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Photolyses of Dibenzyl Ketones in Liquid-Crystalline Media. The Fate of Benzyl Radical Pairs in Various Anisotropic Environments[1]

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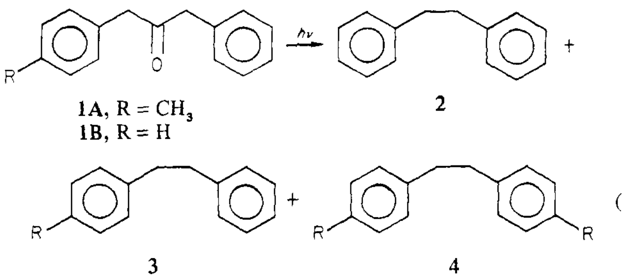
Abstract: Photolyses of 1-(4-methylphenyl)-3-phenylpropan-2-one (**1a**) and 1,3-diphenylpropan-2-one (**1b**) have been conducted in solid, liquid-crystalline, and isotropic phases of a 35/65 (w/w) mixture of cholesteryl chloride/cholesteryl nonanoate (CCl/CN), *trans,trans*-4′-*n*-butylbicyclohexane-4-carbonitrile (BCCN), or *n*-butyl stearate (BS). The fraction of in-cage recombination of benzyl radicals (F_c) produced upon decarbonylation of **1a** depends strongly upon solvent phase. The effects of magnetic field upon F_c for **1a** and the degree of isotopic enrichment of photolyzed **1b** in mesophases are described. The results in BS, especially, indicate that solvent-containment barriers, whose origin does not lie in phase discontinuities or large polarity differences, can influence strongly F_c.

The photolysis of dibenzyl ketones (**1**, eq 1) has been exploited extensively as a means of following the fate of radical pairs. In several anisotropic environments (e.g., micellar solutions,[2] derivatized silica,[3] and uncoated glass surfaces[3a,4]), the reaction has been shown to result in enhanced cage combination of geminate benzyl radicals and in marked ^{13}C enrichment of recovered starting ketones.[5] In virtually all of these cases, the solvent-containment boundaries imposed upon **1** occur as rather drastic discontinuities of the phase or polarity of the medium. From a dynamic standpoint, containment within a fixed region of solvent may be viewed as a consequence of transients from **1** experiencing an increasingly higher free energy of activation for diffusion as they approach a "boundary" (Figure 1).



1A, R = CH_3
1B, R = H
2
3
4
(1)

To determine the role of medium anisotropy on diffusion of benzyl radicals through boundaries in which the phase and polarity of a solvent remain virtually unchanged, we have photolyzed **1a** in several thermotropic liquid-crystalline solvents for which diffusional anisotropies are strongly related to entropic factors.[6] These include a 35/65 (w/w) mixture of cholesteryl chloride/cholesteryl nonanoate (CCl/CN), *trans,trans*-4′-*n*-butylbicyclohexane-4-carbonitrile (BCCN), and *n*-butyl stearate (BS). Our results indicate that the percent of cage reaction derived from photolysis of **1a** in liquid crystals is highly dependent upon and a complex function of both solvent order (phase type) and diffusion (local viscosity).

Experimental Section

1-(4-Methylphenyl)-3-phenylpropan-2-one (**1a**) and 1,3-diphenylpropan-2-one (**1b**) were synthesized as described previously[7] and were shown to be ca. 98% and 99% pure, respectively, by gas chromatographic analyses (GC) on a 6 ft × $^1/_8$ in. 10% SE-30 on 90/100 Anakrom ABS column. A 6 ft × $^1/_8$ in. 10% OV-17 on 80/100 chromosorb W or on 80/100 GasChrom Q column was employed to analyze the diarylethane photoproducts (**2**, **3**, and **4**) and to follow the disappearance of **1a**. Response factors relative to a standard, tetralin or biphenyl, added after the photolyses, were calculated electronically on a Perkin-Elmer M-2 or HP-3390A integrator attached to a Perkin-Elmer 3920B or Varian 3700 flame ionization gas chromatograph after assuming a 1:2:1 statistical ratio for **2**:**3**:**4** upon photolysis of **1a** in hexane.

