Figure 1. Plot of ln (k_{CT}) vs. energy separation arising from solvent interactions, $\Delta E_{solv} - \Delta E_{ether}$, as calculated from eq 5: (●) ether solvents; (■) nitrile solvents; (○) acetone; (△) 1-butanol; (▲) halocarbons; (□) ethyl acetate; (♦) aromatic solvents.

ϵ and refractive index n. $E_1{}^\circ$, $E_2{}^\circ$ and μ_1, μ_2 are the gas-phase energies and dipole moments of states 1 and 2, respectively. In this treatment, solute–solvent interactions are described by the Onsager reaction field model.[13] The molecule is approximated by a point dipole at the center of a spherical cavity of radius "a", usually taken as the molecular radius. This spherical cavity is immersed in the solvent, considered to be a homogeneous dielectric of dielectric constant ϵ. For PAQ, space-filling molecular models give a maximum porphyrin–quinone center-to-center distance of $\simeq 15$ Å (hence $a \simeq 7.5$ Å),[14] which generates a dipole moment $\mu_2 \simeq 72$ D in the charge-separated state. The porphyrin excited singlet state is essentially nonpolar; for this we assumed $\mu_1 \simeq 2$ D. With these parameters the change in energy separation of the two states arising from solvent interactions is given by the last three terms of eq 2,

$$\Delta E_{solv} = -90(f_\epsilon - f_n) - 1600f_n + 2.5(f_\epsilon - f_n/2) \qquad (5)$$

A factor of 0.622 eV/D² Å⁻³ is incorporated into the constants of (5) so that ΔE_{solv} is in electronvolts if "a", the molecular radius, is in angstroms. The dominance of the term involving f_n is a consequence of the large dipole moment in the P⁺–Q⁻ state.

Table I lists the solvation energies relative to that for diethyl ether, where little electron transfer occurs. A plot of ln (k_{CT}) vs. the energy separation resulting from solvent interactions (Figure 1) shows a good qualitative correlation between these two quantities. The actual P⁺–Q⁻ molecular radius, and therefore optimal values of "a" and μ_2, is probably somewhat solvent-dependent. Thus, using a constant value of the molecular radius to determine "a" and μ_2 limits the usefulness of this model to qualitative predictions of solvent effects.

These results are significant because they suggest that in linked donor–acceptor molecules, solvent effects on the energy of the Franck–Condon charge-transfer state can have a profound effect

on the rate of intramolecular electron transfer.

Organic Reactions in Liquid-Crystalline Solvents. 3. Substituted β-Phenylpropiophenones as Photochemical Probes of Solute–Solvent Interactions in Liquid Crystals

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There has been considerable recent interest in the possible effects of liquid-crystalline order on the unimolecular reactivity of dissolved solutes.[2,3] Cyclization reactions have received particular attention,[2] effects on reactivity being expected to the extent that for a rodlike solute, such a process might involve disruption of local solvent order as the transition state is approached. With a few interesting exceptions,[2g,k,l] only small or negligible effects on reactivity have been observed, even with the highly ordered smectic liquid crystals. We wish to report one of the largest effects observed to date of smectic solvents on the energetics of a unimolecular reaction. Furthermore, our results indicate that the ability of smectic phases to inhibit cyclization of even a highly oriented solute may depend critically on structural features defining the "fit" of the solute into the smectic array.

We have measured the triplet lifetimes (τ_T) of two β-phenyl-4-alkoxypropiophenones **1** and **2**[4] between 30 and 95 °C in
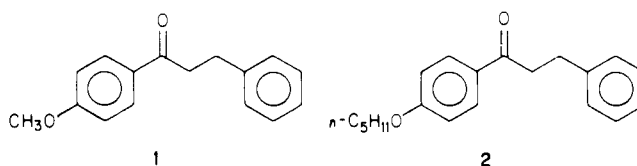
trans,trans-4'-butylbicyclohexyl-4-carbonitrile (BCCN) and the 4'-ethyl homologue (ECCN) by nanosecond laser flash photolysis.[6]

(12) The electron transfer does not occur via a vertical transition to the Franck–Condon coordinates of the product potential energy surface. However, a change in the energy of the Franck–Condon transition should reflect a qualitatively similar change in the activation energy.

(13) Onsager, L. *J. Am. Chem. Soc.* **1936**, *58*, 1486–1493.

