ticancer antibiotic anthracyclinones, in 89% yield and in 85% ee.[11] Friedel–Crafts reaction[12] of **5** with phthaloyl chloride followed by recrystallization of the product afforded nearly optically pure **6** ($[\alpha]^{20}_{D}$ −57.2° ($CHCl_3$))[11] in 68% yield.

The observed enantioface differentiation is kinetically controlled by the relative stabilities of the diastereomeric transition states and is not a result of thermodynamic control governed by the stability of the resulting osmate ester–diamine complex **2**.[13] Further studies are in progress to establish the scope and limitation and to elucidate mechanism of the enantioselective dihydroxylation of olefins by osmium tetroxide employing D_2 symmetric chiral diamine.[14]

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[11] Jew, S.; Terashima, S.; Koga, K. *Chem. Pharm. Bull.* **1979**, *27*, 2351. Arcamone, F.; Bernardi, L.; Giardino, P.; Patelli, B.; Di Macro, A.; Casazza, A. M.; Pratesi, G.; Reggiani, P. *Cancer Treat. Rep.* **1976**, *60*, 829. Kimura, Y.; Suzuki, M.; Matsumoto, T.; Abe, R.; Terashima, S. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 415.

[12] Sartori, G.; Casnati, G.; Bigi, F.; Robles, P. *Tetrahedron Lett.* **1987**, *28*, 1533.

[13] The structure of the osmate ester (**2**, R^1, R^2 = Ph; R^3 = H) was firmly established by ^{1}H and ^{13}C NMR and further established by X-ray crystallography (We are grateful to Prof. Y. Iitaka for X-ray crystallography.). Treatment of excess *dl*-osmate ester (pyridine ligand) (4 equiv), prepared in pyridine, with (−)-**1** gave a nearly 1:1 mixture of two diastereomers. This ligand exchange reaction revealed the nearly equal thermodynamic stability of the diastereomeric osmate esters.

[14] The mechanism of osmium tetroxide oxidations of olefins has been the subject of focused discussion. Schröder, M. *Chem. Rev.* **1980**, *80*, 187. Sharpless, K. B.; Teranishi, A. Y.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **1977**, *99*, 3120. Jørgensen, K. A.; Hoffmann, R. *J. Am. Chem. Soc.* **1986**, *108*, 1867.

Control of Norrish II Reactions of 2- and *sym*-Alkanones by the Ordered Solid Phases of Heneicosane[1]

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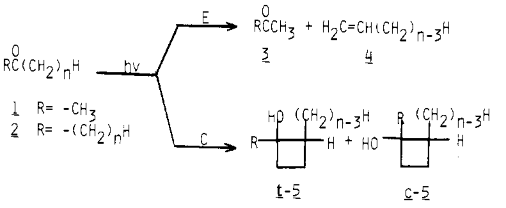
Previously, we exploited the Norrish II reactions of ketones (eq 1) to assess the limitations of the influence of solvent order on solute dynamics.[2] We find that photolyses of 2- and *sym*-alkanones (**1** and **2**) provide sensitive monitors of local solvent order in the smectic B and solid phases of *n*-butyl stearate (BS)[3] and in the aqueous gel phases of potassium stearate, potassium palmitate, and 1/1 potassium stearate/1-octadecanol.[1,4] Each lipophilic solvent molecule consists of a polymethylene chain and a head group.



(1)

Table I. Norrish II Product Ratios from **1** and **2** in the Isotropic (45 °C), the Hexagonal Solid (35 °C; Phase II), and Orthorhombic Solid (25 °C; Phase I) Phases of Heneicosane

