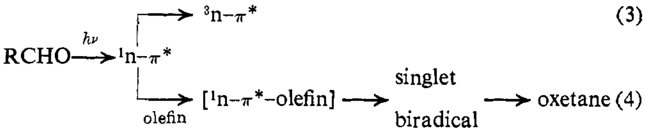
to vary for either isomeric 2-butene. The quantum yield is of the order of 0.13–0.15 in 5 *M* 2-butene indicating that there is an efficient mode of radiationless deactivation of the excited state. There is no detectable isomerization of starting 2-butenes. In view of the known photoreactivity of alkanals toward 1,3-dienes,[9] attempted quenching of oxetane formation by 1,3-dienes was not undertaken.

The Paterno–Büchi reactions of aromatic carbonyl compounds with isomeric olefins are known to give essentially the same mixture of isomeric oxetanes[10] and to cause extensive isomerization of the starting olefins.[11] The reactive intermediate in these reactions is the $^3n-\pi^*$ of the carbonyl compounds or the $^3n-\pi^*$–olefin complex.[3a,3b] Our observations that the photocycloaddition of ethanal to 2-butenes proceeds with a high degree of stereoselectivity and that there is no detectable isomerization of starting 2-butenes during the reaction are in marked contrast to the reactions from aromatic carbonyl compounds, and suggest that the reactions from ethanal proceed *via* its $^1n-\pi^*$.[12] Since the addition is highly stereoselective but not stereospecific, a singlet biradical intermediate may be formed in the reaction. The ring closure of singlet biradicals is known to be appreciably faster than the bond rotation which will cause randomization in the product formation.[13] A secondary biradical intermediate will be formed from the reaction of $^1n-\pi^*$ of an alkanal with either terminal or nonterminal *n*-alkenes. In view of the fact that ethanal reacts with 1-octene photochemically to give 2-decanone and propanal reacts with 1-hexene to give 3-nonanone as the major products, while they react with nonterminal olefins to give oxetanes, the nature of product formed in these reactions is not determined by the stability of the intermediate biradical but rather by the degree of alkylation on the olefinic double bond. Since the carbonyl oxygen is electron deficient in the $n-\pi^*$ states of carbonyl compounds, the $^1n-\pi^*$ of alkanals may interact with the π system of olefins to form an exciplex. The ionization potential of an olefin decreases with an increasing number of alkyl substituents;[14] the ease of exciplex formation will then depend on the degree of alkylation of the olefin. Our results imply that oxetane formation is controlled by the ease of formation of the exciplex which may collapse subsequently to give the biradical intermediate. Turro and his coworkers have suggested such an exciplex as the intermediate in the photocycloaddition of alkanones to a variety of olefins.[2b-d] Since there is no appreciable isomerization of the starting olefin during the reaction, the behavior of $^1n-\pi^*$ of alkanals differs from that of alkanones such that the intersystem crossing of $^1n-\pi^*$ of alkanals or its exciplex is not an important process in the presence of nonterminal olefins (reaction 3). Similar exciplexes from $^3n-\pi^*$ of aromatic carbonyl compounds have been suggested in other Paterno–Büchi reactions.[3a,3b] In conclusion, we propose the following sequence of steps in the Paterno–Büchi reaction of alkanals (reaction 4).



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Nucleation Studies of Supercooled Cholesteric Liquid Crystals

Sir:

Supercooling of liquids before crystallization lends itself to thermodynamic interpretation of the processes involved in nucleation and growth.[1] In this regard, the high degree of supercooling in cholesteric liquid crystals is unique. Here, for example, supercooling of a liquid crystalline compound by 86°K persisted for several minutes. Nucleation proceeds from a semiordered[2] (liquid crystalline) to an ordered (crystalline) phase. We now report the first application of nucleation rate theory to this process using cholesteryl nonanoate and caproate and mixtures thereof.

Samples were placed in glass tubes, which were evacuated and sealed at 10^{-5} mm. The sample was heated to the isotropic state, rotated to ensure a thin liquid coating on the tube, then plunged into a thermostated bath. The time was noted at the first visual evidence of crystallinity, which was always at the liquid crystal–vacuum interface. Nucleation times were corrected for heat transfer from sample tubes to the bath[3] (less than 6 sec). A Perkin-Elmer differential scanning calorimeter (DSC-1B) afforded the enthalpies of transition.

The plot of ln (nucleation rate) (uncorrected for any crystal growth) *vs.* $1/T$ for cholesteryl nonanoate (Figure 1) is typical of mixed and pure systems. The maximum exists because at low temperature nucleation is transport controlled while at high temperatures it is governed by the thermodynamic driving force of supercooling. Turnbull and Fisher[4] and Mandelkern[1] derived an expression for the rate of nucleation in condensed systems

$$N = N_0T\exp(-E_{\mathrm{d}}/RT) \times \exp[-\alpha 8\pi\sigma_{\mathrm{u}}{}^2\sigma_{\mathrm{e}}T_{\mathrm{m}}{}^2/R(\Delta H)^2T(\Delta T)^2] \quad (1)$$

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[1] L. Mandelkern, "Crystallization of Polymers," McGraw-Hill, New York, N. Y., 1964, p 215.

[2] G. W. Gray, "Molecular Structure and the Properties of Liquid Crystals," Academic Press, New York, N. Y., 1962, p 66.

[3] R. B. Bird, W. E. Stewart, and E. N. Lightfoot, "Transport Phenomena," Wiley, New York, N. Y., 1960, p 356.