Samples were prepared by weighing appropriate amounts of **1a** and liquid crystals into ampules and then heating to isotropic temperatures while agitating the mixture. After several heat–agitate and cool cycles, the samples were transferred to rectangular Pyrex capillary tubes (ca. 3-mm o.d.) and heated to isotropic temperatures several times under dry N_2. Transition temperatures for the liquid crystals were depressed by no more than 2 °C upon addition of **1a** in the concentrations employed (see Results Section). The texture patterns of the doped samples, observed under a Kofler micro hot-stage polarizing microscope, indicated that **1a** had been dissolved homogeneously throughout the solvent. The capillary tubes were sealed with Parafilm and placed in an aluminum thermostated cell holder kept at a constant distance (ca. 7.5 cm) from a quartz–water jacketed 450-W Hanovia medium-pressure Hg lamp. In several runs, a 3-kG magnet was placed around the cell holder. After irradiation, the samples were dissolved in either hexane or ether and injected into the GC. Replicate analyses (3–5) or each sample were averaged.

Transition temperatures and melting points were recorded on the micro hot-stage microscope and are corrected. BS, cholesteryl chloride, and cholesteryl nonanoate were prepared and/or purified as described previously.[8] A 35/65 (w/w) CCl/CN mixture exhibited $T_{k\to c}$ 47.5 °C and $T_{c\to i}$ 73.5 °C. BCCN (Merck), $T_{s\to n}$ 56 °C and $T_{n\to i}$ 81 °C (lit.[9] $T_{s\to n}$ 54 °C; $T_{n\to i}$ 79 °C), was used as received.

In the ^{13}C enrichment experiments, 1,3-diphenylpropan-2-one (**1b**), synthetically enriched at the carbonyl carbon[2a] (~55.8% by mass spectrometry), was used to enhance the signal-to-noise ratio in the analysis. Photolyses were performed on ~100-mg samples of a 0.62 wt % mixture of **1b** in BS. The samples were N_2 purged in the isotropic phase of BS (~40 °C) for 15 min, sealed, and photolyzed either at 35 °C in the isotropic phase for 8 min or at 17 °C in the smectic phase for 16 min. A Kratos high-intensity monochromator was used to isolate the 313-nm line from an Oriel 1000-W Xe–Hg arc lamp which was filtered through 10 cm of cooled water and a Corning glass 7-54 filter to eliminate sample heating during photolysis. After photolysis, the samples were dissolved in ether and analyzed by GC as described earlier to determine the per-

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† Columbia University.
‡ Georgetown University.

[1] This paper is part 13 in the Georgetown University series "Liquid Crystalline Solvents as Mechanistic Probes". For Part 12, see: Anderson, V. C.; Weiss, R. G. *J. Am. Chem. Soc.*, accepted for publication.

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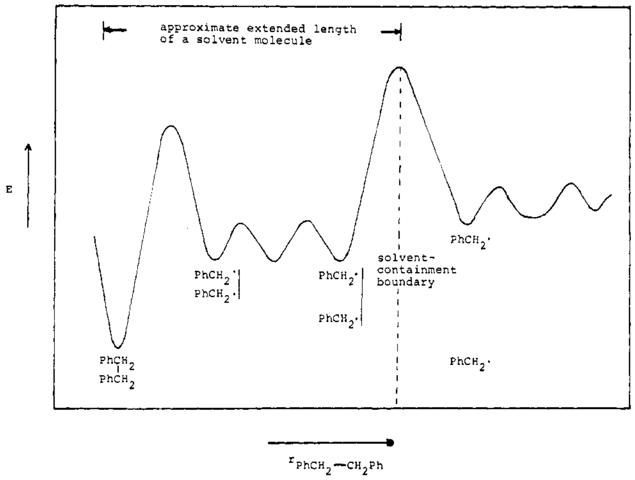

Figure 1. Representation of energy vs. separation of benzyl radical pairs in a smectic phase.

Table I

run	[**1a**], wt %	solvent	temp, °C (phase)[a]	F_c	% conversion of **1a**
1	0.70	CCl/CN	57 (c)	0.16 ± 0.01	50
2	0.82	CCl/CN	51 (c)	0.19 ± 0.02	15
3	0.82	CCl/CN	50 (c)	0.18 ± 0.02	48
4	2.0	CCl/CN	51 (c)	0.18 ± 0.01	45
5	0.70	CCl/CN	78 (i)	0.13[b]	35
6	0.82	CCl/CN	75 (i)	0.13 ± 0.02	20
7	0.82	CCl/CN	78 (i)	0.14 ± 0.01	35
8	2.0	CCl/CN	75.5 (i)	0.14 ± 0.01	54
9	0.43	BS	27 (i)	−0.017 ± 0.019	74
10	1.0	BS	28 (i)	0.021 ± 0.037	75

[a] c = cholesteric; i = isotropic. [b] One injection.

centage conversion of **1b**. BS was removed by preparative TLC (silica gel, 1:9 ether/hexane). GC analysis showed only **1b** and no BS or **2**. Isotopic abundance was then determined by GC/MS as previously described.[2a]

Results

Absolute chemical yields for **2–4** based upon consumed **1a** were determined in several experiments. They were at least 80%. No products other than **2–4** were observed in any of the runs although addition products to solvent would have been missed.

