# SELECTIVITY IN THE PHOTOPRODUCT RATIOS FROM NORRISH II REACTIONS OF A HOMOLOGOUS SERIES OF 2-ALKANONES IN THEIR MELT AND SOLID PHASES. COMPARISON WITH OTHER ENVIRONMENTS*

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Received January 17, 1992
Accepted March 5, 1992

*Dedicated to Professor Václav Horák, our colleague and friend, on the occasion of his 70th birthday.*

The product ratios from Norrish II reactions of 2-tridecanone, 2-tetradecanone, 2-pentadecanone, 2-hexadecanone, 2-heptadecanone, and 2-nonadecanone have been measured at low percents of conversion in the melt and solid phases. Although elimination/cyclization photoproduct ratios from the neat crystals are > 60 in optimal cases, the ratios of cyclobutanol diastereomers (cyclization products) remain near those observed from melt irradiations. From comparisons of the photoproduct selectivities in the neat solids and in their solid solutions, where the solvent molecules are similar in size and shape to the 2-alkanones, it is concluded that the crystalline lattices of some foreign hosts offer environments to the pre-product biradical intermediates, which are at least as restrictive as the environments of the solid 2-alkanones.

The limitations imposed upon the motions of reacting molecules in their excited states by anisotropic environments has eluded a general explanation in spite of the large number of recent investigations (see e.g. ref.[2]). In previous studies, we have attempted to identify the underlying features which lead to substrate control by constrained environments comprised of liquid-crystals[3a,b] especially smectic phases whose constituent molecules pack in layers[3c]. It has been especially fruitful to compare the kinetics and selectivities of Norrish II photoreactions[4] (Scheme 1) suffered by alkanones in layered phases of butyl stearate (hexatic B and solid, smectic E-like phases)[5], aqueous gel phases of potassium stearate (interdigitated bilayers)[6] and potassium stearate/1-octadecanol (bilayers)[6], solid phases of unbranched alkanes[7], and smectic G(J) phases of

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* Part 44 in the series Liquid–Crystalline Solvents as Mechanistic Probes; for Part 43, see ref.[1].

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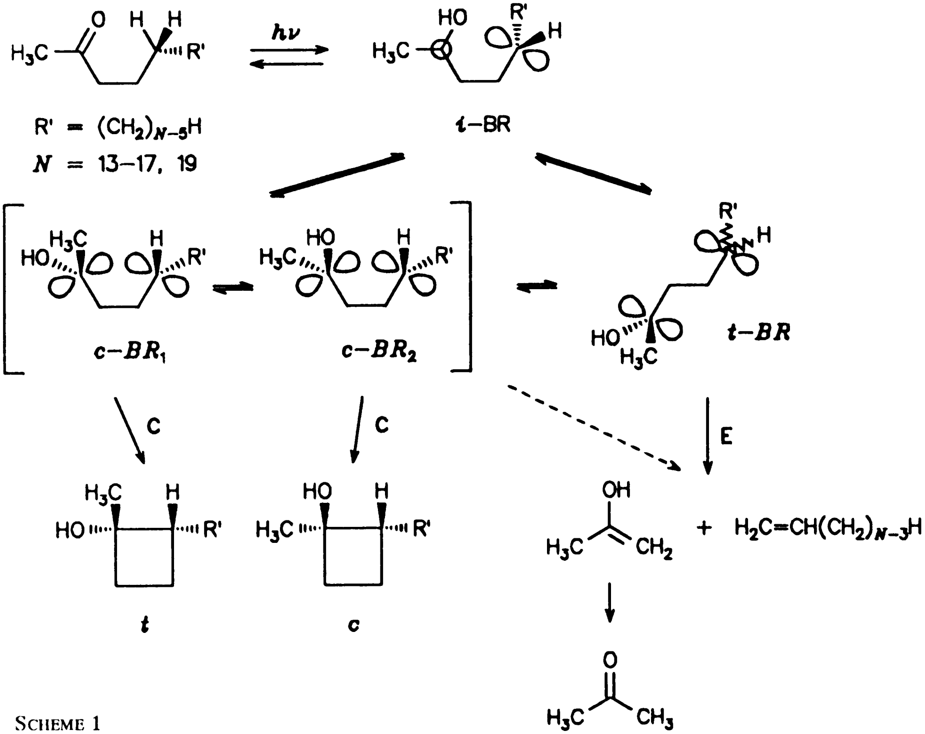
perfluorodecyl decane[8]. In each case, the solvent molecules arrange themselves in extended conformations and with their long molecular axes either perpendicular or tilted with respect to the layer planes. The packing arrangements within a layer vary from hexagonal to orthorhombic to triclinic depending upon the specific phase.

