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Investigations of Cylindrical Reaction Cavities from Ordered Phases of Alkyl Alkanoates and Their Influence on Some Norrish–Yang and Photo-Fries Reactions*

Jon E. Baldvins, Changxing Cui and Richard G. Weiss†

Department of Chemistry, Georgetown University, Washington, DC, USA

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ABSTRACT

The Norrish–Yang photochemistry of three isomeric *p*-alkyl alkanophenones (*p*-propyl nonadecanophenone, *p*-pentyl heptadecanophenone and *p*-octyl tetradecanophenone) and the photo-Fries reactions of 2-naphthyl myristate have been investigated in the ordered (layered) phases of three isomeric alkyl alkanoates. Comparisons of photoproduct selectivity for irradiation of one substrate in the isotropic and ordered phases of one host ester provide information concerning the influence of the cylindrically shaped reaction cavities on the relative motions and conformational changes necessary to convert the reactants to products. Comparisons of photoproduct distributions from one substrate in comparable phases of two or more esters provide details concerning the “wall stiffness” and importance of functional group interactions of the reaction cavities. Finally, comparisons using one substrate and two ordered phases of the same ester indicate the role of wall stiffness on photoproduct selectivity. The results show that the course of the photochemical reactions can be controlled effectively within the ordered media and provide an indication of how to design and select ordered media to effect other photochemical transformations selectively.

INTRODUCTION

Previously, we have examined the influence of organized media (1–5), especially of butyl stearate (BS)‡ (6–8), in

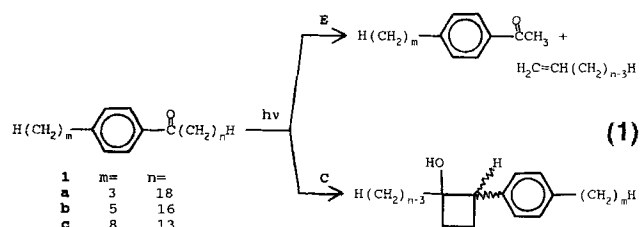
*In memory of Guiseppe Cilento, a friend and an inspiration. He saw light where others did not and shared it selflessly. Um abraço e tschau from R.G.W.

†Author to whom correspondence should be addressed at: Department of Chemistry, Georgetown University, Washington, DC 20057, USA. Fax: 202-687-6209; e-mail: Weissr@gusun. acc.georgetown.edu.

‡Abbreviations: ATR, attenuated total reflectance; bp, boiling point; BS, butyl stearate; c-BR, *cisoid* hydroxy-1,4-biradical; DD, decyl dodecanoate; DSC, differential scanning calorimetry; i-BR, initial hydroxy-1,4-biradical; KI, initial keto intermediate; E/C, fragmentation-to-cyclization ratio; MM', molecular mechanics plus;

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which the host molecules are extended in layers (9–13), on the photochemical reactions of guest molecules, like ketones capable of undergoing Norrish II (14–19) or Norrish–Yang processes (20,21)§ (Eq. 1). Although several mechanistically important aspects of the constraints imposed by the environments surrounding the reacting guest molecules (*i.e.* the reaction cavities (22)) have been identified (2,3), some questions remain unanswered and others have been investigated in only a cursory fashion.

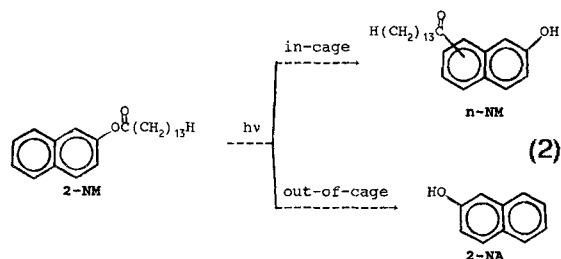


To elucidate further the nature of some of the constraints, we have examined the influence of solvent order imposed by BS and two isomeric alkyl alkanoates, octadecyl butanoate (SB) and decyl dodecanoate (DD) (in which the distance of the carboxy group from a molecular end is changed), on the Norrish–Yang reactions of three isomeric *p*-alkyl alkanophenones, *p*-propyl nonadecanophenone, *p*-pentyl heptadecanophenone and *p*-octyl tetradecanophenone (1a–c, respectively) and the photo-Fries reactions (23,24) of 2-naphthyl myristate (2-NM; Eq. 2) (25). The comportment of the key intermediate of the Norrish–Yang reaction, a hydroxy-1,4-biradical (BR), is contrasted with that of the 2-naphthoxy/myristoyl radical pair from the photo-Fries reactions of 2-NM. The extended lengths of the guest ketones and 2-NM are very similar to those of the host esters. Two

MNDO, modified neglect of differential overlap; mp, melting point; 2-NA, 2-naphthol; n-MN, n-myristoyl naphthol; 2-NM, 2-naphthyl myristate; SB, octadecyl butanoate; TMS, tetramethylsilane; 1a, *p*-propyl nonadecanophenone; 1b, *p*-pentyl heptadecanophenone; 1c, *p*-octyl tetradecanophenone.

§There is deserved sentiment to adopt “Yang reaction” as the name for the cyclization processes (20,21). The Norrish–Yang reaction is the designation that will be used here to describe both the fragmentation and cyclization pathways.

of the media, BS and SB, place their carboxy groups near a chain end. Decyl dodecanoate has its carboxy group near the middle of the molecule. These differing locations alter the interactions of the guest molecules and their intermediates with the host esters constituting the reaction cavities and affect the local order experienced by the reaction centers in the layered solvents.



The choice of solvent media is based upon our prior photochemical studies with alkyl alkanophenones in BS (6) and with 2-naphthyl alkanoates in polyethylene (26,27). Under sterically favorable conditions, the BR from the ketones can form hydrogen bonds with carboxy groups of neighboring BS molecules that influence the distribution of photoproducts (6). Due to the nature of the molecular packing in the ordered host assemblies, their reaction cavities can be envisioned as cylinders with as many as six carboxy groups along a ring in the wall. Results from the prior studies raised questions concerning the link between the projection and direction of the host carboxy groups, with respect to a chain end, and the conformational constraints felt by the intermediate BR. Also, the radical pairs from irradiation of 2-naphthyl alkanoates in polyethylene either recombine (in-cage reaction) or separate (out-of-cage reaction) in ways that are very sensitive to the mesoscopic and microscopic nature of the host reaction cavities (26). This has led to hypotheses concerning the shapes of those cavities that should be tested independently.