The fraction of in-cage radical recombination reaction (yielding exclusively **3**), F_c, was calculated by using eq 2. The relative

$$F_c = \frac{[3] - ([2] + [4])}{[2] + [3] + [4]} \tag{2}$$

concentrations of **2–4** were taken from chromatograms and are corrected for differences in their detector responses.

As can be seen from Table I, neither the percent conversion of **1a** nor its initial concentration in BS or CCl/CN exerts an appreciable effect on the percent of in-cage products.[10] In CCl/CN, the trend to lower F_c with increasing percent conversion is so slight that all of the values are within experimental error of their average. We had expected a larger dependence upon initial concentration since a pronounced effect of acenaphthylene concentration upon the efficiency of its photodimerization in another cholesteric phase has been observed.[8a] The lack of one here is consistent with the small depressions in phase transition temperatures caused by **1a**.

Table II

solvent	temp, °C (phase)[a]	[**1a**], wt %	cage ratio[b]	% conversion of **1a**
CCl/CN	56.5 (c)	2	0.77 ± 0.12	15
CCl/CN	75.5 (i)	2	0.75 ± 0.08	15
BCCN	46–48.5 (s)	0.96	1.0 ± 0.2	20[c]
BCCN	61–62.5 (n)	0.96	0.75 ± 0.2	25[c]
BCCN	82–82.5 (i)	0.96	0.80 ± 0.2	26[c]

[a] c = cholesteric; s = smectic; n = nematic; i = isotropic. [b] Cage ratio = $(F_c)_{3\,kG}/(F_c)_{0\,G}$. [c] Samples irradiated consecutively for 90 min; % conversion is that of the 0-G sample.

Table III

solvent	temp, °C (phase)[a]	F_c[b]	% conversion of **1a**
CCl/CN	51 (c)	0.196 ± 0.018	60
	56 (c)	0.184 ± 0.008	65
	65 (c)	0.143 ± 0.005	60
	70 (c)	0.163 ± 0.012	35
	79 (i)	0.138 ± 0.010	80
	86 (i)	0.133 ± 0.007	70
BCCN	46 (s)	0.088 ± 0.004	20
	61 (n)	0.080 ± 0.004	25
	82 (i)	0.106 ± 0.008	26
BS	9 (k)	0.150 ± 0.010	22
		0.131 ± 0.005	39
	14 (k)	0.183 ± 0.005	20
	17 (s)	0.192 ± 0.011	35
	21 (s)	0.156 ± 0.004	c
	24 (s)	0.085 ± 0.010	68
	28 (i)	0.021 ± 0.037	75
	31.5 (i)	0.007 ± 0.008	c
	35 (i)	−0.001 ± 0.009	57
	45 (i)	0.005 ± 0.005	60

[a] c = cholesteric; i = isotropic; n = nematic; s = smectic. [b] Errors are 1 standard deviation of precision. [c] Not determined.

External magnetic field effects on F_c in BCCN and CCl/CN appear to be virtually phase independent, also (Table II). It is known that the external magnetic field effect on the percent of cage reaction is approximately constant above 1 kG.[11] Thus, the ratios of F_c at 3 kG and at 0 G (external) are representative of a "large" magnetic influence. However, 3 kG is too low a field to align the mesophases of BCCN and CCl/CN.[12]

The ^{13}C isotopic enrichment factor, α,[13] for **1b** (0.62 wt %) photolysis was determined in both the smectic and isotropic phases of BS. After ca. 30% conversion of the starting material the recovered ketone exhibited α of 1.09 ± 0.02 at 17 °C (smectic phase) and 1.03 ± 0.01 at 35 °C (isotropic phase). These results may be compared with α of 1.04 and 1.37 observed at room temperature in benzene and a cationic micelle, respectively.[14]

