyl in partially photolyzed dibenzyl ketone (DBK) [11] result. Here we provide direct evidence for the actual intimate correlation between the magnitude of the  $^{13}\text{C}$  enrichment and the existence of micellar aggregates.

Partial photolysis at room temperature of deaerated solutions of  $^{13}\text{C}$ -labeled DBK (0.005 M, 48%  $^{13}\text{C}$  label

\* Present address: Laboratorium für Organische Chemie, ETH, Zurich, Switzerland.

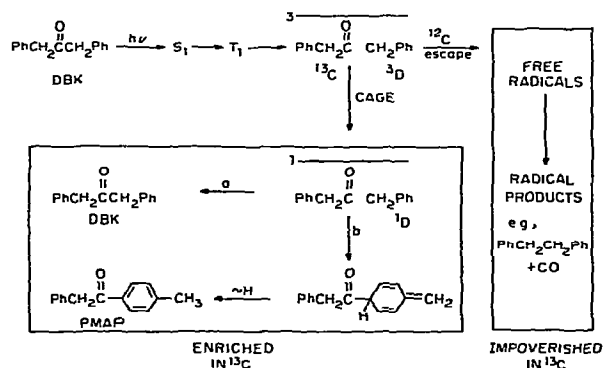
at carbonyl carbon)<sup>\*</sup> in an aqueous solution of the detergent hexadecyltrimethyl ammonium chloride (HDTCl, 0.05 M), followed by the recovery of the remaining starting material and subsequent analysis for its <sup>13</sup>C content provided proof for a strong <sup>13</sup>C enrichment in the carbonyl [11]

### 3. Use of Bernstein's formula as a probe of micelle formation and properties

In analogy to Bernstein's formula [13]<sup>\*</sup> the isotopic enrichment factor can be correlated with photochemical disappearance quantum yields<sup>\*</sup>

$$\alpha \equiv \frac{{}^{12}\Phi}{{}^{13}\Phi} = \frac{\text{efficiency of disappearance of } {}^{12}\text{C ketone}}{\text{efficiency of disappearance of } {}^{13}\text{C ketone}}, \quad (1)$$

where the disappearance quantum yields <sup>12</sup>Φ and <sup>13</sup>Φ stand for the disappearance of unlabeled (<sup>12</sup>C)-DBK and labeled (<sup>13</sup>C)-DBK, respectively. The experimentally derived value, α ≈ 1.47, implies a faster net consumption of <sup>12</sup>C-DBK, the result of more efficient return of the primary radical pair from <sup>13</sup>C-DBK to starting material (scheme 1).



Scheme 1. Mechanism for the enrichment of <sup>13</sup>C in DBK and PMAP.

<sup>\*</sup> Obtained from the correspondingly <sup>13</sup>C-labeled phenylacetic acid (Merck, Sharp and Dohme, Inc.) following the route of Coan and Becker [12].

<sup>\*</sup> Strictly speaking the correlation between the enrichment (expressed with α) and the photochemical disappearance quantum yields is based on an equality of the absorption coefficients of labeled and unlabeled DBK. No other assumptions or approximations were necessary for this derivation.

Similar to the other characteristic micellar cage phenomena [8–10,15]<sup>\*\*</sup> variation of the overall detergent concentration, [det]<sub>tot</sub>, causes variation in the magnitude of the observed enrichment factor α<sub>obs</sub> (fig. 1). A series of deaerated aqueous HDTCl solutions of <sup>13</sup>C-labeled DBK (16.9% <sup>13</sup>C at the carbonyl) with varying detergent concentrations, but with a constant molar ratio ketone:detergent (1:10), were partially photolyzed as described above. Analysis for the <sup>13</sup>C content in the recovered DBK revealed the parallelism between α<sub>obs</sub> and micelle concentration, [mic], shown in fig. 1 (circles). From the data it is clear that the large α<sub>obs</sub> values correlate with the existence of micelles.