C chain length of ketones	*T* (°C)	**1**		**2**	
		E/C	t/c	E/C	t/c
15	45	3.3 ± 0.1	1.9 ± 0.2	1.5 ± 0.1	2.1 ± 0.1
	35	3.7 ± 0.3	2.4 ± 0.2	1.8 ± 0.4	1.8 ± 0.1
	25	16.2 ± 0.4	3.0 ± 0.1	2.6 ± 0.1	1.5 ± 0.1
17	45	3.3 ± 0.2	1.7 ± 0.4	1.4 ± 0.1	2.4 ± 0.1
	35	4.6 ± 0.7	3.4 ± 0.2	2.4 ± 0.1	5.9 ± 0.1
	25	15.0 ± 4.0	2.4 ± 0.4	5.0 ± 0.9	1.5 ± 0.7
21	45	2.4 ± 0.6	1.0 ± 0.1	1.8 ± 0.1	2.5 ± 0.1
	35	5.7 ± 1.3	2.5 ± 0.2	3.5 ± 0.1	24.9 ± 3.0
	25	46.0 ± 16.0	3.6 ± 0.9	69.0 ± 7.0	0.9 ± 0.4
23	45	3.1 ± 0.7	1.9 ± 0.2	2.0 ± 0.1	2.0 ± 0.2
	35	1.6 ± 0.3	2.4 ± 0.2	2.9 ± 0.1	10.8 ± 0.5
	25	3.6 ± 0.1	3.0 ± 0.1	8.1 ± 0.3	9.0 ± 0.8
25	45			2.3 ± 0.4	2.9 ± 0.3
	35			2.9 ± 0.5	18.0 ± 1.0
	25			4.3 ± 0.6	15.0 ± 0.7

To discern how ordered polymethylene chains in the *absence* of a head group influence the Norrish II reactions, we have irradiated **1** and **2** in the isotropic and the two solid phases of heneicosane ($C_{21}H_{44}$). We find that these ordered *n*-alkane phases are more sensitive and selective toward size and shape changes of the ketones than are the analogous phases of BS and the aqueous gels. Above 40 °C, heneicosane is an isotropic liquid in which the alkane chains are weakly correlated with each other and with cylindrically shaped solutes.[5] From 40.2[6] to 32.5 °C, a solid phase (phase II) obtains.[7] The molecules are elongated (approaching *all-trans*) and are stacked hexagonally in layers. Gauche conformational defects are much more prevalent near the ends than in the middle of the chain.[8] Individual molecules rotate rapidly about their long axes, which are perpendicular to the layer planes. This phase bears a close resemblance to the liquid–crystalline smectic B phase of BS[9a] and the lipophilic layer organization of the aqueous gels.[9b]

Below 32.5 °C, another solid phase (phase I) forms in which the molecular rotational motions are quenched and the hexagonal arrangement within layers collapses to orthorhombic.[8] Very little deviation from the *all-trans* conformation is observed. The organizations of phase I and of a smectic E phase or the solid phases of BS[9a] are very similar.

In previous publications we have discussed in detail the mechanistic basis for solvent order induced product selectivity in Norrish II reactions.[2-4] In essence, the immediate precursors to the elimination products (**3** and **4**) and diastereomeric cyclization products (*t*-**5** and *c*-**5**) are different conformers of the same hydroxy 1,4-biradical. If solvent order enhances the population of one conformer over the others, its product will be formed preferentially. The basis for that preference may be related to the ease with which a particular intermediate may be incorporated within a solvent matrix (size and shape considerations) and/or to specific attractive interactions between functional groups on an intermediate molecule and neighboring solvent molecules (e.g., hydrogen bonding). Since the latter is not available to hydroxy 1,4-biradicals in heneicosane, size and shape considerations can be investigated without complications.

The resemblance of **1** and **2** to the shape of heneicosane leads us to conclude[1-4] that the ketones should be incorporated into the solvent layers with their long axes perpendicular to the layer plane.

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[1] Part 27 in our series: Liquid-Crystalline Solvents as Mechanistic Probes. For part 26, see: Treanor, R. L.; Weiss, R. G. *J. Am. Chem. Soc.*, submitted for publication.

[2] (a) Nerbonne, J. M.; Weiss, R. G. *Isr. J. Chem.* **1979**, *18*, 266. (b) Hrovat, D. A.; Liu, J. H.; Turro, N. J.; Weiss, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 7033. (c) Zimmermann, R. G.; Liu, J. H.; Weiss, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 5264.

[3] Treanor, R. L.; Weiss, R. G. *Tetrahedron* **1987**, *43*, 1371.