The effect of phase type on F_c was explored in the three liquid-crystalline solvents at a fixed (1 wt %) initial concentration of **1a** (Table III). The BCCN and CCl/CN samples are only very slightly sensitive to phase and temperature changes. Yet, the magnitudes of F_c indicate that they are not behaving as simply viscous media. **1a** exhibits a remarkable drop in F_c through the smectic phase of BS. Results in the crystalline phase of BS varied from sample to sample and even from aliquot to aliquot. F_c at 9 °C was 0.095, 0.102, 0.112, and 0.131, and 0.150 in five different samples analyzed at Georgetown or Columbia. The source of the variation may be related to the presence of special solute sites, perhaps at crystalline faces: the morphology of the solid phase(s) of BS has not been explored and we have not pursued the exact cause of the lack of reproducibility. As suggested by a reviewer, surfaces within the Pyrex capillaries may affect F_c in solid BS.

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[10] Small systematic differences in the percent of cage reaction have been noted in seemingly identical experiments conducted at Columbia and Georgetown. Only values from Georgetown are presented. While the cause of the laboratory dependency remains unknown, we suspect that it is related to differences in the chromatographic conditions used in analyses.

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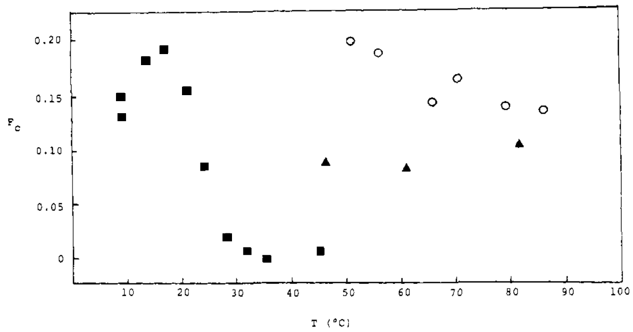


Figure 2. Fraction of in-cage benzyl radical recombination (F_c) from photolysis of **1a** in BS (■), BCCN (▲), and CCl/CN (○) vs. temperature.

In other phases, the type of vessel (and the surface–sample contact areas) exerted no discernable influence upon F_c. The effects of each solvent are displayed graphically in Figure 2.

Discussion

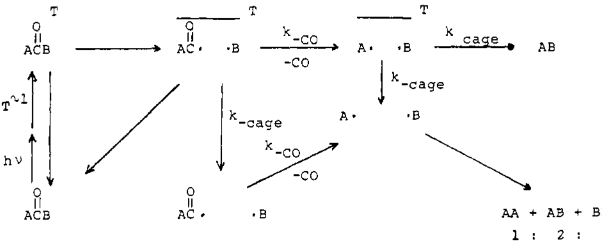
Solvent Order and Diffusion within Mesophases. A nematic phase is characterized on a microscale by individual solvent molecules being aligned (on average) with their long axes parallel to one another.[6b] A cholesteric phase consists of nematic-like layers, each being twisted slightly with respect to its neighbors so that, in toto, they form a macrohelix.[15] A smectic phase is layered also, with the constituent molecules lying at an angle (90° for a smectic A phase) with respect to the plane of a layer.[16] Some smectics, like the B phase of BS, appear to have further orientaitonal order in which molecules in a layer are hexagonally close packed.[17]

Since cholesteric mesophases are non-Newtonian and nematic and smectic phases may not be,[6a,18] it is difficult (and dangerous) to relate macroscopically derived viscosities to rates of microdiffusion (vis-à-vis, the Debye equation). Instead, diffusional coefficents along specific solvent axes should be measured for solutes or solvents. The number of studies of this sort is small. The available rate constants indicate that diffusion coefficients along different directions for a single species (solvent or solute) will differ by no more than ca. 1 order of magnitude.[19]

From a structural standpoint, the existence of directional diffusivity can be rationalized. For instance, if one assumes a cylindrical or cigarlike shape for the constituent molecules of CCl/CN, the cholesteric phase should prefer motion of a relatively small, ball-like radical (e.g., benzyl) along a direction parallel to the long axis of solvent molecules. Similar diffusional preferences of benzyl radicals should occur within the nematic phase of BCCN.