(14) The choice of the center-to-center distance of the "stretched" conformation to evaluate μ_2 and "a" is arbitrary. Ring current calculations[15] (from 500 MHz NMR results) for a similar porphyrin–quinone molecule suggest that a conformation with a separation of $\simeq 11$ Å might be more appropriate. Such a change does not affect the qualitative results of our model.

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(2) (a) Bacon, W. E.; Brown, G. H. *Mol. Cryst. Liq. Cryst.* **1971**, *12*, 229–236. (b) Barnett, W. E.; Sohn, W. H. *J. Chem. Soc., Chem. Commun.* **1971**, 1002–1003. (c) Dewar, M. J. S.; Nahlovsky, B. D. *J. Am. Chem. Soc.* **1974**, *96*, 460–465. (d) Saeva, F. D.; Sharpe, P. E.; Olin, G. R. *J. Am. Chem. Soc.* **1975**, *97*, 204–205. (e) Nerbonne, J. M.; Weiss, R. G. *Isr. J. Chem.* **1979**, *18*, 266–271. (f) Cassis, E. G., Jr.; Weiss, R. G. *Photochem. Photobiol.* **1982**, *35*, 439–444. (g) Otruba, J. P., III; Weiss, R. G. *Mol. Cryst. Liq. Cryst.* **1982**, *80*, 165–178. (h) Anderson, V. C.; Craig, B. B.; Weiss, R. G. *J. Phys. Chem.* **1982**, *86*, 4642–4648. (i) Anderson, V. C.; Craig, B. B.; Weiss, R. G. *Mol. Cryst. Liq. Cryst.* **1983**, *97*, 351–363. (j) Melone, S.; Mosini, V.; Nicoletti, R.; Samori, B.; Torquati, G. *Mol. Cryst. Liq. Cryst.* **1983**, *98*, 399–409. (k) Anderson, V. C.; Weiss, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 6628–6637. (l) Hrovat, D. A.; Liu, J. H.; Turro, N. J.; Weiss, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 7033–7037.

(3) (a) Verbit, L.; Halbert, T. R.; Patterson, R. B. *J. Org. Chem.* **1975**, *40*, 1649–1650. (b) Torgova, S. I.; Kovshev, E. I.; Titov, V. V. *Zh. Org. Khim.* **1976**, *12*, 1593–1594. (c) Pirkle, W. H.; Rinaldi, P. L. *J. Am. Chem. Soc.* **1977**, *99*, 3510–3511. (d) Nerbonne, J. M.; Weiss, R. G. *J. Am. Chem. Soc.* **1978**, *100*, 5953–5954. (e) Eskenazi, C.; Nicoud, J. F.; Kagan, H. B. *J. Org. Chem.* **1979**, *44*, 995–999. (f) Tanaka, Y.; Chiyo, T.; Iijima, S.-I.; Shimizu, T.; Kusano, T. *Mol. Cryst. Liq. Cryst.* **1983**, *99*, 255–266. (g) Otruba, J. P., III; Weiss, R. G. *J. Org. Chem.* **1983**, *48*, 3448–3453. (h) Leigh, W. J.; Frendo, D.; Klawunn, P. *Can. J. Chem.*, in press.

(4) Laser excitation of 1.0 mol % (ca. 0.02 M) solutions of **1** and **2** in these two solvents yields transients that decay with clean first-order kinetics and whose UV absorption spectra ($\lambda_{max} = 395$ nm) are similar to that previously reported for the triplet state of **1**.[5a,b]

(5) (a) Wismontski-Knittel, T.; Kilp, T. *J. Phys. Chem.* **1984**, *88*, 110–115. (b) Netto-Ferreira, J. C.; Leigh, W. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 2617–2622. (c) Wagner, P. J.; Kemppainen, A. E.; Schott, H. N. *J. Am. Chem. Soc.* **1973**, *95*, 5604–5614.
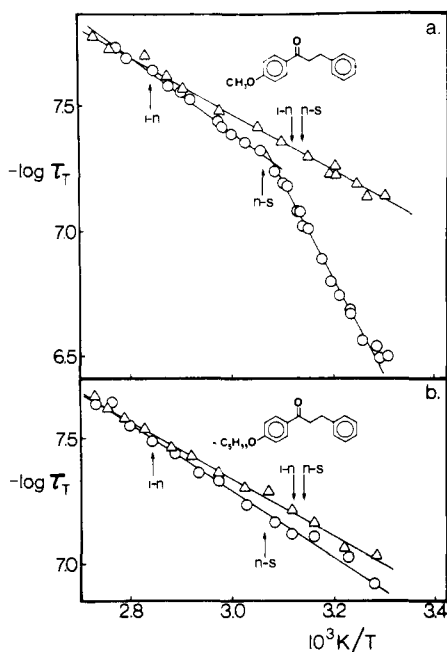
Figure 1. Arrhenius plots for the triplet decay of (a) 1.0 wt % **1** and (b) 1.3 wt % **2**. in BCCN (O) and ECCN (△), monitored at 390 nm. Optically measured transition temperatures for the pure mesogens are indicated.