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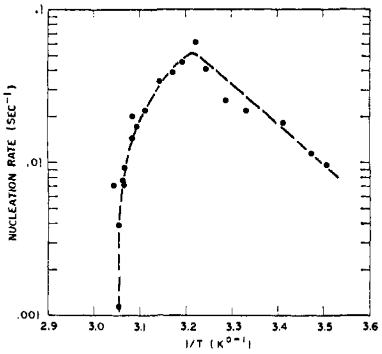

Figure 1. Plot of ln (nucleation rate) *vs.* $1/T$ for cholesteryl nonanoate.

where N is the nucleation rate, E_d is the free energy of activation for transport across the liquid crystal–nucleus interface, σ_e and σ_u represent interfacial energies for cylindrical nuclei, ΔH is the enthalpy of fusion, T_m is the melting point, T is the bath temperature, $\Delta T = T_m - T$, and α represents the proportion by which the homogeneous critical free energy is reduced by secondary nucleation processes. Equation 1 describes the nucleation data. For temperatures below the rate maximum the standard linear least-squares fit of ln (rate/T) *vs.* $1/T$ yielded $E_d = 9.3 \pm 1.0$ kcal/mol for cholesteryl nonanoate.[5] For temperatures above the rate maximum, the interfacial energies were obtained (Table I) from the derived slopes,[6] T_m, and ΔH.

Table I. Enthalpies of Fusion and Interfacial Energies of Cholesteryl Nonanoate–Caproate Mixtures

Material^a	ΔH,^{b} kcal/mol	$\sigma = (\sigma_u^2\sigma_e)^{1/3}$,^{c} erg/cm^2
Cholesteryl nonanoate (N)	5.29 (±0.22)	2.15
Cholesteryl caproate (C)	6.62 (±0.10)	0.871
89.3% N-10.7% C	4.31 (±0.11)	1.49
73.4% N-26.6% C	4.46 (±0.61)	0.336
47.9% N-52.1% C	4.38 (±0.17)	0.327
23.5% N-76.5% C	3.55 (±0.15)	0.444
9.27% N-90.7% C	4.50 (±0.20)	1.04

^{a} Mole percentages. ^{b} Standard deviation given in parentheses. ^{c} ±35%.

The interfacial energies for cholesteryl nonanoate and caproate are an order of magnitude lower than the lowest reported values[7] for other monomeric organic materials. (In order for these energies to approach normal values, α would have to be less than 10^{-3}.) This suggests that on a molecular level the mesophase is more like the solid than the isotropic phase, in accord with the postulate of short-range ordering in the liquid crystalline state.[2] (Short-range ordering should affect nucleation, as it is a rearrangement of molecules and not of domains.)

For the mixtures, the interfacial energies exhibit a minimum which is lower than that of either pure component. This must result from a favorable cooperative interaction of the components in both the mesophase and the crystal phase. Also, of particular interest is the rapid decrease in ΔH upon addition of a few mole per cent of one component to the other (Table I). These data again imply a strong interaction between the components. The nature of the interaction is still under investigation.

We will report the correlation of nucleation rate, interfacial energies, and phase diagrams with structure in subsequent publications.

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[5] Owing to crystallization, we were unable to obtain viscosity data in the supercooled liquid crystal state for correlation with rate below maximum.

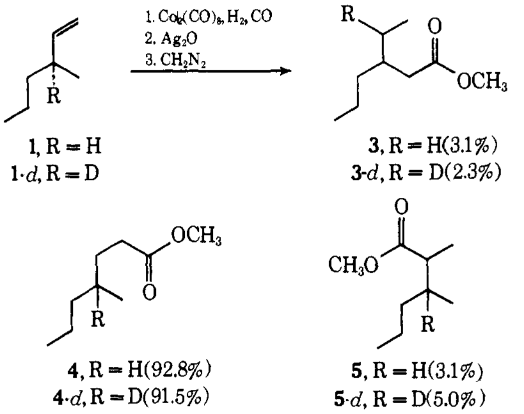
[6] A linear least-squares fit of ln (rate/T) *vs.* $T_m^2/T(\Delta T)^2$ was used, assuming $\alpha = 1$.

[7] D. G. Thomas and L. A. K. Staveley, *J. Chem. Soc.*, 4569 (1952).

Hydroformylation of 3-Methyl-1-hexene-*3-d*$_1$. Evidence Against Direct Formylation of a Methyl Group in the "Oxo" Reaction

Sir:

The hydroformylation of (+)-(*S*)-3-methyl-1-hexene (**1**) under conditions which minimize olefin isomerization[1] has been reported to give 3.1% (*R*)-3-ethylhexanal (**2**) in addition to the normal hydroformylation products 4-methylheptanal and 3,4-dimethylhexanal.[2] Conversion of **2** to the corresponding methyl ester **3** of known absolute rotation indicated that **2** had been formed with 70% net retention of configuration. Consequently, 2-ethyl-1-pentene was excluded as an intermediate in the formation of **2**.



Pino, *et al.*, proposed that **2** arose *via* direct insertion of cobalt into a carbon–hydrogen bond of the methyl group of **1** followed by hydroformylation.[2] The related insertions of transition metals into the ortho carbon–hydrogen bonds of arylphosphines, arylphosphites, benzylamines, and azobenzenes[3] and into the methyl groups of methylphosphines[4] and *o*-tolylphosphines[5] are now well documented. However, this proposed insertion of cobalt into the methyl group of

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[3] G. W. Parshall, *Accounts Chem. Res.*, 3, 139 (1970), and references therein.

[4] J. Chatt and J. M. Davidson, *J. Chem. Soc.*, 843 (1965).

[5] M. A. Bennett and P. A. Longstaff, *J. Amer. Chem. Soc.*, 91, 6226 (1969); R. Mason and A. D. C. Towl, *J. Chem. Soc. A*, 1601 (1970).