The utility of the Norrish II reaction lies in its generality, predictability of the products, and the fact that the transition states are relatively easily inferred from the structures of reactants and products[4]. Thus, motions along the reaction coordinate and, hence, the influence of environmental order on these motions may be visualized.

Recently, we have investigated the Norrish II reactions of *neat* solid and liquid-crystalline phases of *p*-(4-alkylcyclohexyl)alkanophenones[1,9]. In principle, these experiments also allow solute reactions to be observed in the absence of a "foreign" environment*. Due to the lack of a uniform rod-like shape for the alkanophenones,



SCHEME 1

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* In fact, several other groups, most notably those of Scheffer and Trotter[10a], Ramamurthy and Venkatesan[10b], Lahav and Leiserowitz[10c], and Schmidt[10d] have performed exceptionally fine investigations which combine a detailed knowledge of crystal packing and molecular photoreactions in neat solid phases.

results obtained upon irradiation of their layered phases cannot be related easily to those from irradiations of solutes in the aforementioned layered phases. To allow a more direct comparison, we have investigated the photochemistry of a series of homologous 2-alkanones (2-*N*, where $N = 13 - 17$ and 19, the number of carbon atoms in the molecular chain) in their solid, layered phases. X-Ray crystallographic studies[11] have established that crystalline 2-alkanones pack in layers like those of unbranched alkanes, the gels and smectic phases. Thus, a comparison between the selectivities of the Norrish II reactions (defined as the ratio of the photoproduct ratios measured in the solid and isotropic phases) of the 2-alkanones in their neat and dispersed phases should provide an indication of whether the completely undisturbed environment of the neat solid offers a more constrained environment for reaction than those of other layered host molecules.

## EXPERIMENTAL

2-Alkanones were available from previous studies[6], except for 2-tetradecanone and 2-hexadecanone which were prepared from methyllithium and tridecanoic and pentadecanoic acid, respectively, by the method of Rubottom and Kim[12]. The alkanones were > 99% pure by GLPC analyses on a Hewlett–Packard 5890A gas chromatograph equipped with flame ionization detectors and a 3393A integrator using a 10 m × 0.53 mm CP-Sil 19 CB wide-bore capillary column. Melting points (uncorrected) for the ketones are collected in Table I. Photolyses were performed in sealed glass melting point capillaries under nitrogen. Samples (~ 10 mg) were first introduced into the capillaries as solids or melts and either were degassed under vacuum (0.1 – 1.0 Torr), using at least 3 freeze-pump-melt cycles, before being blanketed with nitrogen and flame-sealed or were saturated with nitrogen and flame-sealed. Irradiations were performed with a 450 W Hanovia medium-pressure mercury arc through pyrex in a constant temperature water bath. Temperatures were chosen empirically where no melting of the samples could be discerned or above the melting points (55 °C). Immediately after irradiation, the sealed tubes were stored in a freezer until being analyzed. For product analyses, the contents of the glass capillaries were dissolved in hexane. Each of the resulting

TABLE I
Melting points and layer spacings of 2-alkanones

| *N* | M.p., °C | | Layer spacings[a], Å |
|---|---|---|---|
| | obs. | literature | |
| 13 | 29 - 30 | 29.5 - 30.5[b] | 36.81 |
| 14 | 33 - 34 | 33 - 34[c] | |
| 15 | 38 - 39 | 38.9[a] | 42.60 |
| 16 | 41 - 42 | 44 - 45[d] | |
| 17 | 48 | 48.2[a] | 47.39 |
| 19 | 53 - 54 | 55.6[a] | 52.22 |

[a] Ref.[11b]; [b] ref.[6a]; [c] ref.[13]; [d] ref.[14].

solutions was analyzed thrice using the gas chromatographic system described above, and the average values for product ratios and percentage reaction were calculated. Photoproducts were identified as described previously[6]. Especially at high conversions, small peaks not attributable to Norrish II products appeared. From the total integrated peak areas of all the products divided by the sum of the unreacted ketone and photoproduct peak areas, the percents of conversion were calculated. The data are collected in Table II as elimination/cyclization (E/C) and *trans*/*cis* cyclobutanol (*t*/*c*) ratios. Only the alkene elimination products were used to calculate E/C ratios.