Table I. Triplet Lifetimes and Arrhenius Parameters for Triplet Decay of β-Phenyl-4-alkoxypropiophenones in the Smectic, Nematic, and Isotropic Phases of BCCN and ECCN[a]

ketone	solvent (phase)	$\tau_T^{30\,°C}$, ns[b]	E_a, kcal/mol	log A, s^{-1}	$\Delta S^{\ddagger}$, eu[c]
1	BCCN (Sm)	370	16.7 ± 1.4	18.5 ± 0.9	24.0 ± 4.4
	BCCN (Nem)	122	6.7 ± 0.3	11.8 ± 0.2	−6.7 ± 0.8
	ECCN (Isot)[d]	104	5.2 ± 0.3	10.9 ± 0.2	−10.9 ± 0.8
2	BCCN (Sm)	120	5.3 ± 1.4	10.8 ± 1.0	−11.4 ± 4.6
	BCCN (Nem)	140	6.4 ± 0.6	11.5 ± 0.3	−8.1 ± 1.8
	ECCN (Isot)[d]	102	5.3 ± 0.3	10.8 ± 0.2	−11.8 ± 1.3

[a] Measured by nanosecond laser flash photolysis. Errors are quoted as ±2σ. [b] Extrapolated from the Arrhenius plots. [c] Calculated from standard Eyring plots. [d] Arrhenius parameters obtained using lifetime data throughout the entire temperature range examined.

BCCN forms a smectic phase[7] from 29 to 54 °C and a nematic phase from 54 to 79 °C, while ECCN is smectic from 28 to 46 °C and is an isotropic liquid above 48 °C.[8] Figure 1 shows Arrhenius plots for these data, and the calculated Arrhenius parameters are collected in Table I.

The short n,π* triplet lifetime of β-phenylpropiophenone (ca. 1 ns at 30 °C) is the result of efficient intramolecular deactivation

via exciplex interactions between the carbonyl group and the β-phenyl ring;[9,10] accordingly, the activation energy for triplet decay in fluid solution is roughly that for C_α-C_β bond rotation.[5b,11] 4-Methoxy substitution as in **1** renders the lowest triplet state π,π* and lengthens its lifetime considerably[5] (ca. 60 ns in isooctane at 30 °C). Nevertheless, the photostability of **1**[12] and comparison of its triplet lifetime to that of 4-methoxyaceto-phenone[14] indicate that β-phenyl quenching provides the dominant decay mechanism in this case as well (presumably via thermal population of the proximate n,π* triplet state[5b,c]) and that the activation parameters for triplet decay reflect the energetics of the various motions involved in achieving the quenching geometry.

Striking differences are observed in the Arrhenius parameters for triplet decay of **1** in the smectic and nematic phases of BCCN, E_a being ca. 10 kcal/mol higher and $\Delta S^{\ddagger}$ ca. 30 eu more positive in the highly ordered smectic phase relative to the values in the more fluid nematic phase. These indicate that smectic order has a pronounced inhibitory effect on the bond rotations (C_α-C_β + C_β-C_{phenyl}) required for intramolecular quenching in the triplet state of **1** and that local smectic order is severely disrupted as these motions occur.