Comparison of the results from irradiations in the isotropic phase and ordered phase of one ester provides information about the influence of cavity shape and wall stiffness (2,3). Comparison of the results from irradiation of one guest in comparable phases of two (or more) esters or of more than one isomeric guest ketone in one ordered phase of one ester host provides information concerning specific functional group interactions and gradations of wall stiffness.

MATERIALS AND METHODS

Instrumentation. The NMR spectra were acquired on a Bruker Instruments AM-300 WB spectrometer with an Aspect 3000 computer. Infrared spectra were recorded on a Mattson Galaxy 5020 FT spectrometer and a Specac ZnSe attenuated total reflectance (ATR) accessory with 45° crystal faces. Melting points, from a Kofler hot-stage and a Bausch and Lomb microscope equipped with polarizing films, are corrected. Gas chromatographic analyses of photoproduct mixtures from **1** (GC) employed a Perkin-Elmer 8500 GC or a Perkin-Elmer Autosystem GC with flame ionization detectors. Both were equipped with a Hewlett-Packard HP-17 (50% phenyl and 50% polysiloxane) 10 m × 0.53 mm fused silica capillary column. Photoproduct mixtures from 2-NM were analyzed by HPLC using a Waters chromatograph, an Alltech 250 mm × 4.4 mm 5 μ silica gel column (ethyl acetate/hexane as eluent) and a UV (254 nm) detector.

Syntheses of guest molecules. The *p*-alkyl alkanophenones, gifts from Dr. Zhiqiang He (6,28), were prepared *via* a standard Friedel-

Crafts procedure employing commercially available alkylbenzenes and acyl chlorides. The syntheses of 2-NM and its photoproducts have been described in detail recently (25).

Syntheses of *n*-alkyl esters. Decyl dodecanoate and SB were synthesized according to standard acid chloride-alcohol coupling techniques using commercially available acid chlorides and alcohols. A typical procedure for octadecyl butanoate is reported.

1-Octadecanol (Aldrich 99%), 27.0 g (0.10 mol), was warmed to its liquid state. Butanoyl chloride (Aldrich 98%), 17 mL (0.15 mol), was added dropwise under an N₂ atmosphere during a 15 min period. The solution was refluxed for 30 min after which the heating mantle was removed. Fractions from vacuum distillation were analyzed by GC and the purest fraction was recrystallized several times from acetone.

SB. Yield 98%, 98% pure, melting point (mp) 23.9°C. ¹HNMR (CDCl₃/tetramethylsilane [TMS]): δ 4.06 (2 H, t, J = 6.74 Hz, -OCH₂-), 2.28 (2 H, t, J = 7.46 Hz, -C(O)-CH₂-), 1.64 (4 H, m, -OCH₂CH₂- and -C(O)CH₂CH₂-), 1.26 (30 H, m, CH₃(CH₂)₁₅-), 0.95 (3 H, t, J = 7.38 Hz, -OCH₂CH₂CH₃), 0.90 (3 H, t, J = 6.74 Hz, CH₃(CH₂)₁₅-). ¹³CNMR (CDCl₃): 173.7 (C=O), 64.4 (-OCH₂-), 36.3 (-C(O)CH₂-), 32.0, 29.7-28.7 (unresolved peaks), 25.9, 22.7, 18.5, 14.1 and 13.7 ppm. IR (neat): 2955, 2927, 2854, 1741, 1467, 1179 cm⁻¹. Transition temperatures from differential scanning calorimetry (DSC) heating curves: α₃-α₂, 3.3°C; α₂-α₁, 11.3°C; α₁-i, 23.9°C.

DD. 66% yield, 99% pure, mp 20.0°C (from DSC heating curves). ¹HNMR (CDCl₃/TMS): δ 4.05 (2 H, t, J = 7.03 Hz, -OCH₂-), 2.28 (2 H, t, J = 7.30 Hz, -C(O)CH₂-), 1.61 (4 H, m, -OCH₂CH₂- and -C(O)CH₂CH₂-), 1.26 (30 H, m, CH₃(CH₂)₁₅-), 0.88 (6 H, m, -OCH₂(CH₂)₈CH₃ and CH₃(CH₂)₁₅-). ¹³CNMR (CDCl₃): 173.8 (C=O), 64.3 (-OCH₂-), 34.4 (-C(O)CH₂-), 31.9, 29.6-29.3 (unresolved peaks), 29.2, 28.7, 25.9, 22.6, and 14.1 ppm. IR (neat): 2955, 2921, 2853, 1740, 1466, 1172 cm⁻¹.

BS (29). Boron trifluoride etherate (Aldrich, purified, redistilled), 100 mL (0.81 mol), was added to 50.0 g (0.18 mol) of stearic acid (Aldrich 99+%) in 400 mL of previously distilled *n*-butanol (Baker, reagent, boiling point [bp] 114-115°C). The BF₃-etherate was cannulated under an N₂ atmosphere from the reagent bottle into the reaction vessel. The mixture was refluxed under N₂ for 4 h. Upon cooling to room temperature, 500 mL anhydrous ether was added. The organic fraction was extracted with distilled water (2 × 200 mL), 20% (wt/vol) aqueous sodium bicarbonate (2 × 200 mL), distilled water (2 × 200 mL) and aqueous saturated sodium chloride (2 × 200 mL). The organic layer was dried (MgSO₄) and evaporated *in vacuo* on a rotary evaporator to yield 60.6 g of colorless oil. The oil was irradiated with the Pyrex-filtered output of a Hanovia 450 W medium pressure Hg arc for 40 h and passed through a 2 cm (diameter) column, which contained 2.5 cm of alumina and 2.5 cm of silica at ca 80°C. The resulting clear oil was distilled under vacuum to yield 46.2 g (77%) of a colorless liquid (bp 174°C, 0.07 mm). It was free of both stearic acid and 1-butanol (>99% purity according to GC analyses). Phase transition temperatures, determined from the onset of DSC heating curves: α₃-α₂, 11.0°C; α₂-α₁, 14.7°C; α₁-i, 26.0°C (from the literature (9,10) 11.1°C, 14.8°C and 26.1°C).