Cage phenomena such as the magnetic isotope effect in radical pair reactions can be used as probes for the properties of micellar (and other) cavities. Based on the "second phase approximation" [14], represented in eq. (2) for the relation between [mic], [det]<sub>tot</sub> and the average aggregation number,  $\bar{n}$ , eq. (3) is empirically found<sup>\*\*</sup> (solid line in fig. 1), which provides a linear correlation between α<sub>obs</sub> and the calculated [mic] (where α<sub>aq</sub> = observed enrichment factor below cmc, α<sub>mic</sub> = calculated enrichment factor for pure micellar phase and [det]<sub>mic</sub> = global concentration of detergent in the micellar phase):

$$[\text{mic}] = (1/\bar{n}) ([\text{det}]_{\text{tot}} - \text{cmc}) = (1/\bar{n}) [\text{det}]_{\text{min}}, \quad (2)$$

$$\frac{\alpha_{\text{obs}} - \alpha_{\text{aq}}}{\alpha_{\text{mic}} - \alpha_{\text{aq}}} \approx \frac{[\text{det}]_{\text{mic}}}{[\text{det}]_{\text{tot}}} = \frac{[\text{det}]_{\text{tot}} - \text{mic}}{[\text{det}]_{\text{tot}}}. \quad (3)$$

The predominant solubilization of DBK in the micellar phase was confirmed experimentally by the observation that the OD (300 nm, 1 cm path) of saturated aqueous solution of DBK was 0.09, whereas the OD for saturated micellar solutions (0.05 M detergent) was 4.3. The following values were thus estimated from a fit of the experimental data using eq. (3): α<sub>aq</sub> ≈ 1.06, α<sub>mic</sub> ≈ 1.47 and cmc ≈ 4 × 10<sup>-3</sup> M. The estimate for the cmc of aqueous HDTCl is in good agreement with values similarly indicated from the results obtained by the photolysis of

<sup>†</sup> This approximation is suitable only at detergent concentrations above cmc; see also discussions in refs. [8,9,14].

<sup>‡</sup> Cella et al. [16] obtained a value of 1.5 × 10<sup>-3</sup> M as cmc for HDTCl.

<sup>\*\*</sup> Eq. (3) can be derived exactly for the limiting case where the average occupancy of the micelles throughout a dilution series is constant.

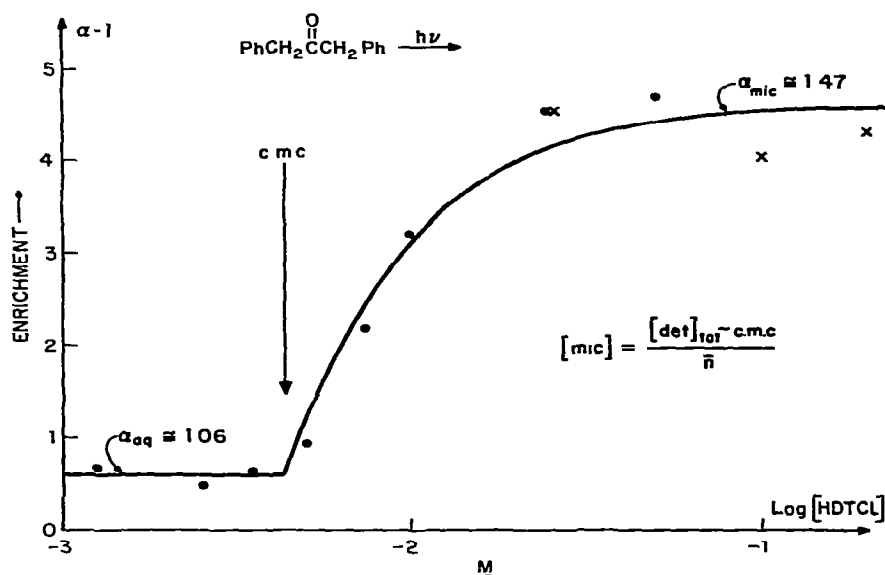


Fig. 1.  $^{13}\text{C}$ -enrichment of recovered dibenzyl ketone (DBK) from photolysis in aqueous hexadecyltrimethyl ammonium chloride (HDTCl): plot of the observed enrichment factor  $\alpha$  versus concentration of HDTCl (stirred, deaerated solutions,  $25^\circ\text{C}$ , Hanovia medium pressure Hg lamp, quartz vessels).  $\bullet$  =  $[\text{DBK}]:[\text{HDTCl}] = 1 \cdot 10$ ,  $\times$  =  $[\text{DBK}]:[\text{HDTCl}] = 2 \cdot 5 \text{ mM}$ .