In one set of irradiations, the pyrex and water-filtered output of an Osram HBO 500W high pressure mercury arc was focused onto capillary tubes containing 2-heptadecanone which were mounted behind a Corning 7-51 filter. Irradiations were conducted at 30 °C for 5 days in order to obtain the results reported in Table III.

## RESULTS AND DISCUSSION

In other attempts to dissect the factors which contribute to the selectivity of solute reactions in constrained environments, we have discussed at length the salient features of Norrish II reactions of alkanones[3,5,6 – 9]. In essence, the initially formed biradical (*i-BR*) must undergo a conformational change to yield either an elimination (E) or a diastereomeric *trans* or *cis* cyclobutanol (*t* or *c*) product (Scheme 1). Since the motions leading to each product are different and the *BR* conformation which is a precursor of each product has different steric requirements, two distinct environmental factors influence the eventual product ratios. One is the resistance of the medium to the motions required to convert *i-BR* to any of the preproduct *BR* conformations (*t-BR*, $c\text{-}BR_1$, and $c\text{-}BR_2$) and the other is the "fit" of each *BR* conformation in the constrained environment*.

Since the *i-BR* → *c-BR* motions entail only a nominal twist by ca 90° about the α C–C bond, but formation of *t-BR* requires a ca 90° twist about the α C–C bond and a ca 180° twist about the β C–C bond, cyclobutanols should be the major photoproducts if the least motion pathway from *i-BR* dominates. Furthermore, since $c\text{-}BR_1$ and $c\text{-}BR_2$ from 2-alkanones are very similar in shape[3], the ratio of cyclobutanol photoproducts should be comparable regardless of whether the solvent matrix is isotropic or anisotropic. Only in those cases in which the steric differences between $c\text{-}BR_1$ and $c\text{-}BR_2$ can be exacerbated (e.g., by solvent interactions) should *t*/*c* deviate significantly from the norm. On the other hand, *t-BR* is the most rod-like of any of the *BR* conformers and, as such, should disturb least a solvent matrix comprised of layers of similarly shaped molecules. Thus, elimination is expected to dominate if the *BR* conformers are able to

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* The reaction occurs via the short-lived singlet and the longer-lived triplet n, π* states[4]. Although both multiplicity states may lead to *i-BR*, constrained or high viscosity media favor the triplet. While some elimination products may derive from *c-BR*, available evidence indicates that, in systems like those under study, the vast majority of the *c-BR* cyclize[3].

equilibriate before collapsing to products. The data presented in Tables II and III clearly favor the compatibility of *BR* "fit" in the alkanone layered matrices as the more important product-determining factor. To similar extents, foreign host matrices comprised of layered rod-like molecules also favor the formation of elimination products upon irradiation of guest alkanones[3].

There appear to be few, if any, single crystal X-ray studies performed on unbranched alkanones*. However, as early as 1925, it was recognized from X-ray powder diffractograms[11c] that 2-alkanones crystallize in layers. These results have been corroborated by later studies[11a,b] which demonstrate the similarities in the crystal packing of 2-alkanones, butyl stearate[11a,15] and the unbranched alkanes[16]. Additionally, the diffraction patterns give a reflection corresponding to Bragg distances about twice the length of a 2-alkanone molecule[11]. From this, it may be inferred that the carbonyl groups from adjacent layers tend to aggregate near one interface while the long alkyl chains of adjacent layers prefer to reside near the opposite interface. Although we have not been able to find a report of the layer spacing for any of the irradiated 2-*N* with an even number of carbon atoms, the layer spacing of 2-octadecanone, 50.0 Å (ref.[11c]), fits the trend of 2-*17* and 2-*19*. Thus, the irradiated even-numbered 2-*N* should pack like their odd homologues.

It is known from IR and NMR investigations of the solid layered phases of unbranched alkanes that a layer middle is much more ordered than its extremities[17]. The occurrence of gauche twists in polymethylene chains is smallest near a layer middle. In the rotator phase of solid unbranched alkanes, the probability of gauche bends near the terminal carbon of a molecule is much higher. From solid state $^2$H NMR studies on 2-alkanones and symmetric alkanones with deuterium atoms at the carbons alpha to the carbonyl groups[18], we arrive at the same conclusion for the alkanones.