Sample preparations and irradiations of **1.** Each *p*-alkyl alkanophenone (2.0 wt%) was dissolved in the appropriate solvent and the solution was bubbled with N₂ for 10 min. Aliquots were transferred to Pyrex capillary tubes (ca 1 mm i.d.), purged again with N₂ and the tubes were then flame-sealed. The samples were heated to their isotropic phase, immediately quenched to the desired temperature and thermostated for at least 15 min prior to irradiation. The tubes, immersed in a circulating water bath, were irradiated with a Hanovia 450 W medium-pressure Hg arc with a Pyrex filter. Irradiation times were varied empirically from 30 to 300 s to maintain <25% conversion. After irradiation, the contents of the tubes were dissolved in pentane (Mallinkrodt, HPLC grade) and analyzed by GC. The fragmentation-to-cyclization ratios (E/C) are an average of triplicate injections of three samples (nine data points) and are uncorrected for detector response.

The fragmentation products and GC retention times from the irradiation of both **1a** and **1b** were previously identified (6,28). The 1-dodecene fragmentation product from **1c** was identified by coinjection with an authentic sample. The identity of the cyclization

products was inferred from their GC retention times, which are slightly shorter than those of the corresponding reactant ketone.

We assume that because **1a–c** and their cyclization products have the same molecular weight, they have the same flame ionization detector response in GC analyses. Similarly, the sum of the peak areas for the alkene and truncated ketone has been used to calculate the contribution of the fragmentation process. Thus, E/C is taken as the sum of the peak areas from the alkene and truncated ketone divided by the sum of the peak areas from the diastereomeric cyclobutanols.

Sample preparations and irradiations of 2-NM. 2-Naphthyl myristate (1 wt%) was dissolved in isotropic BS and the solutions were deoxygenated by bubbling with nitrogen for 10 min. Aliquots were transferred rapidly to capillary tubes that were flame-sealed immediately. The tubes were irradiated as indicated above in a thermostated water bath (after being equilibrated for 10 min). At least three chromatograms of irradiated aliquots that had been dissolved in the eluent mixture were averaged. Peak areas were scaled according to the molar extinction coefficients of the products to obtain the relative yields reported.

RESULTS AND DISCUSSION

Phase morphology

Butyl stearate is known to form one liquid-crystalline and two crystalline phases below 26°C (9,10). The nature of the phases is based on polarized optical microscopy, powder X-ray diffraction, DSC, NMR, IR and dielectric absorption measurements. Between 15.3°C and 26°C, the α_1 phase is regarded as a hexatic smectic B (S_{BH}) in which molecules are arranged in layers in extended chain conformations with their long axes normal to the layer plane (10,13). Molecules within each layer are hexagonally packed and rotate about their long molecular axes (30). There are positional correlations that are three dimensional and long range (31), permitting shear both within and between molecular layers.

The crystalline α_2 phase occurs between 11°C and 15°C (10). In it, rotations about the long molecular axis are restricted and packing becomes orthorhombic (10). Below 11°C, a second crystalline phase (α_3), similar to the α_2 phase but with even more restricted rotations, is formed.

There is limited information regarding mesomorphic behavior of other *n*-alkyl alkanooates. However, many compounds become mesomorphic due to alkyl substituents.

Octadecyl butanoate, a component in a variety of mammalian scent systems such as the cotton-top tamarin (*Saguinus oedipus*) (33) and the marmoset (*Saguinus fuscicollis*) (34) and in both the secretions of *Melissodes* bees (35) and the aphrodisiac pheromones of the sulfur butterflies *Colias eurytheme* and *Colias philodice* (36), is not mentioned as a liquid crystal in the extensive compendium of Demus and coworkers (37,38).

A combination of X-ray diffraction and DSC measurements demonstrate that SB and BS are completely miscible in all of their condensed phases (J. E. Baldvins and R.G. Weiss, unpublished). Like that of BS, the mesophase of SB is hexatic smectic B (S_{BH}) and molecular packing in the solid phases mimics that of BS. In fact, the phase transition temperatures are affected only slightly by addition of one molecular species to the other. Additionally, DSC heating curves of 1% 2-NM in BS or 2% **1** in neat BS, SB, DD and mixtures of BS and SB show no new transitions, nor are the ones intrinsic to the alkyl alkanooates affected in a substantive way. We conclude that the guest molecules at these loadings are dispersed completely in all of the host phases; they are

Table 1. Layer thicknesses of host molecules in their various ordered phases according to X-ray diffraction data and calculated extended molecular lengths

Molecule	T (°C)	Phase	Lengths/layer thicknesses (Å)*
BS†	5	α_3	31.2
	13	α_2	31.5
	18	α_1	31.4
SB†	1	α_3	30.8
	9	α_2	30.7
	18	α_1	31.0
DD†	10	Solid	29.4
1a–c			(34.8)
2-NM			(25.5)

*Numbers in parentheses are from MM2/MM+ calculations.

†Calculated extended van der Waals lengths from MM2 force field calculations of the alkyl alkanooates are 32.0 Å.

the concentrations used for the irradiation experiments. Pertinent layer thicknesses of the ordered host phases and the calculated extended molecular lengths of the host the guest molecules are collected in Table 1.

The DSC and X-ray diffraction data show that DD passes directly from its layered solid to isotropic phase (J. E. Baldvins and R. G. Weiss, unpublished). Decyl dodecanoate has a low-angle reflection that corresponds to molecular layers of 29.4 Å thickness. Increased disorder near the center of a DD layer, caused by the carboxy group, may be responsible for it being thinner than the comparable layers of BS and SB; data from the solid phases of layered *n*-alkanes (39–41) indicate that packing disorder is more easily accommodated when it occurs near the ends of a molecular layer.