1-*p*-tolyl-3-phenyl-acetone [10], the fluorescence lifetime of pyrene [15], and other reports in the literature [16]

#### 4. Observation of a new recombination product from the benzyl-phenacetyl radical pair

A plot strikingly similar to fig. 1 is obtained when the *chemical yield* of a sideproduct of the photolysis of DBK, 1-phenyl-*p*-methylacetophenone PMAP (scheme 1), is represented as a function of the concentration of the detergent, HDTCl (for the same set of experiments in fig. 1), as shown in fig. 2. Indeed the similarity of the two plots reflects a mechanistic correlation, between the  $^{13}\text{C}$  enrichment in DBK and the formation of PMAP: in the micellar solution of HDTCl two recombination channels for the photogenerated phenacetyl-benzyl radical pair are important — one of which, recombination at the site of fragmentation gives back the starting material, DBK (channel a, scheme 1), a second path, attack of the acyl radical on the para position of the benzyl radical, also occurs to an important extent (channel b). The cross conjugated hexatriene thus formed gives PMAP after tautomerization  $^{**}$ .

This new recombination product of the photogenerated radical pair gives preparative access to a second recombination pathway that was postulated by Langhalls and Fischer [17] on the basis of CIDNP evidence. An emission in the  $^1\text{H}$  CIDNP spectrum of DBK was assigned to the methyldene-group of the intermediate cage product, the hexatriene, but PMAP could not be isolated from homogeneous aprotic solutions. This was explained by rapid trapping of the cross conjugated triene by the photogenerated radicals [17].

The chemical yield of PMAP in the photolyses was highest ( $\approx 5.5\%$  at  $25^\circ\text{C}$ ) with the full output of the medium pressure Hg-lamp  $^{**}$ , uses of pyrex filters or illumination with sunlight gave lower chemical yields

$^{**}$  DBK was dissolved in the aqueous detergent solution, an aliquot was placed into a quartz tube and was deaerated by  $\text{N}_2$ -bubbling for 20 min and photolyzed under stirring with a Hanovia medium pressure 450 W Hg-lamp; reaction samples were drawn from the solution, extracted with dichloromethane and the residue was analyzed after evaporation of the solvent. vpc analysis with 1/8 in  $\times$  6 ft 10% SE-30 on Chromosorb W., column temperature  $180$ – $200^\circ\text{C}$ , analysis by  $^1\text{H}$  NMR and combined vpc-ms.

$^{**}$  PMAP obtained by photolysis of DBK in deuterated aqueous HDTCl solution incorporates one deuterium (mass spectral analysis: the molecule ion is increased by one mass unit).

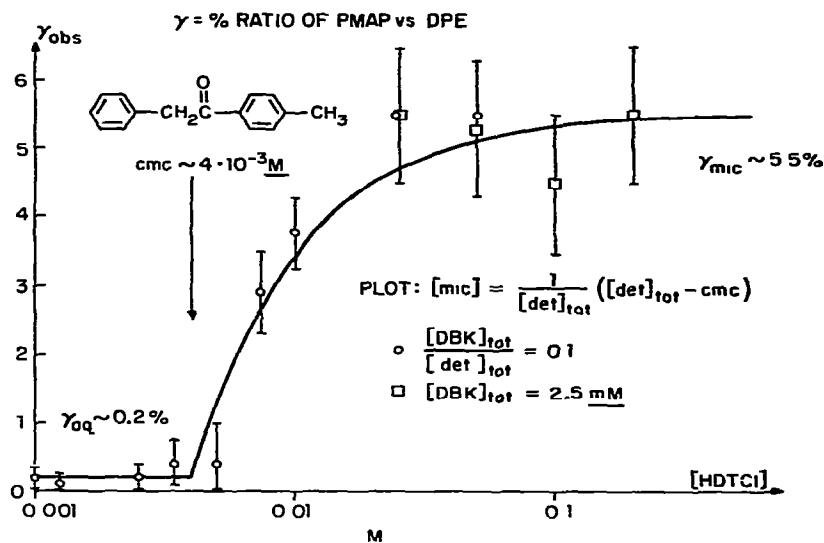


Fig. 2. Yield of 1-phenyl-*p*-methyl acetophenone (PMAP) from photolysis of DBK in aqueous HDTCl solutions: plot of the yield versus concentration of HDTCl (same experimental conditions as for fig. 1).

