C–H bond cleavage in the transition state.[11] This is not consistent with an E2 mechanism. (ii) Addition of *t*-butylthiol depresses reaction rates. This observation is consistent with an ElcB mechanism or at least with an E2 process that lies well to the carbanion side.[11]

Rate constants for ethoxide reactions cover a 10^{11}-fold range of reactivity. Reactions with compounds Ia and Ib were too fast to measure in ethanol; estimates from rate constants obtained in water are included. The enormous difference between the constants for the first (Ip) and second (Ib and Ic) row onium salts[12] strongly suggests participation of d orbitals in stabilization of the intermediate carbanion. As expected, the sulfonamide Ik and the carboxamides Im and Io are less reactive than the corresponding esters If and Ij. Further, the phenyl sulfone Ig is more reactive than the methyl sulfone Ih, and these sulfones are much more reactive than the corresponding sulfoxides Il and In.

A rectilinear relationship is found between log $k_{\text{elimination}}$ and the limited available values of σR^-,[13] confirming that direct resonance interaction between the substituent and the intermediate carbanion is important. This correlation makes it likely that in the expression for the rate constant, k_{obsd}, of this second-order ElcB process, $k_{\text{obsd}} = Kk_2$, the magnitude of k_{obsd} is primarily controlled by the dissociation constant, K.[14] The observed rate constants thus provide a measure of the effects of these substituents on the dissociation of the adjacent C–H bond. Support for the conclusion that the magnitude of k_2 is insensitive to the nature of the activating substituent comes from the effect of substituents in the eliminated aryloxy group upon the rate of elimination. In the substrates Ic, Ig, and Il, whose rate constants cover a range of 10^5, approximate Hammett ρ values so far obtained differ only very slightly.

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(12) With the onium salts as with some other substrates, such as Ii, elimination of the activating group is formally possible as a competitive reaction. In all cases quantitative yields of phenol are obtained, together with high yields of products derived from olefin II.

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(14) If so, a direct relationship between elimination rate and the thermodynamic acidity of the substrate should exist. Acidity data in this range of pK_a is too sparse, scattered, and inconsistent to be of very much value in this respect.

J. Crosby, C. J. M. Stirling
Department of Chemistry, King's College,
Strand, London, W.C. 2, England

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Complete Determination of the Alignment of CH_2Cl_2–CD_2Cl_2 Molecules in Poly-γ-benzyl-L-glutamate Solution by the Nuclear Magnetic Resonance of ^{35}Cl, ^{2}D, and ^{1}H. Comparison of Electric and Magnetic Ordering[1]

Sir:

Concentrated solutions of poly-γ-benzyl-L-glutamate dissolved in CH_2Cl_2 (and CD_2Cl_2) are liquid crystalline[2] and acquire order when placed in magnetic[3,4] and electric[5,6] fields. Solute ordering constrains the motion of the *solvent* molecules so that their intramolecular traceless tensor interactions are not averaged to zero.

We have determined additional *nmr characteristics of the solvent* in the liquid crystalline state of this system.[3,4] Comparison of the integrated signal intensity of the high-resolution (hr) proton magnetic resonance (pmr) with that of a measured quantity of added TMS indicates that to within experimental error *all* the solvent molecules contribute to the hr pmr spectra.

We have extended the nmr measurements to the ^{35}Cl and ^{2}D nuclei to extract, insofar as possible, information about the ordering of the solvent. The anisotropic motion is reflected by the residual dipolar splitting of the pmr,[7,8] by the quadrupolar splitting of the deuterium magnetic resonance (dmr),[8] and by the occurrence of quadrupolar-induced satellites in the ^{35}Cl nmr spectrum, reported here for the first time.