Diffusion within a smectic phase along the long axis of a solvent molecule should be relatively facile *as long as a layer boundary is not crossed*: the existence of a potential barrier to diffusion of molecules between layers is the major characteristic distinguishing smectic from nematic phases; were transfer of solvent molecules from layer to layer a facile process, smectic order would be destroyed. As in a nematic phase, diffusion in a direction perpendicular to the long axis should be equally probable but more difficult. Of extreme importance in this study is the probability that a radical fragment of **1a** will traverse the layer barriers in the smectic phases of BS and BCCN. Unfortunately, these numbers are not available. The greater smectic viscosity of BS than of BCCN (smectic BS does not flow perceptibly whereas smectic BCCN is more liquid-like)[20] indicates that even if the activation energy ratios for transverse to parallel diffusion in the two smectic phases are approximately equal, the absolute energies for diffusion will be larger in BS.

Scheme I. Possible Routes to Diarylethanes (AA, **2**; AB, **3**; BB, **4**) from 1,3-Diarylpropan-2-one (AC(=O)B) Photodecarbonylations



Of special interest is the low fraction of in-cage recombination which is observed in solid BS. In a completely immobile matrix, F_c is expected to approach unity. That F_c in BS at 9 °C is only about one-tenth of unity is a clear indication that, whatever its other aberations, BS is not a completely immobile solid. We suspect that the solvent chains remain somewhat flexible and the phase may even be a plastic crystal.[17b] In addition to the source of the lower than expected F_c, several other questions concerning the "solvent" properties of solid BS (e.g., the irreproducibility of F_c and the tendency of F_c to increase as the temperature is raised toward the melting point) remain to be answered by future work: the relatively low F_c may indicate that **1** is dissolved both within and between solvent layers.

Kinetic Considerations. A mechanism for photolysis of **1a** is presented in Scheme I, where A is $C_6H_5CH_2$ and B is p-$CH_3C_6H_4CH_2$. Excitation to the excited singlet state of **1a** is followed by intersystem crossing ($\Phi_{ST} \sim 1$; $k_{ST} > 10^8$ s^{-1})[21] and a small amount of fluorescence. Within $<10^{-10}$ s, triplets of **1a** either return to the ground state or undergo lysis to give a radical pair.[21,22] In fact, a 4/6 preference for A vs. B lysis has been shown to occur.[23] Since the fraction of initially formed radicals which recombine to yield **1a** is independent of the mode of carbonyl–methylene bond cleavage, the mechanism in Scheme I need include only one initial lysis mode: the rates of carbon monoxide loss from AC(=O)· and BC(=O)· are indistinguishable.[23]

We assume that the diffusional coefficients of AC(=O)·, A·, and ·B (as well as BC(=O)·) are nearly equal in the solvents employed. Their similar size (which is smaller than that of the solvent molecules) and shape make this approximation a reasonable one. Thus only one rate constant, $k_{-\mathrm{cage}}$, need be included to express the loss of one radical partner from a pair within a solvent cage. Similarly, one rate constant for decarbonylation, $k_{-\mathrm{CO}}$, is assumed to express events involving a radical pair or a single cage-escaped radical. With these assumptions, the empirical measure of F_c can be correlated with Scheme I by eq 3.

$$F_c = \frac{k_{-\mathrm{CO}}}{k_{-\mathrm{CO}} + k_{-\mathrm{cage}}} \frac{k_{\mathrm{cage}}}{k_{\mathrm{cage}} + k_{-\mathrm{cage}}} \qquad (3)$$

The activation parameters for decarbonylation have been determined recently in several isotropic solvents.[24] They indicate

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(15) Gibson, H. W. In ref 6b, Chapter 3.

(16) Petrie, S. E. B. In ref 6b, Chapter 4.

(17) (a) Krishnamurti, D.; Krishnamurthy, K. S.; Shashidhar, R. *Mol. Cryst. Liq. Cryst.* **1969**, *8*, 339. (b) We thank Prof. S. Chandrasekhar of the Raman Institute of Bangalore, India, for helpful discussions concerning the nature of BS phases.

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(19) See for instance: (a) Miesowicz, M. *Nature (London)* **1946**, *158*, 27. (b) Hakemi, H.; Labes, M. M. *J. Chem. Phys.* **1974**, *61*, 4020. (c) Murphy, J. A.; Doane, J. W.; Hsu, Y. Y.; Fishel, D. L. *Mol. Cryst. Liq. Cryst.* **1973**, *22* 133. (d) Chu, K.-S.; Ailawadi, N. K.; Moroi, D. S. *Ibid.* **1977**, *38*, 45. (e) Yun, C. K.; Fredrickson, A. G. *Ibid.* **1970**, 12, 73. (f) Urbach, W.; Hervet, H.; Rondelez *Ibid.* **1979**, *46*, 209. (g) Hervet, H.; Urbach, W.; Rondelez, F. *J. Chem. Phys.* **1978**, *68*, 2725. (h) Kneppe, H.; Schneider, F. *Mol. Cryst. Liq. Cryst.* **1981**, *65*, 23. (i) Kneppe, H.; Schneider, F.; Sharma, N. K. *J. Chem. Phys.* **1982**, *77*, 3203.