(presumably a consequence of secondary photolysis of PMAP under these latter conditions). PMAP could be easily detected by vpc-analysis, but no indication for the corresponding ortho isomer was found. Structural proof for PMAP arose from spectral and vpc comparison with a sample independently synthesized via a Friedel-Craft acylation of toluene with phenacetyl chloride.

Parallel to the  $^{13}\text{C}$  enrichment in DBK, the chemical yield of PMAP (as expressed by the ratio of formation of PMAP divided by the disappearance of DBK) was also found to be approximately linearly dependent upon the calculated relative micelle concentration. Only at detergent concentrations sufficiently above the critical micelle concentration (cmc) was the yield of PMAP near the calculated limiting value  $\gamma_{\text{mic}} \approx 5.5\%$  for the pure micellar phase at  $25^\circ\text{C}$ . Below cmc the formation of PMAP was very small, but still noticeable with a yield of  $0.2\%$  ( $\approx \gamma_{\text{aq}}$ ).

##### 5. Dependence of isotopic enrichment on the average occupancy of micelles

Variation of the average occupancy of the micelle from ca. 10 molecules DBK ( $[\text{HDTCl}] = 2.5 \times 10^{-2} \text{ M}$ ,  $[\text{DBK}] = 2.5 \text{ mM}$  assuming  $\bar{n} \approx 100$  [10]) near the

maximum solubility per micelle, to only about one DBK per micelle ( $[\text{HDTCl}] = 0.20 \text{ M}$ ,  $[\text{DBK}] = 2.5 \text{ mM}$ ) does not affect significantly the dynamic behavior of the photogenerated primary radical pairs, as evidenced by a lack of significant variance of  $\alpha_{\text{obs}}$  and  $\gamma_{\text{obs}}$  under these conditions (crosses in figs. 1 and 2). Apparently, concentrating the ketone DBK and the photo-product diphenylethane inside the micelle, does not result in noticeable changes of the relevant micellar properties, such as the solubility of solutes as well as the micelle-monomer equilibrium of the detergent in water.

##### 6. The magnetic isotope effect on PMAP

A significant fraction of the photogenerated phenacetyl-benzyl radical pairs have to be able to recombine in order to observe the enrichment of  $^{13}\text{C}$  in DBK and the formation of PMAP. The radical pair, generated in the triplet electronic spin state ( $^3\text{D}$  in scheme 1), has to intersystem cross to its singlet state ( $^1\text{D}$  in scheme 1) in order to be able to recombine and form a ground state molecule. In the absence of strong external magnetic fields, hfc provides for a mechanism of intersystem crossing in a radical pair. However, only fast intersystem crossing is able to compete with the rapid decarbonylation of the phenacetyl radical (half-life on the order of

$10^{-8}$  s at  $25^{\circ}\text{C}$ ) [18]. The most significant hfc in the pertinent radical pair arises from a  $^{13}\text{C}$  in the carbonyl of the phenacetyl radical ( $a_{^{13}\text{C}} \approx 120$  G) [19] allowing  $^{13}\text{C}$  labeled radical pairs to intersystem cross most successfully. As a result, an increase of the  $^{13}\text{C}/^{12}\text{C}$  ratio should occur in the singlet radical pair, finally reflecting itself in an enrichment of the  $^{13}\text{C}$  content of the recombination products. Both DBK and PMAP should, therefore, show an enriched content of  $^{13}\text{C}$  in their carbonyl carbon. Indeed, mass spectral and  $^1\text{H}$  NMR analysis of the  $^{13}\text{C}$  content of DBK and PMAP isolated from partial photolysis of a micellar HDTCl solution of DBK (with 16.9% or 47.6%  $^{13}\text{C}$  in the carbonyl originally) showed both isomers to have an increased  $^{13}\text{C}$  content in their carbonyl (see fig. 1 of preceding paper). Characteristic and in accord with the mechanism presented in scheme 1, *the enrichment of  $^{13}\text{C}$ , gradual in DBK, is sizeable in PMAP even at very low conversions (with a single stage enrichment factor for PMAP  $\alpha' \approx 1.27$ )*. The interdependence of the  $^{13}\text{C}$  enrichment in the two compounds, DBK and PMAP, as well as the experimental correlation with photochemical quantum yields have been established (see previous paper).