Consistent with these structural observations, Slivinskas and Guillet[19] and we[5c] have noted that symmetric alkanones are virtually photostable in their solid phases. Apparently, even the motions required to bring the γ-hydrogen into adequate proximity to the carbonyl oxygen from an all-*transoid* conformation are not possible during the excited state lifetimes of the symmetric alkanones. However, protracted irradiation of solid symmetric alkanones *does* lead to small amounts of Norrish II products whose distribution is similar to that observed from the melt or isotropic solutions[5c]. Reaction, when it does occur, proceeds in molecules at sites which are not indicative of the normal crystal structure (e.g., at defect sites).

By contrast, 2-alkanones react rather efficiently in their neat solid phases. The additional motional freedom associated with the ends of the molecules is sufficient to

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* A search of the Cambridge Crystallographic File using "alkanone" as the key word resulted in no pertinent "hits".

TABLE II
Product ratios from irradiation of neat phases of 2-*N* with the pyrex-filtered output of a 450 W medium pressure arc, and selectivities from the neat phases and from anositropic solution

| *N* | *T*, °C | Conversion, % | E/C | *t*/*c* | Selectivity[a] | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | P = solid[b] | P = hexatic B[c] | P = solid[c] | P = Phase II[d] | P = Phase I[d] |
| 13 | 55[e] | 7 | 3.2 ± 0.2 | 1.3 ± 0.1 | | | | | |
| | 8 | 6 | 13.9 ± 3.5 | 2.5 ± 0.5 | 4.3 | 1.1 | 1.2 | | |
| | 8 | 12 | 10.4 ± 1.3 | 3.5 ± 1.7 | 3.3 | | | | |
| | 8 | 14 | 8.4 ± 1.4 | 2.6 ± 1.4 | 2.6 | | | | |
| 14 | 55[e] | 10 | 3.3 ± 0.2 | 1.3 ± 0.1 | | | | | |
| | 7 | 5 | 25.4 ± 3.9 | 1.0 ± 0.2 | 7.7 | | | | |
| | 7 | 14 | 11.6 ± 1.7 | 2.0 ± 0.4 | 3.5 | | | | |
| | 7 | 29 | 4.5 ± 0.2 | 2.1 ± 0.1 | 1.4 | | | | |
| | 55[e] | 5 | 4.5 ± 0.3 | 1.4 ± 0.1 | | | | | |
| | 23 | 6 | 21.0 ± 3.2 | 2.5 ± 0.4 | 4.7 | 3.2 | 5.4 | 1.1 | 4.9 |
| | 23 | 8 | 16.6 ± 0.9 | 3.0 ± 0.6 | 3.7 | | | | |
| | 23 | 8 | 12.7 ± 1.6 | 4.4 ± 1.0 | 2.8 | | | | |
| | 23 | 14 | 11.9 ± 0.6 | 1.9 ± 0.1 | 2.6 | | | | |
| | 23 | 16 | 8.6 ± 0.1 | 1.5 ± 0.1 | 1.9 | | | | |
| | 23 | 30 | 5.8 ± 0.2 | 1.3 ± 0.1 | 1.3 | | | | |
| | 23 | 34 | 5.3 ± 0.2 | 1.3 ± 0.1 | 1.2 | | | | |
| 16 | 55[e] | 3 | 7.6 ± 0.3 | 0.6 ± 0.4 | | | | | |
| | 17 | 5 | 17.0 ± 1.4 | 1.9 ± 0.2 | 2.2 | | | | |
| | 17 | 11 | 16.8 ± 0.4 | 1.3 ± 0.2 | 2.2 | | | | |