(20) The viscosity of isotropic BS at 27 °C is 8.0 cP.[20a] The viscosity of BCCN does not appear to have been measured.[20c] (a) Otruba, J. P. O., III; Weiss, R. G. *Mol. Cryst. Liq. Cryst.* **1982**, *80*, 165. (b) Ganapthy, S.; Weiss, R. G., unpublished results. (c) Private communication from Dr. F. V. Allan, EM Chemicals.

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(22) Robbins, W. K.; Eastman, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 6077.

(23) (a) Johnson, L. J.; de Mayo, P.; Wong, S. K. *J. Am. Chem. Soc.* **1982**, *104*, 307. (b) Hutton, R. S.; Roth, H. D.; Kraeutler, B.; Cherry, W. R.; Turro, N. J. *Ibid.* **1979**, *101*, 2227.

(24) (a) Lunazzi, L.; Ingold, K. U.; Scaiano, J. C. *J. Phys. Chem.* **1983**, *87*, 529. (b) Turro, N. J.; Gould, I. R.; Baretz, B. H. *Ibid.* **1983**, *87*, 531.

that $k_{-\mathrm{CO}}$ is nearly medium independent and allow us to reduce the number of unknowns in eq 3 to k_{cage} and $k_{-\mathrm{cage}}$.

If the $\overline{AC(=O)\cdot\cdot B^T}$ pairs are produced with thermal translational velocities, any $\overline{A\cdot\cdot B^T}$ pairs derived therefrom should undergo intersystem crossing and combine more rapidly than escaping from the cage (i.e., $k_{\mathrm{cage}} \gg k_{-\mathrm{cage}}$). If the initial A··B separation calculated by Sterna et al.,[25] ~9 Å, is correct, spin rephasing of the radical pair should occur without inhibition by correlation effects. Given the high macroviscosities of BS and CCl/CN (at least), diffusion in any direction is "slow". By comparison, Burkhart[26] and Fischer[27] have demonstrated that benzyl radicals, generated singly or initially as pairs, combine in low-viscosity isotropic solvents at rates which are within experimental error of being diffusion controlled. Apparently, each radical–radical encounter includes a sufficient number of collisions for the 25% of singlet pairs to find an appropriate orientation to combine and for the 75% of triplet pairs to undergo intersystem crossing and then combine.

Therefore, eq 3 can be simplified and rearranged to eq 4 in order to isolate $k_{-\mathrm{cage}}$. If a plot of log $[(1/F_c - 1)k_{-\mathrm{CO}}]$ vs. $1/T$ for the

$$k_{-\mathrm{cage}} \simeq (1/F_c - 1)k_{-\mathrm{CO}} \tag{4}$$

three points from the smectic phase of BS is forced to a straight line, the slope can be correlated to $E_a(-\mathrm{cage}) \sim 30$ kcal mol^{-1}. Obviously, with only three points and a 7 °C temperature range, $E_a(-\mathrm{cage})$ is subject to a very large error. However, it is clear that the activation energy is larger than for the same process in the isotropic phase of BS. If the assumptions and model in Scheme I are correct, then $k_{-\mathrm{cage}}$ *must* pertain in large part to solvent disorganization caused by penetration of a radical through a smectic layer interface.[28] Large activation parameters have been observed by us previously for a unimolecular isomerization within the smectic phase of BS.[20a,b] There, again, the contributions of solvent to the activation parameters appear dominant.