## 7. Micelles as dynamic "super cages"

The enrichment of  $^{13}\text{C}$  in the carbonyl of DBK (and PMAP) and the formation of PMAP correlate nicely with the existence of micelles in the aqueous detergent solutions of HDTCl. The short-lived photogenerated radical pairs suffer a different chemical fate, depending on whether they are formed inside a micelle (a "super cage") or in homogeneous solution. In the latter case, they diffuse apart efficiently and little recombination is found. Low enrichment of the  $^{13}\text{C}$  in the carbonyl of DBK ( $\alpha_{\text{aq}} \approx 1.06$ ) and low chemical yield of PMAP ( $\gamma_{\text{aq}} \approx 0.2\%$ ) result. A short-lived radical pair, generated within a micelle, however, stays in this "super cage" (probably for relevant time intervals of the order of  $10^{-6}$  to  $10^{-7}$  s $^*$ ). Thus "cage state" has two important consequences: confinement in the micelle preserves the spin correlation of the radical pair over extended periods of time (until one radical escapes or decarbonylates) helping to control the spin dynamics of such a pair via

\* Estimated in analogy to the residence times of small aromatic compounds in various micelles; see ref. [20].

hfc and boosting the magnetic isotope effect. Also, during the time interval of residence in the micelle, the radical pair is constrained to a reduced reaction space, where the local concentration of radicals is high (in an HDTCl micelle a radical pair corresponds to  $\approx 0.1$  M of radicals). A high probability for (repetitive) encounter results, followed by efficient recombination, if the electronic spin state is a singlet. The effect on the enrichment of DBK ( $\alpha_{\text{mic}} \approx 1.47$ ) and on the formation of PMAP ( $\gamma_{\text{mic}} \approx 5.5\%$ ) shows this dramatically.

The fate of DBK in an aqueous detergent solution therefore depends largely upon the probability that the ketone is situated within a micelle or in the aqueous bulk of the solution. The direct and linear correlation found here for the  $^{13}\text{C}$  enrichment of DBK and of the yield of PMAP on the concentration of the micelles in an aqueous solution of HDTCl demonstrates the effect of "reduced dimensionality" on the dynamics and reactivity of a radical pair.

From the radical pair theory of CIDNP [3,4] the probability of a radical pair recombination can be computed by the equation

$$P \approx \epsilon \int_0^{\infty} F(t) |C(t)|^2 \exp(-kt) dt, \quad (4)$$

where  $\epsilon$  is the probability of  $^1\bar{\text{D}}$  to recombine to a specific product,  $F(t)|C(t)|^2 \exp(-kt)$  is the probability that a radical pair generated at time  $t = 0$  re-encounters to give  $^1\bar{\text{D}}$  at time  $t$ ;  $|C(t)|^2$  describes the spin dynamics of the pair;  $F(t)$  describes its diffusional motion; and  $\exp(-kt)$  describes the pair disappearance due to a first-order chemical reaction. Qualitatively the primary effect of a micellar cage on the dynamics of a radical pair should be reflected in a proper function  $F(t)$ . For a fluid, homogeneous solution  $F(t)$  approaches zero rapidly with time (a measure of diffusive escape), while for a micellar environment  $F(t)$  must allow for a high probability of re-encounter of the spin correlated radical pair even after a prolonged period of its existence. The cage reactivity of a spin correlated benzyl-phenacetyl radical pair correspondingly is limited by reactivity toward diffusive separation in homogeneous solution ("diffusive escape"), while in a micelle the "chemistry" of the radical pair determines its cage reactivity ("reactive escape" [21]) as the residence time of the radical pair (order of  $10^{-6}$  s) [20] is more than an order of magnitude longer than the half-life due to decarbonylation.