TABLE II
(*Continued*)

| *N* | *T*, °C | Conversion, % | E/C | *t*/*c* | Selectivity[a] | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | P = solid[b] | P = hexatic B[c] | P = solid[c] | P = Phase II[d] | P = Phase I[d] |
| 17 | 55[e] | 5 | 2.4 ± 0.1 | 1.8 ± 0.1 | | | | | |
| | 39[f] | | 3.9 ± 0.5 | 3.1 ± 0.2 | | | | | |
| | 19 | 4 | 20.6 ± 1.2 | 1.5 ± 0.2 | 8.6 | 4.1 | 7.3 | 1.4 | 4.5 |
| | 19 | 8 | 38.5 ± 0.8 | 3.8 ± 0.2 | 16.0 | | | | |
| | 19 | 10 | 28.0 ± 0.5 | 2.7 ± 0.2 | 11.7 | | | | |
| 18 | | | | | | 4.1 | 8.4 | | |
| 19 | 23[f] | 23 | 4.5 ± 0.3 | 2.1 ± 0.2 | | 4.1 | 5.6 | | |
| | 23 | 10 | 32.5 ± 1.0 | 3.4 ± 0.9 | | | | | |
| | 23 | 13 | 20.8 ± 2.9 | 2.3 ± 0.5 | | | | | |
| | 23[g] | 17 | 16.1 ± 1.4 | 2.3 ± 0.8 | | | | | |
| | 23 | 43 | 7.8 ± 1.3 | 1.6 ± 0.5 | | | | | |
| | 23 | 46 | 3.8 ± 0.3 | 1.3 ± 0.2 | | | | | |
| 20 | | | | | | 2.6 | 4.9 | 3.7 | 33.7 |

[a] $(E/C)_p/(E/C)_i$; P anisotropic phase type, i isotropic phase. [b] Neat phase. [c] Butyl stearate, ref.[5c]. [d] Heneicosane, ref.[7]. [e] Melt phase. [f] Hexane solution, ref.[6a]. [g] Average of 2 analyses only.

permit formation of *i-BR* and then its conversion to the preproduct *BR* conformations. Due to experimental complications with such measurements, we have not attempted to compare the quantum efficiencies for formation of photoproducts from the 2-alkanones studied here. Instead, we have measured the ratios of E/C and *t/c* photoproducts in hopes of relating them to the chain flexibility experienced by the alkanones. It should be noted that the photoproduct ratios probe a *specific* set of related chain motions rather than a simple probability of encountering single *cisoid* bends along the total carbon chain.

Examination of the data in Table II reveals that all of the 2-*N* yield similar E/C and *t/c* ratios upon irradiation in their melt or isotropic solution phases. Comparison of those ratios with photoproduct ratios obtained from the solid phases at various percents of conversion provides the selectivity of the reaction expressed by the alkanone's lattice structure. There is no discernible correlation between the E/C selectivities from the 2-*N* solid phases and their reduced temperatures, $T_{mp} - T_{h\nu}$ (the difference between the melting point and irradiation temperature). Although the magnitude of the reduced temperature must be of some importance, it does not appear to be a significant factor in the range explored.

The very small selectivity in cyclobutanol diastereomers is reminiscent of results found upon irradiation of the same 2-*N* in aqueous gel phases comprised of layers of stearate or stearate and 1-octadecanol[6]. In those systems, the absence of selectivity in *both* E/C and *t/c* ratios could be attributed to solvation of the *BR* by water molecules[4]. Although the neighboring 2-alkanone molecules of the neat solid phase cannot act as hydrogen-bond donors to a *BR*, they can be (and probably are) hydrogen-bond acceptors since their carbonyl groups will be adjacent in a layer to the hydroxyl group of a *BR* (ref.[11a]). We have demonstrated in another ordered phase that hydrogen-bonding interactions between a *BR* and neighboring rod-like host molecules can mediate both Norrish II reactivity and selectivity[5a]. Similar considerations should apply here; however, in the absence of additional factors which augment the small steric differences between *c-BR*$_1$ and *c-BR*$_2$ from 2-alkanones, almost no selectivity in the *t/c* ratios is to be expected[3].

All of the 2-*N* (except 2-*17*) produce E/C ratios which decrease significantly at even modest percents of conversion. We believe that the disturbance created by the forced introduction of photoproducts into the lattice after one molecule reacts leads to much lower selectivity in the photoconversion of neighboring alkanones when they undergo photolysis. Also, although we have not measured quantum yields, we suspect that the efficiency of conversion of alkanones at disturbed sites is greater than at ones which are pristine. Both the presence of disturbed sites and the enhanced ability of alkanones near them to undergo reactions may contribute to the reason why the solid photoproduct ratios approach the values found from the melt as the percent of conversion increases.