Norrish–Yang reactions in ordered media: general considerations (2, 3, 19)

The quantum efficiency of intersystem crossing (Φ_{isc}) for alkanophenones is nearly unity. Hence, photoreaction emanates from the triplet manifold. When the lowest triplet state is n, π^* and steric and energy factors allow (18, 42, 43), a γ -hydrogen atom can be abstracted intramolecularly by the carbonyl oxygen via a six-membered transition state. The resulting hydroxy-1, 4-biradical can reform the original ketone, fragment to an enol and an olefin or cyclize to cyclobutanols. The existence of triplet hydroxy-1,4-biradicals has been confirmed both spectroscopically and by direct trapping experiments (44).

Figures 1 and 2 show various pathways available to the initial hydroxy-1,4-biradical (i-BR) and emphasize the shape differences and conformational relationships among various mechanistically important intermediates. Fragmentation produces an enol, which usually ketonizes in a subsequent dark reaction and an alkene. It may occur from the family of *cisoid* biradicals (c-BR), but several studies demonstrate that the principal source is *transoid* biradicals (t-BR) in the absence of steric constraints. For steric reasons, cyclization products, diastereomeric cyclobutanols, must have c-BR as their immediate precursor.

Current evidence indicates that rates of triplet \rightarrow singlet intersystem crossing for t-BR and c-BR, that must precede

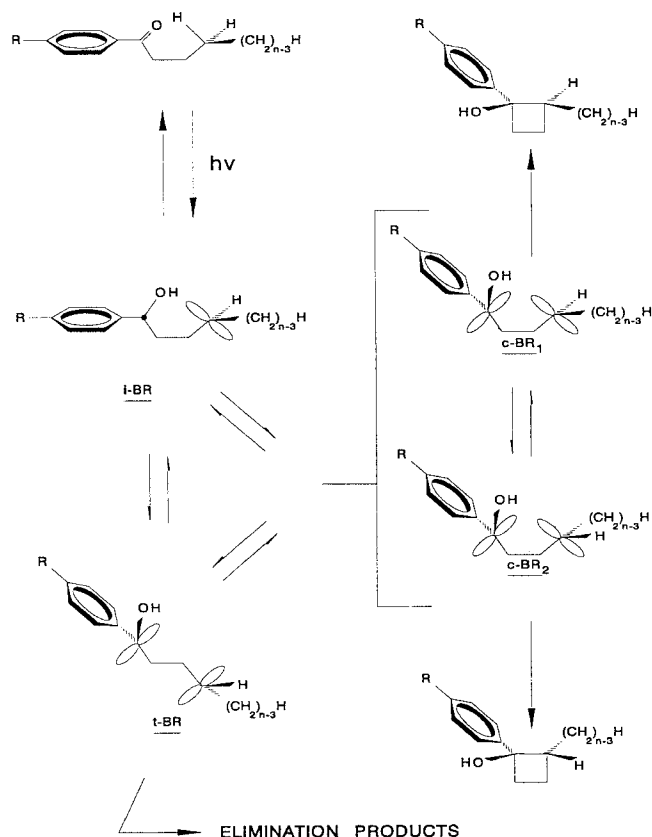


Figure 1. The formation of Norrish–Yang cyclization photoproducts showing some mechanistically important BR intermediates.

or accompany product formation, are comparable (18, 45, 46). Accordingly, E/C reflects the ratios of the populations of the triplet t-BR and c-BR at the time of intersystem crossing. Because c-BR is less rodlike than t-BR, it is reasonable to assume, and available results support, that the ordered phases of host molecules comprised of layers of rodlike molecules enhance the t-BR conformer and, therefore, fragmentation.

Photo-Fries rearrangements of 2-NM in ordered media: general considerations (26, 47)

In isotropic media, the principal course of the photochemical reactions of 2-NM is described in Fig. 3 (23, 25). Lysis of the acyl-oxy bond occurs in the excited singlet state manifold, resulting in a radical pair whose fate is controlled by the shape, size and functional groups of the initial reaction cavity and by the ability of the radicals to escape from it. In prior studies, we have demonstrated that the distribution of photoproducts is sensitive to each of these factors as well as to the conformation of the 2-NM singlet state from which lysis occurs (25–27). In very ‘stiff’ cavities that afford very little opportunity for radical pair motion, the dominant course is recombination to afford ground-state 2-NM. Thus, in both the orthorhombically (at 25°C) and hexagonally organized (at 36°C) layered solid phases of heneicosane (48) ($C_{21}H_{44}$; 28.7 Å layer thickness by X-ray diffraction (48)), a rodlike molecule that can be thought of as an analogue of the BS, SB and DD alkyl alkanolate host molecules, but in which the carboxy groups have been excised, no photoreac-

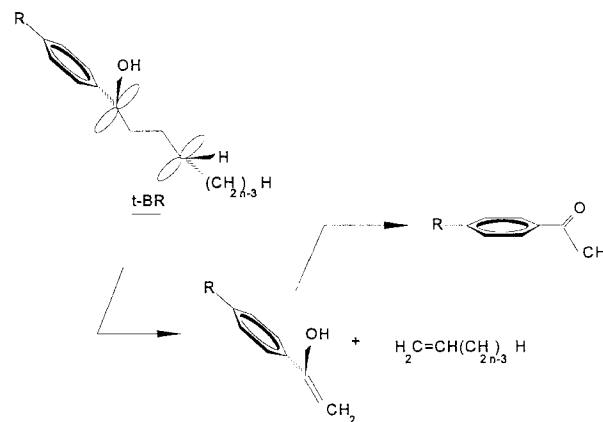


Figure 2. The formation of Norrish type II fragmentation photo-products showing some mechanistically important BR intermediates.

tions of 2-NM are discernible after irradiation periods sufficient to convert virtually all of the 2-NM in the mesophase of BS to photoproducts (27).