For calculating the "distortion theory" orientation parameters, S_{ii},[7] we defined a molecule-fixed frame in which the $1 = x$ axis is parallel to the Cl–Cl direction, the $2 = y$ axis is parallel to the H–H direction, and $3 = z$ is the C_{2v} axis, and assumed that the axis of constraint[7] of the solvent was directed along the magnetic field H_0 ($\Omega = 0$). Neglecting asymmetry parameters, the frequency separation, in hertz, between the two lines in the dmr in CD_2Cl_2 is[7,8]

$$\Delta_{\mathrm{D}}{}^{\mathrm{Q}} = \pm\frac{e^2Qq(\mathrm{D})}{2h}[-S_{11} + S_{22}(3\sin^2\alpha - 1) + S_{33}(3\cos^2\alpha - 1)] \quad (1)$$

where $eq(\mathrm{D})$ is the gradient along the CD bond, assumed to be the largest component of the electric field gradient, and $2\alpha = 112.0°$ is the DCD bond angle.

The frequency separation between the outer two lines of the triplet ^{35}Cl nmr is

$$\Delta_{\mathrm{Cl}}{}^{\mathrm{Q}} = \pm\frac{e^2Qq(^{35}\mathrm{Cl})}{3h}[S_{11}(3\sin^2\beta - 1) - S_{22} + S_{33}(3\cos^2\beta - 1)] \quad (2)$$

where $2\beta = 111.8°$ is the Cl–C–Cl bond angle.

The separation, in hertz, between the two dipolar components of the solvent pmr is

$$\Delta_{\mathrm{HH}} = \pm 3h(\gamma/2\pi)^2 R_{\mathrm{HH}}{}^{-3} S_{22} \quad (3)$$

where $\gamma/2\pi = 4.257 \times 10^3$, and $R_{\mathrm{HH}} = 1.771$ Å.

For ^{35}Cl, $e^2Qq/2h$ is 36.2 MHz.[9] We deduced $e^2Qq(\mathrm{D})/h = 150$ kHz for deuterium from a dmr T_1 measurement.[10] The values of $\Delta_{\mathrm{Cl}}{}^{\mathrm{Q}}$, $\Delta_{\mathrm{D}}{}^{\mathrm{Q}}$, and Δ_{HH} measured at 24° in solutions which contained ten solvent molecules for each monomer residue are given in Table I.

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Table I. Measured Residual Quadrupole Splittings of the Nmr Spectra of Deuterium (Δ_D^Q) and of ^{35}Cl (Δ_{Cl}^Q) and the Residual Dipolar Splitting of the Proton Nmr (Δ_{HH}) in the CH_2Cl_2 + CD_2Cl_2 Solvent Molecules of a Magnetically Aligned Concentrated Solution of PBLG

$\Delta_D^Q = \pm(368 \pm 3)$ Hz
$\Delta_{Cl}^Q = \pm(112 \pm 20) \times 10^3$ Hz
$\Delta_{HH} = \pm(107 \pm 2)$ Hz

Eight sets of solutions to eq 1–3 are possible when all combinations of signs are considered. From the magnitudes of the splittings alone it is not possible to select the correct set of S parameters and additional information is necessary. In our case it was obtained from the pmr "powder pattern" [11] and the orientation by an electric field. Either of these observations yields the sign of S_{22}.

Immediately after the cholesterically ordered sample[2a] is placed in the magnetic field, the pmr and dmr spectra replicate those of proton pairs in polycrystalline solids[11] except that the interaction in the liquid crystal is attenuated by 10^3.

We draw the analogy and attribute the intensity at the shoulders of the pmr spectrum to proton pairs aligned parallel to H_0. In the course of alignment the intensity of the pmr and dmr shoulders increases at the expense of that in the center of the pattern, and we interpret this change as a proliferation of proton pairs aligned parallel to H_0. This conclusion provides us with the additional information necessary to establish the signs of eq 1–3. These conditions are, then, (a) $\Sigma S_{ii} = 0$, (b) $S_{22} > 0$, and (c) $S_{22} > S_{11}$.

From eq 3 and restriction b, we obtain $S_{22} = +1.7 \times 10^{-3}$, and from the molecular bond angles the remaining S parameters are calculated by eq 2 and 3 (Table II).