The large effect of smectic order on β-phenyl quenching in **1** in BCCN suggests that the probe is solvated fairly tightly in this phase. In its trans conformation, **1** is one carbon atom shorter than BCCN and thus might indeed reside "comfortably" within the solvent layers with only minor disruption of local order. Lengthening the probe by four carbon atoms yields a molecule (**2**) which is (when fully extended) somewhat longer than BCCN; the observation (Figure 1b) that the triplet behavior of this molecule is *phase independent* indicates that the nature of its solvation in smectic BCCN is different from that of **1**. Since thermal microscopy indicates that **2** disturbs the mesophase to a larger extent than does **1**[8] but that bulk smectic order is preserved in the smectic **2**–BCCN mixture, it must be that the excessive length of **2** causes enough *local* disruption in solvent order that the bond rotations leading to intramolecular quenching are unimpeded.[15] The local solvent structure seen by **2** is a stable one, since sample annealing has no effect on the triplet lifetimes of **2** in smectic BCCN.[16] The present results bear some analogy to the recent report that the product distributions obtained from the Norrish Type II reactions of phenylalkyl ketones in smectic n-butyl stearate depend on relative solute/solvent lengths.[21]

The triplet states of both **1** and **2** exhibit phase-independent behavior in the homologous ECCN (Figure 1, Table I). While the reason for the ineffectiveness of smectic ECCN toward in-

(6) Laser flash photolysis experiments employed the pulses (337.1 nm, 8 ns, ca. 10 mJ) of a Molectron UV-24 nitrogen laser for excitation. Samples, deoxygenated by bubbling dry nitrogen through the isotropic melts or three freeze–pump–thaw cycles followed by sealing, were contained in 0.7 × 7 mm rectangular Pyrex tubes, and transient absorption was monitored at 390 nm. For full details of equipment and experimental design and general data processing, see: Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747–7753.

(7) (a) There is some question as to the type of smectic phase formed by BCCN. Its texture is consistent with the SmB structure,[2k,7b] and both the 4′-propyl and 4′-pentyl homologues have been shown to exhibit SmB phases by X-ray diffraction.[7c] However, preliminary DSC evidence indicates that BCCN may form a higher order smectic phase than either ECCN or the 4′-propyl homologue.[7b] Complete characterization of the smectic phases of BCCN and ECCN is in progress and will be reported in a full paper. (b) Leigh, W. J.; Mitchell, D. S., unpublished results. (c) Brownsey, G. J.; Leadbetter, A. J. *J. Phys. (Les Ulis, Fr.)* **1981**, *42*, L135–L139.

(8) Transition temperatures (uncorrected) for samples of BCCN and ECCN and their mixtures containing 1.0 wt % **1** and 1.3 wt % **2** were measured by thermal microscopy. They are as follows: BCCN, 53.5–54 °C (S→N), 80 °C (N→I); 1/BCCN, 52.5–53 °C (S→N), 78.5–79 °C (N→I); 2/BCCN, 51.5–52 °C (S→N), 77–77.5 °C (N→I); ECCN, 46–46.5 °C (S→N), 48.5 °C (N→I); 1/ECCN, 45–45.5 °C (S→N), 47–47.5 °C (N→I); 2/ECCN, 45–45.5 °C (S→N), 46.5–47 °C (N→I).

(9) (a) Wagner, P. J.; Kelso, P. A.; Kemppainen, A. E.; Haug, A.; Graber, D. R. *Mol. Photochem.* **1970**, *2*, 81–85. (b) Scaiano, J. C.; Perkins, M. J.; Sheppard, J. W.; Platz, M. S.; Barcus, R. L. *J. Photochem.* **1983**, *21* 137–147.

(10) Whitten, D. G.; Punch, W. E. *Mol. Photochem.* **1970**, *2*, 77–80.

(11) If rotation about this bond is prohibited, the triplet lifetime is extended to ca. 2 ms at room temperature and phosphorescence is observed. See: Casal, H. L.; Scaiano, J. C. *Can. J. Chem.* **1984**, *62*, 628–629.

(12) In laser flash photolysis experiments with reactive ketones in smectic BCCN, such as 4-methoxyvalerophenone, the appearance of the triplet decay profile changes markedly as the number of laser pulses delivered to the sample accumulates. This is presumably the result of substrate depletion, since diffusion of fresh subtrate into (and products out of) the monitoring path is severely restricted by the high viscosity of the medium.[13] Samples of **1** and **2** in smectic BCCN have been subjected to hundreds of laser pulses with no apparent decrease in signal intensity or change in the appearance of the decay profiles.

(13) Leigh, W. J., unpublished results.

(14) The triplet lifetime of 4-methoxyacetophenone, measured in the various phases of BCCN and ECCN, was found to be 50–80 times greater than that of **1** under the same conditions; thus, intramolecular quenching is the dominant decay pathway in all phases over the temperature range examined, and contributions to triplet decay from bimolecular quenching by adventitious impurities can be safely ignored.