Irradiations in unstretched and stretched polyethylene films indicate that somewhat flexible and rod-shaped cavities favor 3-myristoyl-2-naphthol (3-MN) and, when some directed diffusion is allowed, 6-myristoyl-2-naphthol (6-MN) (26,27). If the cavity is less rod-shaped, the principal rearrangement product in isotropic media, 1-myristoyl-2-naphthol (1-MN), is formed in large quantities and 8-myristoyl-

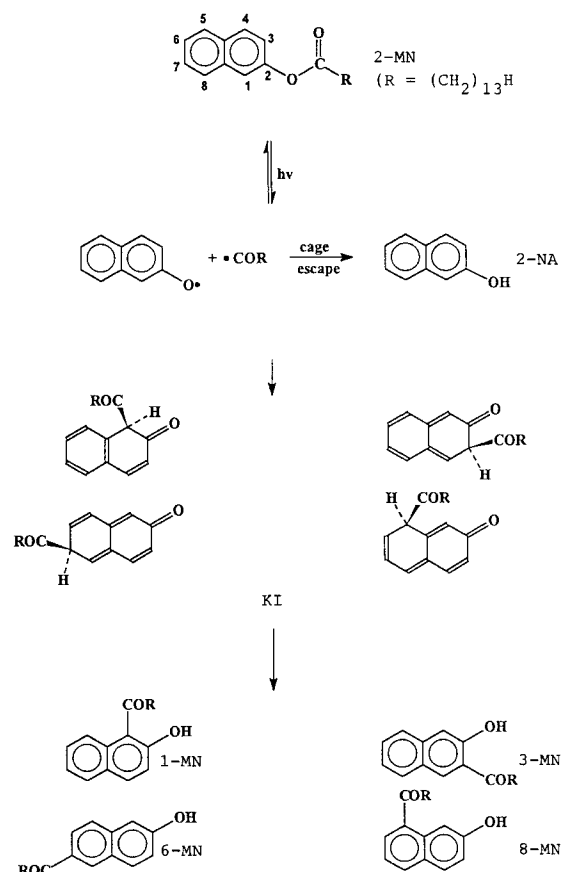


Figure 3. A stepwise mechanism for the photo-Fries reactions of 2-NM.

Table 2. Fragmentation/cyclization ratios from 2 wt% **1a** ketone in BS, SB and their mixtures as a function of temperature and host composition.

% SB	Fragmentation/cyclization ratios (percent conversion)		
	5°C	18°C	30°C
0	80 ± 21 (21 ± 3)	24 ± 4 (11 ± 2)	7 ± 6 (11 ± 1)
25	90 ± 20 (19 ± 4)	25.8 ± 0.8 (16 ± 3)	6 ± 3 (13 ± 4)
50	70 ± 15 (18 ± 4)	24 ± 3 (17 ± 3)	5.5 ± 0.8 (21 ± 4)
75	90 ± 18 (21 ± 4)	23 ± 1 (15 ± 4)	5 ± 1 (15 ± 4)
100	100 ± 20 (14 ± 3)	17 ± 2 (16 ± 2)	5.0 ± 0.4 (15 ± 3)

2-naphthol (8-MN), a produce of similar shape but which requires diffusional motion to form, is produced in small amounts. Each of the MN isomers is isolated after the corresponding initial keto intermediate (KI) undergoes enolization; at the relatively low temperatures and conversions of 2-NM utilized here, other processes are not competitive with enolization of KI. When the initial radical pair separates before combining (*i.e.* cage escape), the 2-naphthoxy radical abstracts a hydrogen atom from solvent to yield 2-naphthol (2-NA). Existing evidence indicates that all of the rearrangement products are the result of in-cage recombinations and all of the 2-NA emanates from out-of-cage reaction (25); once cage-escape occurs, the radical pair does not recombine in condensed media like those employed here.

Photoproduct distributions from irradiations of **1** in BS, SB, their mixtures and DD

The Norrish–Yang reaction products from **1** were previously characterized and their GC retention times are known (6). Although both diastereomeric cyclobutanols were formed, at least upon irradiations in the isotropic phases, their ratios were not determined because the GC columns employed did not resolve them completely.

Small amounts of other products were detected, but with the low conversions used, they represent <2% of the peak areas for initially formed elimination products (assuming equivalent detector response). If these peaks are the result of α -cleavage (Norrish type I) or photoreduction of molecules of **1**, they have no influence on the E/C ratios; even if they emanate from secondary reactions of fragmentation products, their small amounts introduce inconsequential errors in E/C. The blue-shifted absorption spectra of the cyclobutanols (<300 nm) makes them unlikely candidates for precursors to the small peaks; if they were, their small yields would create large errors in the E/C ratios.

Because photoproduct ratios from alkanones similar to **1** irradiated in other isotropic solvents are unaffected by temperature in the region of this investigation (5,6), any change in E/C ratios in Tables 2–4 can be attributed to factors related to solvent order.

The E/C ratios from irradiation of **1a** or **1b** in the liquid-crystalline phases of BS, SB and their mixtures (Tables 2

Table 3. Fragmentation/cyclization ratios from 2 wt% **1b** in BS, SB and their mixtures as a function of temperature and host composition.

% SB	Fragmentation/cyclization ratios (percent conversion)		
	5°C	18°C	30°C
0	>200 (14 ± 3)	26 ± 9 (11 ± 4)	5 ± 1 (22 ± 3)
25	>200 (22 ± 3)	31 ± 3 (22 ± 2)	5.4 ± 0.5 (14 ± 4)
50	132 ± 7 (22 ± 2)	27 ± 2 (15 ± 4)	5.3 ± 0.8 (12 ± 3)
75	>200 (19 ± 6)	24 ± 2 (20 ± 3)	4.4 ± 0.3 (20 ± 1)
100	>200 (20 ± 3)	20 ± 4 (18 ± 3)	6.7 ± 0.8 (14 ± 7)

and 3) are three to six times those found for the corresponding isotropic phases, and the α_3 solid phases at 5°C yield much higher values still. Although there are distinct differences between E/C values for different phases, those within one phase type are rather similar; it must be remembered that small errors in the amount of cyclobutanols will create very large errors in E/C when the total amount of cyclization product is small (as in the ordered phases).

The E/C ratios (=4–7) for irradiations of both **1a** and **1b** in the isotropic phases should be considered within the experimental error for accuracy. In the liquid-crystalline state, the E/C ratios increase to 17–31. While initial inspection of the data might suggest that the experiments with **1b** yield higher E/C ratios than with **1a**, almost all of the results are, with one exception within experimental error of one another.