By contrast, $E_a(-\mathrm{cage}) \simeq 9$ kcal mol^{-1} is obtained for points from both the cholesteric and isotropic phases of CCl/CN. This is a more resonable value for a diffusional process in a viscous medium[29] and is near the activation parameters for diffusion within a cholesteric phase.[8b,30]

Turro et al.[31] have determined that the rate constant for disappearance of benzyl radicals generated from **1b** in HDTCl micelles is expressed best by two single-order rate constants, $k_f = 2.5 \times 10^6$ s^{-1} and $k_s = 2.1 \times 10^4$ s^{-1}. Presumably, disappearance reflects the rate constants for intersystem crossing of radical triplet pairs within the initial cage (k_f) and rates of diffusion of benzyl radicals within a micelle (k_s). Taking the viscosity within a micelle as ~30 cP,[32] diffusion should be faster there than in at least the smectic and cholesteric mesophases:[6b,18] viscosities within several thermotropic smectic phases are on the order of 10^2–10^3 cP;[33a] cholesteric mixtures exhibit highly temperature dependent viscosities (~10–10^3 P) which are discontinuous near the c → i transitions and <1 P above them;[33b] nematic viscosities for molecules similar in size to BCCN are <100 cP and are *smaller* than in the corresponding isotropic phase.[33c]

Thus, if k_{cage} in the mesophases is limited by intersystem crossing, k_f should represent an upper limit to k_{cage}. Diffusion of the radical pair to a distance at which spin rephasing is rapid and then diffusion back to a collisional distance from which product can form will be slower in the liquid crystals than in a micelle.

Cage Considerations in Mesophases. The thickness of a smectic layer in BS (31.6 Å[17]) and in BCCN (~17 Å[34]) as well as the cylindrical shapes of the individual molecules places additional constraints upon the motion of an $\overline{A\cdot\cdot B^T}$ pair and requires a further definition of "cage". Assuming that a molecule of **1a** is aligned parallel to neighboring solvent molecules, cleavage within 10^{-8} s after excitation[21] will propel the AC(=O)· and ·B fragments away from one another and toward the layer boundaries. If one of the two radicals does not escape to a neighboring layer, the fragments will diffuse preferably in a recoil motion toward one another (in competition with transverse motions within a layer). The space defined by the initial cage motion is a cylinder whose diameter is that of a benzyl "ball" (ca. 4–5 Å) and whose length is that of a solvent molecule. This volume, then, defines a smectic cage, escape from which will occur most easily via lateral diffusion.[35] Considering (1) the breathing motions of the BS chains or BCCN rings about an A· or B· radical to approximate the effect of collisions between a solute and solvents of about equal size (i.e., $D \simeq 10^{-6}$ cm^2 s^{-1} [19]) and (2) twice the cylinder length to be the *maximum* distance that an A··B pair need traverse within a cage before reencountering one another, then the time between encounters in smectic BS is about $(2 \times 31 \times 10^{-8}\ \mathrm{cm})^2/(2 \times 10^{-6}\ \mathrm{cm^2\ s^{-1}})$ (or ~10^{-7} s) and in smectic BCCN is $(2 \times 17 \times 10^{-8}\ \mathrm{cm})^2/2 \times 10^{-6}\ \mathrm{cm^2\ s^{-1}}$ (or ~5×10^{-8} s).[36] Of course, these values will be altered by orders of magnitudes if the diffusion coefficients of A· and B· for motion within the cylinders are either larger or smaller than expected. In fact, the diffusion coefficients are predicted to vary drastically with temperature.[19] Despite these uncertainties, we believe that k_{cage} will be limited by diffusion rather than intersystem crossing in all mesophases employed.[37]

Isotopic Enrichment Studies in BS. It has been demonstrated that large solvent viscosities, alone, are insufficient to induce significant ^{13}C isotopic enrichments in **1b** which is recovered after partial photolysis.[2a,5] In the most viscous isotropic solvent in which the distribution has been measured, ethylene glycol (η 13.8 cP), the yields of **2**–**4** remain statistical.[2b] Pines[25] and Buchachenko[38] have analyzed the factors contributing to α and predict that it will be largest at "intermediate" viscosities. Given that directional diffusivity within a layer along any axis of BS molecules may be "low", it is not unreasonable that the F_c be large and α be small. In fact, α 1.09 (smectic) and α 1.04 (isotropic) could arise from BS viscosities which lie on the high and low sides, respectively, of the intermediate value at which α is maximized.

Conclusion

We have demonstrated that the probability of recombination of benzyl radical pairs produced upon decarbonylation of 1-(4-methylphenyl)-3-phenylpropan-2-one is very sensitive to the nature of the local solvent organization. Environmental barriers which

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do not involve polarity or phase discontinuities can influence strongly the diffusion of benzyl radicals. A model for analyzing their fates in more than one phase (including a liquid-crystalline one) of a solvent has been devised. From it, we conclude that variations in viscosity, alone, cannot account for changes in the recombination probability.