[4] Treanor, R. L.; Weiss, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 3137.

[5] (a) Lemaire, B.; Bothorel, P. *J. Polym. Sci.: Polym. Lett. Ed.* **1978**, *16*, 321. (b) Lamotte, M.; Joussot-Dubien, J. *Chem. Phys.* **1973**, *2*, 245. (c) Clement, C.; Goulin, J.-C. *C. R. Acad. Sci.* (*Paris*) **1978**, *286C*, 597.

[6] Heneicosane in this work (Aldrich, recrystallized 5× from 95/5 ethanol/toluene), mp 39.2–39.5 °C (uncorrected) was >99.5% pure by GLC analysis.

[7] (a) Schaerer, A. A.; Busso, C. J.; Smith, A. E.; Skinner, L. B. *J. Am. Chem. Soc.* **1955**, *77*, 2017. (b) Muller, A. *Proc. R. Soc.* (*London*) **1932**, *138A*, 514.

[8] (a) Maroncelli, M.; Strauss, H. L.; Snyder, R. G. *J. Chem. Phys.* **1985**, *82*, 2811. (b) Maroncelli, M.; Qi, S. P.; Strauss, H. L.; Snyder, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 6237.

[9] (a) Krishnamurti, D.; Krishnamurthy, K. S.; Shashidar, R. *Mol. Cryst. Liq. Cryst.* **1969**, *8*, 339. (b) Vincent, J. M.; Skoulios, A. *Acta Crystallogr.* **1966**, *20*, 432, 441, 447.

0002-7863/87/1509-6215$01.50/0

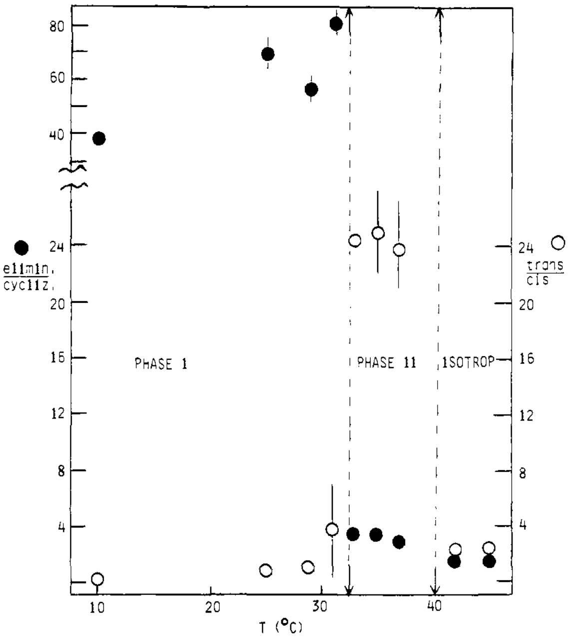

Figure 1. Norrish II product ratios from 11-heneicosanone in *n*-heneicosane versus temperature. Note the break in the E/C scale.

In fact, all of the ketones at 1% (w/w) concentration appeared to be well-dispersed in the solvent matrices. No evidence for two coexisting phases or for microcrystallites could be adduced from optical microscopy. Also, it is known that crystalline *n*-alkanones do not undergo Norrish II reactions.[3,10]

In Table I, elimination/cyclization (E/C) and trans/cis cyclobutanol (t/c) ratios are presented for **1** and **2** which are shorter than, the same length as, and longer than heneicosane. The ratios were obtained from irradiations[11] at three representative temperatures, which include the isotropic phase (45 °C), phase II (35 °C), and phase I (25 °C).

None of the t/c ratios for 2-alkanones in any of the solvent phases differs appreciably from what is found (and expected[3]) in the isotropic phase. This result can be attributed to two principal factors: (a) the diastereomeric precursors of *t*-**5** and *c*-**5** (from **1**) are very similar in size and shape; (b) the locus of reaction in **1** is near the most disordered part of a solvent layer.