The same factors may explain why the correlation between photoproduct ratios and percents of conversion (especially for 2-*17*) is not smooth. If, as assumed, the disturbed sites facilitate further product formation, the ratios reported are a weighted average of the selectivities exhibited by a myriad of different sites; even experiments at the same percent of conversion may yield somewhat different ratios depending upon the size of crystals, their orientation with respect to the lamp, the light flux, and the size of powder grains.

In spite of these uncertainties, it is possible to establish that the ambience associated with the undisturbed lattice environments of the 2-*N* (i.e., the crystal before irradiation) is able to control some motions of ***i-BR*** leading to products much more effeectively than others. Thus, *t*/*c* values are not very different from the melt and the solid, but E/C ratios appear to have *limiting values* (i.e., those when the percent of conversion approaches zero) from the solids which are several fold higher than from the melts.

In an attempt to ascertain how high the limiting values might be, we allowed only the extreme red edge of the n → π* band to absorb the incident radiation by passing it through a 7-51 filter (Fig. 1). Under these circumstances, the probability that molecules near the surface of the reaction capillary will undergo reaction is attenuated, also. More

TABLE III
Product ratios from irradiation of neat solid 2-*17* with the pyrex and 7-51 glass filtered output of a 500 W high pressure mercury arc at 30 °C

| Conversion, % | E/C | *t*/*c* |
|---|---|---|
| 3.3 ± 0.1 | 61.9 ± 7.7 | 2.9 ± 0.9 |
| 3.7 ± 0.5 | 47.5 ± 8.2 | 1.8 ± 0.4 |
| 6.9 ± 1.5 | 14.9 ± 1.0 | 4.1 ± 3.9 |

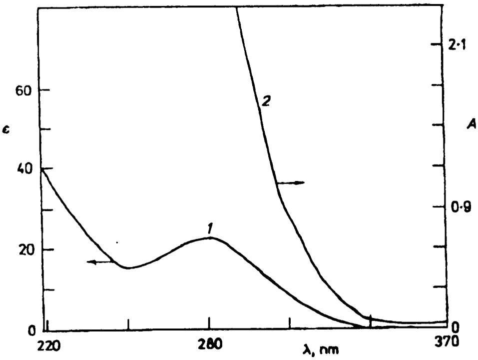

FIG. 1
Absorption spectra of 2-heptadecanone in hexane (*1*) and of 7-51 filter (*2*)

importantly, molecules throughout the sample have an almost equal probability of being excited. Thus, the mole fraction of alkanones which are excited in disturbed lattice sites at any percent of conversion is decreased significantly, allowing photoproduct ratios at low percents of conversion, especially, to reflect the true selectivity of the medium. The data from Table III for irradiation of 2-*17* indicate that the *t/c* ratios remain isotropic-like even under these stringent conditions. However, the E/C ratios are very high, and suggest that limiting ratios near 100 should be expected.

These results and those obtained from irradiations of the same alkanones in layered phases of foreign hosts offer some interesting comparisons (Table II). When irradiated in either of the solid phases of heneicosane, (2-*13*) yields non-selective Norrish II photoproduct ratios; the 2-*15* and 2-*17* alkanones exhibit some selectivity only when irradiated in the more ordered solid phase (Phase I) of heneicosane[7]. In fact, 2-eicosanone (2-*20*), a 2-alkanone expected to fit well in the layered heneicosane matrices, yields E/C *and t/c* ratios from solid solutions which are higher than the limiting ratios from the neat crystals[7,18]. The *t/c* ratios from 2-*17* in the solid and hexatic B phases of butyl stearate are, again, non-selective; the E/C ratios are comparable to those measured from the neat solid[5c].

Thus, we conclude that *the neat crystals confer no special order upon the reactive sites of the 2-alkanones.* Even in undisturbed lattice sites, the reacting ketones experience a "soft-crystalline" environment which is less rigid than that produced upon dissolution of 2-*20* into Phase I of heneicosane. Although the cybotactic region afforded by a neat crystal will always be more ordered (and more constrained with respect to molecular motions) than the melt phase, the conformational freedom available to individual functional groups on molecules in neat solid phases may be greater than when those molecules are imbedded in a foreign host.

*We thank the National Science Foundation and the Naval Research Laboratory for financial support of this work. Dr Alberto Nuñez is thanked for his technical assistance and advice.*

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