(15) Note Added in Proof: The behavior exhibited by **1** in BCCN has also been observed for the 4-ethoxy and 4-n-propoxy derivatives. The behavior of the 4-n-octyloxy derivative, on the other hand, is similar to that of **2**. Details will be reported in the full paper.[13]

(16) Annealing the mixtures of **1** and **2** in BCCN and ECCN for 7 days at 40 °C produces homeotropically aligned (i.e., glassy) samples. While such treatment has no effect on the triplet lifetimes of **1** or **2** in these phases, it does provide much better samples for UV absorption measurements than ones used immediately after cooling from the nematic phase.

hibiting β-phenyl quenching in either probe may indeed be the same as applies for BCCN (ECCN is one carbon shorter than **1**), it is also possible that ECCN forms a different type of smectic phase than does BCCN.[7] This solvent does, however, provide a model isotropic solvent against which to compare the behavior of **1** and **2** in BCCN. Such comparisons indicate that nematic order may as well have some effect, albeit small, on the energetics of β-phenyl quenching in **1** and **2**. The magnitude of the effect (1–2 kcal/mol in E_a) is similar to those reported for other cyclization reactions in nematic and cholesteric solvents.[2]

In conclusion, our results indicate that smectic liquid-crystalline order can drastically inhibit the intramolecular mobility and reactivity of a rodlike solute, provided that the solute is of an appropriate length to fit within the solvent layers. Experiments to better define the interrelationship between solute and solvent molecular length and the effects of smectic order on solute mobility are currently in progress.

Photoactivated Oxidation of Alcohols by Oxygen

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Primary and secondary alcohols can be converted to the corresponding aldehyde or ketone by using O_2 and visible light. The process is catalyzed by the presence of H_2PtCl_6 and $CuCl_2$.[1] This

$$RCH(OH)R' + {}^1/_2O_2 \xrightarrow[h\nu]{\substack{H_2PtCl_6, \\ CuCl_2}} RC(=O)R' \qquad (1)$$
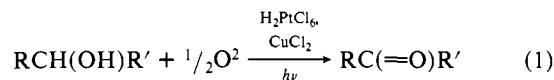
photoassisted catalytic reaction occurs at room temperature under 1 atm of O_2 in neat alcohol. The mild reaction conditions coupled with the ability to employ high substrate concentrations favors good product yields with high selectivity compared to more standard oxidation methods. For example, both aliphatic and allylic primary alcohols are oxidized to aldehyde without overoxidation to the carboxylic acid. The catalytic cycle is stable for several days when using primary or secondary substrate alcohols. Further, the consumption of expensive reagents is avoided. The concept of using H_2PtCl_6 in this reaction extends from the observation that $[PtCl_6]^{2-}$ can be photoreduced first to Pt(II) and then to Pt–metal in the presence of alcohols with visible light.[2] A catalytic process is possible if a lower oxidation state of platinum can be intercepted and reoxidized prior to conversion to Pt–metal. On thermodynamic grounds O_2 should be capable of this oxidation under acidic conditions; however, experimentally we do not find this to occur. Addition of $CuCl_2$ to the reaction mixture as a

Table I. Two-Electron Oxidation of Alcohols[a,h]

alcohol	product	time, h	equiv formed[e]	$\Phi^{P\,g,h}$
ethanol[b]	acetaldehyde	20	25	0.05
benzyl alcohol[d,f]	benzaldehyde	24	27	0.03
cinnamyl alcohol[d]	cinammaldehyde	24	13	0.02
n-hexyl alcohol[b,d]	n-hexanal	24	10	0.02
isopropyl alcohol	acetone	24	45	0.06
cyclopentanol[c]	cyclopentanone	18.5	23	0.04
cyclohexanol[c]	cyclohexanone	24	11	0.02