The largest E/C ratios are for irradiations in the solid phase. Ratios from **1a** are between 70 and 100. Those from **1b** can only be estimated; they are greater than 200 because the amount of cyclization products is less than 0.5% of the yield of fragmentation products.

A second set of experiments was conducted to compare the interactions of BS and DD with **1a** and **1c** and their hydroxy-1,4-biradicals. The polar functional groups of **1c** and its BR should be able to interact effectively with the carboxy group of neighboring DD molecules in the layered

Table 4. Fragmentation/cyclization ratios from 2 wt% **1a** and **1c** in BS and DD as a function of temperature (phase)

Guest/host	Fragmentation/cyclization ratios (percent conversion)	
	10°C, solid	30°C, isotropic
1a /BS	80 ± 21* (21 ± 3)	7 ± 6 (11 ± 1)
1c /BS	110 ± 20 (15 ± 1)	5.5 ± 0.2 (20 ± 3)
1a /DD	22 ± 3 (16 ± 1)	6.0 ± 0.1 (21 ± 1)
1c /DD	50 ± 6 (21 ± 1)	5.4 ± 0.1 (16 ± 4)

*Temperature = 5°C.

Table 5. Relative photoproduct yields from irradiations ($\lambda > 300$ nm) of 2-NM (1% wt) in N_2 -saturated butyl stearate*

T/°C (phase)	% Conversion	% Yield			
		1-MN	3-MN	6-MN	2-NA
32 (isotropic)	24 (3)	9 (1)	22 (1)	8 (1)	68 (4)
	28 (2)	7 (1)	18 (1)	2 (1)	73 (3)
20 (smectic)	5 (2)	<3	20 (1)	7 (1)	70 (3)
	5 (2)	<3	20 (1)	11 (1)	65 (3)
	6 (2)	<3	17 (1)	9 (1)	72 (3)
	7 (2)	<3	16 (1)	8 (1)	73 (3)
13 (α_2 solid)	2 (1)	†	5 (1)	6 (1)	89 (4)
	3 (1)	†	6 (1)	6 (1)	88 (4)

*No 8-MN was detected.

†A trace amount was detected.

solid phase. Due to the lack of a DD mesophase, the photochemistries of **1a** and **1c** could be compared only in the isotropic and solid phases of BS and DD (Table 4). As expected, insignificant differences exist among results from irradiations in the isotropic phases. In the solid phases, the E/C ratios are much larger. However, the smallest increase occurs for **1a** and DD: $(E/C)_{\text{solid}}/(E/C)_{\text{iso}} \approx 3.7$; the corresponding ratios for **1a** in BS and for **1c** in DD are *ca* 11.4 and 9.3, respectively. The much larger increase in the **1c** in BS system $((E/C)_{\text{solid}}/(E/C)_{\text{iso}} \approx 20)$ occurs in spite of the fact that carbonyl (or hydroxyl) interactions with carboxyl groups of BS are predicted to be sterically forbidden (*vide infra*).

Product distributions from irradiations of 2-NM in BS

As mentioned, DSC thermograms of BS with and without 1% of 2-NM are virtually identical, indicating that the 2-NM is solubilized in all condensed phases of BS. Above 1.5% of 2-NM, a new transition at 18.1°C, perhaps from a eutectic mixture, appears.

In all irradiations, no 8-MN could be detected (Table 5). Measurable quantities of all of the other photoproducts in Fig. 3 were present in the irradiation mixtures. However, the relative yield of 1-MN, the least rodlike isomer present, decreases precipitously from the isotropic to smectic phase and from the smectic to the α_2 solid phase. Although the relative yields of the other photoproducts are nearly the same in the isotropic and smectic phases, the relative yields of 3-MN and 6-MN are diminished significantly in favor of 2-naphthol in the α_2 phase. Very small changes are detected in the photoproduct distribution when 2-NM is irradiated in solvents that remain isotropic throughout the temperature range explored in Table 5. Qualitatively, the quantum efficiency for conversion of 2-NM decreases, as expected, when temperature decreases (and phase order increases).

An analysis of the influence of cylindrical reaction cavities

From the molecular lengths and layer thicknesses in Table 1, it is clear that 2-NM and each of the isomers of **1** should be able to replace a molecule in an ordered ester matrix while retaining nearly all-*transoid* conformations for their alkyl chains. However, the cross-sectional area of an aro-

matic ring is larger than that of a methylene chain. As a result, some disorder should be introduced into the layered matrices of the host molecules in the vicinity of a guest, and it should be greatest near the locus of reaction. This disorder must contribute to the ability of the cavity to permit molecules of excited **1** to undergo the shape changes necessary to afford products.

In a general sense, we can classify the Norrish–Yang and photo-Fries reactions as processes in which each guest molecule leads to one or more different species in the product-forming step(s). For the Norrish–Yang reaction, the eventual products are based upon the conformations adopted by one key product-determining intermediate, a BR. For the photo-Fries reaction, the relative motions of two key intermediates, a radical pair derived from one species, determine the nature of the products. In isotropic media that afford reaction cavities whose walls are flexible and whose shapes and volumes can be adjusted in the time frame defined by transformation of the key intermediates to their various products, internal steric and energetic constraints of the reactant and its intermediate control, primarily, the course of reaction. For instance, the extra volume needed when a hydroxy-1,4-biradical in the Norrish–Yang reaction fragments to an enol and an alkene or the change in shape (and volume) that occur when the biradical cyclizes to a hydroxycyclobutane are accommodated easily by expansions, contractions and redistributions of volume within the reaction cavity.

We have used the modified neglect of differential overlap (MNDO) approach to calculate the van der Waals volumes of the fragmentation and cyclization products from a model ketone, 2-nonanone. The molar volumes of the *cis*- and *trans*-hydroxycyclobutanols (alkyl substituents *cis* and *trans*, respectively) are 81.6 and 82.3 cm³; for the initial fragmentation products, 1-hexene and propen-2-ol, the volumes are 51.8 and 36.7 cm³ (or a sum of 88.5 cm³). The 6–7 cm³/mol difference between the volumes of the cyclization and fragmentation products represents an upper limit to the differences among the transition state volumes: the volumes for the transition states for cyclization are larger than those of the product cyclobutanols because the radical centers move to distances that are smaller than the sums of their van der Waals radii; the volumes of the transition states for fragmentation are smaller than the sum of the enol and truncated alkene products because the carbon atoms of the σ -bond separating the radical centers move to distances that are at least as long as the sum of their van der Waals radii. Although the volume differences for the 2-nonanone and **1a–c** systems should be nearly the same, they are much smaller fractions of the total volumes of the latter. In fact, the primary shape changes associated with formation of the various photoproducts, localized in the region of the radical centers, may have a greater impact than volume changes on interactions with a host reaction cavity.