Table II. The S_{ii} Parameters as Calculated from the Data of Table I, Eq 1–3, and Restrictions a–c

Signs of Δ_D^Q, Δ_{Cl}^Q	Nucleus			
	Deuterium		^{35}Cl	
	$\Delta_D^Q(+)$	$\Delta_D^Q(-)$	$\Delta_{Cl}^Q(+)$	$\Delta_{Cl}^Q(-)$
$S_{22} \times 10^3$	+1.7	+1.7	+1.7	+1.7
$S_{11} \times 10^3$	−3.2	+6.6	+6.0	−2.8
$S_{33} \times 10^3$	+1.5	−8.3	−7.7	+1.1

S parameters corresponding to $\Delta_D^Q(+)$ and $\Delta_{Cl}^Q(-)$ are self-consistent, as are those corresponding to $\Delta_D^Q(-)$ and $\Delta_{Cl}^Q(+)$. The former set is chosen to conform with condition c and to be consistent with the molecular geometry.

Using the S parameters derived from the pmr and ^{35}Cl nmr and substituting into eq 1, we calculate $e^2Qq(\mathrm{D})/h$ = 160 kHz, in agreement with the T_1-derived value of 150 kHz.

We emphasize that the unique assignment of the S parameters was possible because the pmr and dmr "powder patterns" reveal the parallel and perpendicular splittings; the time development of the spectra establishes $S_{22} > 0$. Similar use of such observations has been made by others.[12] For mesophases which have short reorientation times the "powder pattern" would not be observable. The sign ambiguity in such cases may be resolved by the application of electric fields which orient the mesophases; the dependence of the spectrum upon the angle between the electric and magnetic fields should suffice to establish the sign of the orientation parameters.

The pmr spectra observed when the samples were subjected to electric fields revealed that electric-field ordering is prompt and always dominates the magnetic ordering for fields of 5 kV cm^{-1}. For periods shorter than 30 min between successive applications of E fields, the ordering influence of H_0 may be neglected. When $\vec{E}$ is parallel to $\vec{H}_0$, the pmr spectra are unperturbed; the dipolar splitting exhibits the angular dependence ($3\cos^2\Omega - 1$) when Ω is the angle between $\vec{E}$ and $\vec{H}_0$. We deduce that the pattern of ordering is identical in $\bar{E}$ and in $\bar{H}$ fields.

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D. Gill,[13] M. P. Klein, G. Kotowycz[14]
Chemical Biodynamics Laboratory
Lawrence Radiation Laboratory
University of California, Berkeley, California 94720

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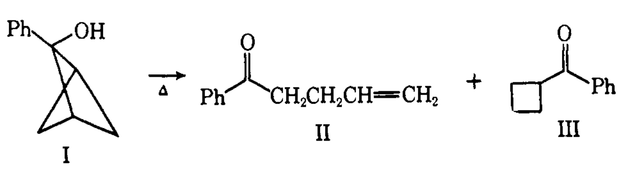
Thermal Reorganization of Phenylbicyclo[1.1.1]pentanol[1]

Sir:

Recent studies on the Norrish type II photoelimination suggests that the abstraction of the γ hydrogen is reversible and can occur from either the excited singlet or triplet state.[2] The lines of evidence implicating the reversibility of the hydrogen-transfer step are based on kinetic data[3,4] and are reinforced by stereochemical[5,6] and deuterium isotope effects.[7,8] We felt that it should be possible to gain further insight into the nature of the reverse hydrogen-transfer step by generating the 1,4 diradical by a nonphotochemical route. The present study reports on the ground-state generation of such a species and shows the behavior of the diradical to be the same as is observed in the Norrish type II process.

Thermal decomposition of 2-hydroxy-2-phenylbicyclo[1.1.1]pentane[9] (I) in the gas phase (20 mg in a 100-ml carefully neutralized tube sealed at −78° at 0.05 mm) at 135° afforded a mixture of 1-phenyl-4-penten-1-one (II; 65%) and cyclobutyl phenyl ketone (III; 35%).



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