[a] Unless otherwise noted, a solution of 0.009 M H_2PtCl_6 in neat alcohol with 2 equiv of $CuCl_2$ was purged with O_2. The reactants were then irradiated with 488-nm (85 mW) illumination from an Ar^+ laser while O_2 was passed over the stirred solution. [b] 3 equiv of $CuCl_2$ were used. [c] 0.006 M H_2PtCl_6 was used. [d] A 50% by volume mixture of alcohol and acetone was used. [e] Equivalents were determined using FID GC[4] and internal standards and are relative to moles of H_2PtCl_6 initially. The values reported here do not reflect limiting values. [f] 0.007 M H_2PtCl_6. [g] Quantum yields, Φ^P, were measured in terms of product (ketone, aldehyde) appearance as follows: Carbonyl product yields were ascertained by GC analysis[4] by using a Perkin-Elmer Sigma 3B, FID gas chromatograph with H.P. 3390A integrator. Photon yield was determined by using a beam-expanded argon ion laser (488 nm) adjusted to low intensity as the light source. The photon flux was monitored by a NRC model 815 radiometer. The accuracy of the radiometer is ±5% NBS traceable. Data were obtained as a function of time. Only yields that were time independent over the course of the reaction are reported. In carrying out these experiments a neat alcohol solvent was employed of which only a few percent was converted to product. [h] See ref 3a.

charge-transfer mediator, however, does cause the reaction to become catalytic in Pt(IV); although, $CuCl_2/O_2$ in the absence of H_2PtCl_6 does not produce organic products with visible-light photolysis.

As can be seen from the data in Table I this system is capable of carrying out the specific two-electron oxidation of a variety of alcohols. For example, ethanol is converted to acetaldehyde in 94% yield under the conditions reported in Table I. Even low redox potential alcohols such as benzyl alcohol show no tendency to be overoxidized to the acid. Further, reactivity is not influenced by the presence of sites of unsaturation near the alcohol functionality. Thus, as demonstrated by using cinnamyl alcohol, (Table I) conjugated aldehydes can be generated in good yield. There does appear to be a steric effect on the turnover rates obtained, with larger substrates being oxidized more slowly. Presumably, this steric effect can be related to the ease with which the substrate coordinates to the Pt complex.

In a typical synthetic procedure a 10-mL solution containing H_2PtCl_6 (8 mmol, 0.06 mol %) and $CuCl_2$ (16 mmol, 0.12 mol %) in neat alcohol was purged with O_2 prior to irradiation (5 min). The solution was then statically maintained under 1 atm of O_2 using an oil bubbler while being irradiated with a tungsten–halogen source.[3a] In the case of isopropyl alcohol after 37 h of irradiation a solution that was 0.18 M in acetone (by GC analysis[4]) was obtained. As an alternative procedure the reactants were diluted with acetone. For example, photolysis[3b] of cyclopentanol in a solution consisting of alcohol (70 mmol), H_2PtCl_6 (3.5 mmol, 5 mol %), and $CuCl_2$ (7 mmol, 10 mol %) and O_2 purged as described above provided a 98% yield[4] of cyclopentanone.

In order to ascertain overall reaction parameters the oxidation of isopropyl alcohol to acetone has been studied in detail. At room

(1) This process is stoichiometrically similar to the recently published[8] $O_2/CuCl_2$ oxidation of alcohols using 2,2,6,6-tetramethylpiperidinyl-1-oxy as an electron mediator with the exception that secondary alcohols that are unreactive in that system produce good product yields in the current case. Thus, a more general catalytic oxidation scheme is possible.

(2) That this reaction is occurring is proven by ${}^{195}Pt$ NMR studies and parallel GC analysis of the ketone formed. These studies indicate that prior to metal formation a large fraction of $[PtCl_6]^{2-}$ has been converted to $[PtCl_4]^{2-}$ and $[PtCl_3(ROH)]^-$ with concomitant formation of ketone. $[PtCl_6]^{2-}$ yields a singlet in its ${}^{195}Pt$ spectrum which we have employed as the reference signal. The NMR spectrum of $[PtCl_4]^{2-}$ is composed of a singlet 16 016 ppm upfield of $[PtCl_6]^{2-}$.

(3) (a) A variety of light sources have been employed to carry out this reaction, in the case of white light sources such as tungsten–halogen lamp or a xenon lamp a UV cutoff filter was employed to avoid photolysis of the product. An IR filter ensured the solution remained at 25 °C. An argon ion laser running at low power was employed as an alternate source to simplify quantum yield determinations (Table I). (b) For this particular reaction a low-power, beam-expanded argon ion laser (90 mW) operating at 488 nm was employed.

(4) Gas chromatography analysis was carried out on a Perkin-Elmer Sigma 3B FID instrument with a 3% Carbowax 20 M chromosorb WHP column. The inlet temperature was maintained at 180 °C and a ramp rate of 2 °C/min was employed (initial temperature 35 °C). All solutions were analyzed prior to irradiation and appropriate dark controls were also executed.