Additionally, the “porosity” of the cavity walls (2,3) is an important factor in determining whether the initially formed radical pair in the photo-Fries will react with each other or diffuse apart and react singly.

We view the reaction cavities afforded by the ordered, layered phases of BS, SB and DD as cylinders whose wall stiffness is dependent upon whether a solid (stiffer, less flexible) or liquid-crystalline (looser, more flexible) phase is be-

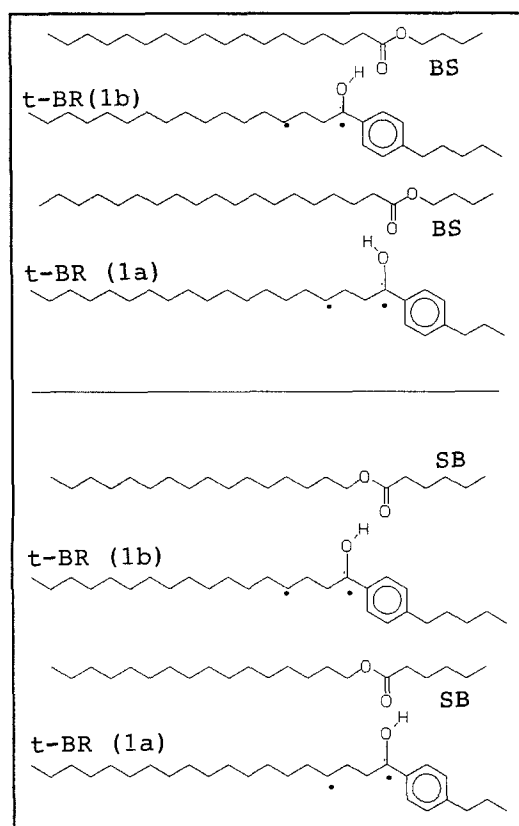


Figure 4. Probable approximate positions of hydroxy groups of *t*-BR intermediates from **1a** and **1b** with respect to the carboxy groups of host molecules in the layered phases of BS and SB.

ing employed, and whose ability to interact specifically with functional groups of the guest molecules and their pre-product intermediates is controlled by simple spatial factors. As mentioned previously, even within one cylinder, there are gradations of wall stiffness: in the absence of disturbing groups, the greater stiffness is felt near the middle of a cylinder (middle of a layer) and the greatest flexibility is near the cylinder ends (layer interfaces) (39–41). The presence of carboxy groups in the cylinder walls contributes also to a more flexible local environment. When the groups are near the middle of a cylinder, as in the solid phase of DD, the increase in flexibility is greater than when they are near the intrinsically less-ordered ends.

Hydrogen-bonding interactions can be another major source of enhanced photoproduct selectivity (6). Although specific group–group interactions between a guest and the walls of a host reaction cavity may have strict spatial requirements, an average of six carboxy groups surrounds each guest molecule in the liquid-crystalline and solid phases of the esters. Only one of them need be oriented appropriately. More important is the location of the carboxy groups (as a “ring” in the cylindrical cavity) with respect to the position of the carbonyl (or hydroxy) group in the extended guest molecule. As predicted by Fig. 4, BS should be able to make hydrogen bonds more easily with the BR from **1a** than with that from **1b** (or **1c**). The model suggests also that the layered phases of SB and DD should be able to make hydrogen bonds most easily with the BR from **1a** and **1c**, respectively.

The ability of guest molecules and their intermediates to diffuse laterally within a layer will be greater than their ability to diffuse across layers, but both types of motion will be greater in the liquid-crystalline than in the solid phases. Thus, the layered phases afford reaction cavities that discourage globular guest shapes but should not impede reactions along coordinates in which guests retain rodlike shapes. This model has been shown to accommodate the results from irradiation of other ketones in BS and several other layered hosts (5,19).

We observe qualitatively that the irradiation time required to effect a fixed conversion of **1** or 2-NM to products in an ester increases on passing from the isotropic to the liquid-crystalline to the solid phase. These observations are consistent with greater return by the radical pair to 2-NM and increasing difficulty to change from the most stable all-*transoid* conformation of **1** to a skewed one that brings a hydrogen atom on a γ -carbon to within an abstractable distance of the carbonyl oxygen; without attainment of this conformation during the triplet lifetime of **1**, hydroxy-1,4-biradicals cannot be formed and no Norrish–Yang products are possible. Alternatively, a small fraction of **1** (or 2-NM) may reside in “defect sites,” cavities that promote skewed conformations (or radical pair separation). Excitation of guest ketones in such sites would lead to rapid and efficient *i*-BR formation. Depending upon the wall stiffness of the sites, one might expect enhanced return to **1** (back H-atom transfer) and/or cyclization instead of fragmentation. The results indicate that the fraction of such sites is very small. Regardless, the *E/C* ratios and Fries photoproduct distributions relate primarily to the fates of the various hydroxy-1, 4-biradicals and radical pairs that do not return to reactant molecules.

Irradiations of **1** and 2-NM in BS show a clear trend toward a diminished ability to form more globular-shaped intermediates and products in the ordered phases. For instance, the results in Table 5 show that the least rodlike of the isomers detected, 1-MN, is formed in progressively smaller relative amounts as BS order is increased: the 1-MN/(3-MN + 6-MN) ratio decreases from *ca* 0.3 (isotropic) to <0.1 (smectic) to *ca* 0 (solid). In a narrow, cylindrical reaction cavity, this comportment is expected because the acyl carbon atom of the myristoyl radical will experience progressively greater difficulty to move to the vicinity of the 1-carbon of the 2-naphthoxy radical in the ordered phases. Analogous results are found upon irradiations of **1a–c** in BS where the relative yields of the fragmentation products suffer large increases as solvent order increases.