When, as in **2**, the locus of reaction is moved to the more ordered center of a solvent layer, very different t/c cyclobutanol selectivities are found. Although both phase I and phase II direct the product ratio, they respond very differently to changes in the length of **2**. Most notable is very low t/c ratios from **2** shorter than or equal to the length of solvent and the rather high t/c ratios from longer ketones. Since molecular models indicate that the 2-derived biradical precursors to *t*-**5** and *c*-**5** are very different in shape, we expected that the more ordered solid phase would be the more selective (but see ref 3).

The E/C ratios from **1** and **2** indicate that phase I does exert greater control over the biradical precursors of **3** (or **4**) and **5** than does phase II. However, the magnitude of that difference (in fact, the near lack of E/C selectivity in phase II) was not anticipated. Comparison of E/C ratios in phase I from 11-heneicosanone and 12-tricosanone indicates that extending the solute length by ca. 3 Å (two C–C bonds) is sufficient to reduce product selectivity by a factor of 10!

Figure 1 shows, in detail, the influence of solvent phase on the product ratios from 11-heneicosanone, the ketone whose length matches solvent best. It is noteworthy that in the ordered phase which influences greatly one product ratio, the other is near its isotropic values. The E/C ratios in phase I and the t/c ratio in phase II are the largest observed for any of the ketones investigated: the greatest selectivity obtains when the initial ketone is incorporated best into the solvent matrix. Similar selectivities, but smaller magnitudes, have been observed by us and Leigh in other ordered solvents.[1-4,12] Additionally, Snyder et al.[13] have shown that the phase behavior of an *n*-alkane can be modified by the addition of a different *n*-alkane as solute.

Further evidence for this assertion was found in studies of phase II–isotropic phase transitions when heneicosane was doped with ketone. Almost no depressions of the melting point or expansions of the melting range were detected at 1% ketone doping (where the photochemistry was conducted). Large changes in both the transition temperature and melting range were observed when the ketone, present in 10% loading, was much longer or shorter than heneicosane. However, 10% of 2-heneicosanone or 11-heneicosanone caused very slight depressions in the transition temperature (ca. 1 deg) and expansions of the melting range (<1 deg) of heneicosane.

The data presented here provide clear evidence that solvent order that does not rely upon strong attractive forces can control the dynamics of the Norrish II reaction.[14] They also show that slight changes in phase order can result in drastic changes in solute reactivity. The trends of solvent effects on product ratios observed with heneicosane are the same as, but more pronounced than, were reported with the analogous (but less ordered) phases of BS[3] or amphiphile gels.[1,4]

We intend to investigate further the solvent-related factors that are responsible for the abrupt changes in product ratios and to explore how other solid phases of longer alkanes[8] affect solute reactivity.

Acknowledgment. We thank Richard L. Treanor for his help in some aspects of this work. Financial support form the National Science Foundation (Grant CHE85-17632) is gratefully acknowledged.

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(10) Slivinskas, J. A.; Guillet, J. E. *J. Polym. Sci.: Polym. Chem. Ed.* **1973**, *11*, 3043.

(11) All irradiations were performed with a Pyrex-filtered 450-W medium-pressure Hg lamp on N_2-saturated samples containing 1% (by weight) of ketone. Analyses by GLC were conducted at least in triplicate and conversions of ketones for E/C ratios were always $\leqslant$15% (where no secondary irradiation products could be detected); t/c ratios were determined on aliquots irradiated to ca. 65% conversion, but did not differ from those measured at $\leqslant$15% conversion. Other experimental procedures are similar to those described in ref 3.

(12) Leigh, W. J.; Stephanus, J. *Tetrahedron* **1987**, *43*, 1393.

(13) Maroncelli, M.; Strauss, H. L.; Snyder, R. G. *J. Phys. Chem.* **1985**, *89*, 5260.

(14) For other examples of control by restricted environments of Norrish II selectivities, see: (a) Ariel, S.; Ramamurthy, V.; Scheffer, J. R.; Trotter, J. *J. Am. Chem. Soc.* **1983**, *105*, 6959. (b) Turro, N. J.; Wan, P. *Tetrahedron Lett.* **1984**, *25*, 3655. (c) Casal, H. L.; de Mayo, P.; Miranda, J. F.; Scaiano, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 5155.