The parallelism between the cage phenomena, the  $^{13}\text{C}$  enrichment in DBK and the formation of PMAP, with respect to their dependence on the concentration of the detergent HDTCl and the correlation of both phenomena with the concentration of micelles in the aqueous solutions of this detergent supports strongly such a picture. Indeed from the dependence of the yield of PMAP on the existence of micelles one can estimate the recombination of the photogenerated benzylphenacetyl radical pair inside a micelle to be roughly 20–30 times more probable than in an aqueous detergent solution below cmc.

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### References

- [1] J. Bargon, H. Fischer and U. Johnson, *Z. Naturforsch.* 22a (1967) 1551, 1556, 23a (1968) 2109.
- [2] H.R. Ward and R.G. Lawler, *J. Am. Chem. Soc.* 89 (1967) 5518; R.G. Lawler, *J. Am. Chem. Soc.* 89 (1967) 5519.
- [3] R. Kaptein, *Chem. Phys. Letters* 2 (1968) 261, R. Kaptein and L.J. Oosterhoff, *Chem. Phys. Letters* 4 (1969) 195, 214.
- [4] G.L. Closs and L.E. Closs, *J. Am. Chem. Soc.* 91 (1969) 4549, 4550; G.L. Closs, *J. Am. Chem. Soc.* 91 (1969) 4552.
- [5] A.L. Buchachenko, E.M. Galimov, V.V. Ershov, G.A. Nikoforov and A.D. Pershyn, *Dokl. Akad. Nauk SSSR* 228 (1976) 379; *Proc. Acad. Sci. USSR* 228 (1976) 451.
- [6] R. Sagdeev, T. Leshina, M. Kamha, A. Resvukin and Yu. Molin, *Chem. Phys. Letters* 48 (1977) 89.
- [7] A.L. Buchachenko, *Zh. Fiz. Khim.* 51 (1977) 2461; *Russian J. Phys. Chem.* 51 (1977) 1445.
- [8] J.H. Fendler and E.J. Fendler, *Catalysis in micellar and macromolecular systems* (Academic Press, New York, 1975).
- [9] K.L. Mittal, ed., *Micellization, solubilization and microemulsions* (Plenum Press, New York, 1977).
- [10] N.J. Turro and W.R. Cherry, *J. Am. Chem. Soc.* 100 (1978) 7431.
- [11] N.J. Turro and B. Kraeutler, *J. Am. Chem. Soc.* 100 (1978) 7432.
- [12] S.B. Coan and E.I. Becker, in: *Organic synthesis, coll. Vol. 4*, ed. N. Rabjohn (Wiley, New York, 1963) pp. 174, 176.
- [13] R.B. Bernstein, *J. Phys. Chem.* 56 (1952) 893.
- [14] N.J. Turro and A. Yekta, *J. Am. Chem. Soc.* 100 (1978) 5951; D. Meisel and J. Rabani, *J. Am. Chem. Soc.* 100 (1978) 117.
- [15] N.J. Turro and N.E. Schore, in: *Micellization, solubilization and microemulsions*, ed. K.L. Mittal (Plenum Press, New York, 1977) p. 75.
- [16] J.A. Cella, D.R. Noel, D.N. Eggenberger, H.J. Harwood and C.A. Harriman, *J. Am. Chem. Soc.* 74 (1952) 2061.
- [17] H. Langhals and H. Fischer, *Chem. Ber.* 111 (1978) 543.
- [18] W.K. Robbins and R.H. Eastman, *J. Am. Chem. Soc.* 92 (1970) 6076.
- [19] H. Paul and H. Fischer, *Helv. Chim. Acta* 56 (1973) 1575.
- [20] M. Almgren, F. Grieser and J.K. Thomas, *J. Am. Chem. Soc.* 101 (1979) 279.
- [21] R.S. Hutton, H.D. Roth, B. Kraeutler, W.R. Cherry and N.J. Turro, *J. Am. Chem. Soc.* 101 (1979) 2227.