Molecular mechanics plus (MM⁺) calculations for 2-naphthyl acylates in the absence of solvent predict that conformations placing the carbonyl oxygen atom of the acyl group near C-1 and C-3 are almost equal in energy (25). However, the shape of the reaction cavity in the ordered phases of BS should favor the conformation with the acyl group nearer C-3 because it produces the more rodlike shape. Thus, the reaction cavity prejudices the radical pair to yield 3-MN and makes motions that allow 1-MN to be produced more difficult. The presence of 6-MN in amounts comparable to the yield of 3-MN demonstrates that some translational and/or rotational motion of the radical pair is possible even in the solid phase of BS. Because the distance traversed by the acyl

carbon to reach C-6 of 2-naphthoxy is greater than that to reach C-1 (starting from a position in which the acyl carbon is near the oxygen atom on C-2), the paucity of 1-MN is a consequence of the inability of the reaction cavity to undergo the shape changes necessary to accommodate bond formation at C-1.

Another aspect of the reactions of 2-NM in BS that merits comment is the increasing fraction of cage-escape products that accompanies increasing order of BS phases. Intuitively, one would expect that the diffusion needed for cage escape (and 2-NA formation) should diminish in solid BS; the much lower quantum yields for conversion of 2-NM indicate that it does. We hypothesize that the fraction of 2-NM singlets that yield the radical pair is nearly the same in all three phases of BS. However, a much larger portion of the radical pairs recombines to yield 2-NM in the smectic and solid phases than in the isotropic phase. Of those that do not in the solid phase, many are separated, perhaps through lateral diffusion that follows small longitudinal movement of the radical pair toward opposite layer boundaries; the two radicals can diffuse longitudinally without traversing a layer boundary since 2-NM is *ca* 6 Å shorter than a BS layer (Table 1).

The E/C ratios in Tables 2 and 3 show that **1a** and **1b** cannot distinguish clearly among the cavities provided by BS, SB and their mixtures. Only in the 50/50 BS/SB solid and SB smectic phases are there indications of somewhat less-restrictive reaction cavities. However, the decrease in E/C in comparison with ratios for other mixtures of the same phase is too small to merit conjecture. The carbonyl groups of both ketones (and the hydroxy groups of their BR intermediates) are situated so that they can interact with the ester groups of nearby host molecules in their layered phases (Fig. 4). The somewhat larger solid-phase ratios from **1b** are consistent with the reaction center of its BR residing closer to the layer middle than that of **1a**. In the corresponding smectic phases there appears to be a much smaller differential influence of the position of the BR reaction centers on the E/C ratios; the walls of the smectic reaction cavities must be similar in their flexibility along the region where the radical centers of the BR from **1a** and **1b** lie.

The results in both the solid and smectic phases demonstrate that the cylindrical reaction cavities make it much more difficult for a BR to attain a more globular *c*-BR conformation. Once formed, an *i*-BR must undergo rapidly those motions that lead to *t*-BR. In essence, the relative energy of the *c*-BR and the energy barrier for *t*-BR → *c*-BR is increased by the cylindrical shape of the smectic and solid-phase reaction cavities.

Secondary interactions from hydrogen-bonding to ester groups and relative reaction-site positioning can also influence the E/C ratios. These factors have been explored by irradiating **1a** and **1c** in BS and DD (Table 4). As shown in Fig. 5, the carbonyl groups of **1a** and the hydroxy group of the corresponding BR cannot interact with the carboxy group of neighboring DD molecules if both are incorporated in layers; however, strong interactions between **1c** (or its BR) and DD are sterically feasible. The results in Table 4 show that placement of a carboxy group near the (most-ordered) middle of an alkyl alkanate, as in DD, results in layered assemblies with reduced order. The E/C ratios from **1a** in solid DD are *ca* one-

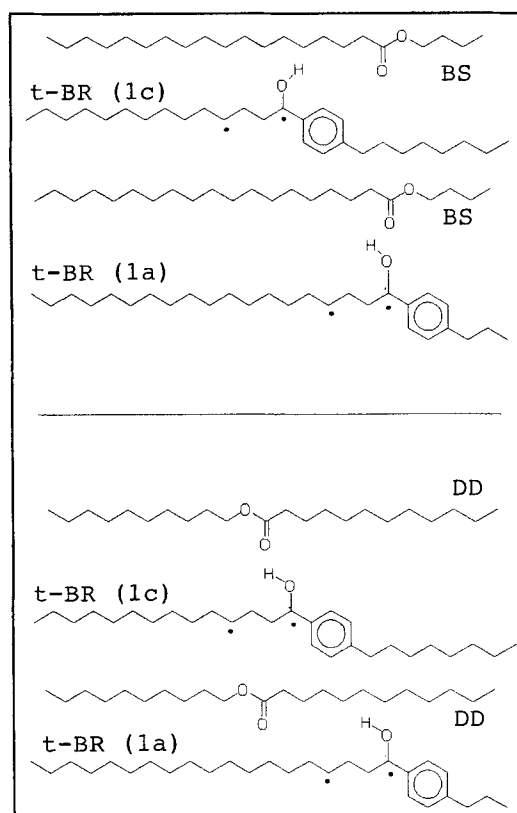


Figure 5. Probable approximate positions of hydroxy groups of *t*-BR intermediates from **1a** and **1c** with respect to the carboxy groups of host molecules in the layered phases of BS and DD.

quarter those in solid BS. More to the point, the E/C ratios from **1c** in solid DD (where carbonyl/hydroxy interactions with carboxy groups of neighboring host molecules are possible) is less than one-half that of **1c** in solid BS (where the interactions are not possible). These results provide a striking demonstration of the importance to E/C selectivity that the middle of a layer be highly ordered even if the reaction center is not in its vicinity. In spite of the BR from **1c** being able to form hydrogen bonds with neighboring host DD molecules, the selectivity is lower than in solid BS. We conclude that the stiffness of the walls of a cylindrically shaped reaction cavity is more important in directing the reactions of the guest molecules than specific interactions between groups in the cavity walls and those attached to the guests.

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