The nature of the processes leading to products appears very complex and, in *n*-butyl stearate especially, merits further attention.

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Registry No. 1a, 35730-02-0; **1b**, 102-04-5; benzyl radical, 2154-56-5.

Synthesis of *dl*-Pentalenolactones E and F

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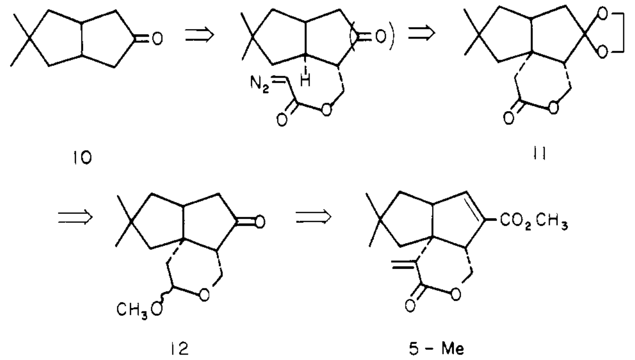
Abstract: The methyl esters of (±)-pentalenolactone E (**5**-Me) and F (**6**-Me) have been synthesized by a route based on the intramolecular insertion of an α-acylcarbene into an unactivated C–H bond to effect closure of the key fused δ-lactone ring system. Thus 7,7-dimethylbicyclo[3.3.0]octan-3-one (**10**) was assembled in seven steps from dimethyl 3,3-dimethylglutarate (**13**). The requisite (diazoacetoxy)methyl side chain was appended to **10** by a sequence of carbomethoxylation, ketalization, side-chain reduction, acylation with glyoxalyl chloride tosylhydrazone, and base-catalyzed elimination of *p*-toluenesulfinate. Ring closure to the desired δ-lactone **31** was effected in 43–47% yield by using $Rh_2(OAc)_4$ catalyst in refluxing Freon TF. Lactone reduction, deketalization, and selective acetalization of the derived lactol provided **34** as a mixture of epimers. By use of the method previously described by Paquette, **34** was converted to pentalenolactone E methyl ester (**5**-Me). Stereoselective epoxidation of the exomethylene double bond of **5**-Me provided pentalenolactone F methyl ester (**6**-Me). The use of α-diazo β-keto esters for the elaboration of bicyclo[3.3.0]octanones was also explored as an approach to the synthesis of pentalenolactone (**1**) itself. Thus exposure of **38** to $Rh_2(OAc)_4$ in refluxing Freon TF gave a 3:2 mixture of the corresponding bicyclo-[3.3.0]octan-3-one **39** and the spirocyclobutanone **40**. When **53** was subjected to the identical cyclization conditions, however, only the spirocyclobutanone adduct **54** was formed, without any evidence for the generation of the desired bicyclo[3.3.0]octan-3-one **55**.

Since the initial isolation and identification of the *Streptomyces* antibiotic pentalenolactone (**1**),[2] members of the pentalenane family of sesquiterpenes have continued to attract the attention of synthetic and bioorganic chemists. Over the last several years additional representives of this group of novel metabolites have been reported, including pentalenolactones G (**7**),[3] H (**8**),[4] and P (**9**),[5] pentalenic acid (**4**),[4] deoxypentalenic acid glucuronide (**3**),[5] and the parent hydrocarbon itself, pentalenene (**2**) (Chart I).[6] Our own group has reported the isolation and structure determination of two further metabolites, pentalenolactones E (**5**)[7] and F (**6**).[8] Many of these latter substances are believed to be intermediates or shunt metabolites in the biosynthesis of pentalenolactone. In biosynthetic investigations already reported from this laboratory we have established the mevalonoid origin of the pentalenolactones,[9] demonstrated that pentalene is a precursor of **4**, **5**, **6**, and **8**,[10] and isolated a cell-free enzyme preparation which catalyzes the conversion of farnesyl pyrophosphate to pentalenene.[10]

Scheme I



At the same time, the considerable synthetic challenge presented by these novel polyquinane systems has inspired a number of interesting synthetic approaches. In an extensive investigation of biomimetic cyclizations of humulene and its derivatives, Matsumoto and Shirahama have prepared several members of the pentalenane family of metabolites. These studies, which are of considerable theoretical importance, have resulted in the total synthesis of pentalenene[11] and, by an extension of the basic ring-forming methodology, more oxidized derivatives such as

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