In the case of the tripeptide, Z-Gly-Gly-Phe-OPCP, when prepared by the usual procedure, only 52% optical purity was obtained at −10°, while the "complex" gave 99% optically pure product in 85% yield at room temperature.[17]

Generally the use of the "complex" at room temperature resulted in higher yields and optical purity of esters. This raised the possibility that Z-Gly-Phe-OH makes a direct nucleophilic attack on the aromatic nucleus of "A." This reaction path was eliminated by O^{18} studies.[18] Z-Gly-OH, used as a model, containing 1.52% O^{18} in the carboxyl group, when allowed to react with the PCPOH- or PFPOH-isourea "complexes," gave DCU with 0.76% O^{18}; no labeled DCU would have resulted from a direct nucleophilic attack. Reaction of Z-Gly-Phe-OH with the PCPOH "complex," when followed by infrared spectroscopy, showed that at 8 min, *ca.* 68% oxazolone (5.47 μ),[11,19] 14% active ester (5.60 μ), and some unreacted DCC (4.72 μ) were present, and 85% DCU was isolated at the same time. This excludes anhydride and O-acylisourea as major identifiable intermediates. These results can be explained by the dissociation of the "complex" into DCC and PCPOH followed by reaction of the Z-peptide acid with DCC, forming oxazolone through the O-acylisourea.

However, the interception of the intermediate acylisourea by the phenols is not completely excluded, based on the following observations. Infrared studies showed that active ester formation is substantially faster during the reaction of Z-Gly-OH, PCPOH, and DCC than during the reaction of $(Z\text{-}Gly)_2O$, PCPOH, and DCC, as base catalyst, present in 1:2:1 ratio; this indicates that the Z-Gly-OPCP active ester is formed preferably through direct attack by the PCPOH on the acylisourea intermediate.

We conclude that the more acidic PCPOH or PFPOH which is present in excess contributes to depress the base (DCC) catalyzed racemization of the oxazolone,[19] and also opens the ring faster than *p*-nitrophenol. This faster ring opening was established by infrared studies of the reaction of PCPOH and NPOH with the oxazolone of Z-Gly-Phe-OH as well as by yields of the PCPOH and NPOH esters prepared by method b under identical conditions.[12]

In the Anderson test[4] Z-Gly-Phe-OPCP in DMF or dioxane gave 89 and 94% Z-Gly-Phe-Gly-OEt, respectively, and no DL isomer was detected in either case. This also indicates that peptide PCPOH esters can form amide bonds without racemization in the same solvent (DMF) and under similar conditions used for polymerization.[2] Z-Gly-Phe-OPFP in the Anderson test, in DMF, also gave no racemate. Bz-Leu-OPCP in dioxane at room temperature or chloroform at 0° gave no racemate using Young's test,[5] while in THF at 0°, 9.5% DL-Bz-Leu-Gly-OH was obtained, indicating that unfavorable conditions can cause racemization.

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[17] Z-Gly-OH was coupled to HBr·H-Gly-Phe-OPCP by the mixed anhydride procedure. This tripeptide active ester exhibits polymorphism; from ethyl acetate mp 171–172°, from chloroform–petroleum ether, mp 137–138.5°; $[\alpha]^{21}\text{D}$ −34.8° (*c* 1.00, DMF). We reported previously[2d] mp 112–113°, $[\alpha]^{25}\text{D}$ −10° (*c* 1, chloroform). Based on this $[\alpha]$ value, the previously reported[2d] material is considered to be a partially racemized product.

[18] The O^{18} analyses were carried out by Dr. James E. Morgan, Morgan and Schaffer Corp., Montreal, Canada.

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Characterization of the Reactive Excited State in the Photochemistry of a Cyclohexadienone[1]

Sir:

The characterization of the reactive excited state(s) involved in the conversion of 2,5-cyclohexadienones to lumiproducts is a matter of extensive current interest. Fisch and Richards[2] observed that the santonin–lumisantonin photoconversion was sensitized by benzophenone and was totally quenched by solvent piperylene (although the expected *cis–trans* isomerization was not observed in dilute solution), strongly implicating triplet states in the rearrangement. They suggested the configuration of the reacting triplet was π,π^*. Zimmerman and Swenton[3] proposed that a triplet was involved in the conversion of 4,4-diphenylcyclohexadienone to its lumiproduct on the basis of sensitization by acetophenone, although quenching by naphthalene was not observed, and they assigned an n,π^* configuration to the reacting triplet. Phosphorescence was observed in both studies, the emission being broad and unresolved for santonin[2] and resolved into vibrational bands for 4,4-diphenylcyclohexadienone.[3] Saltiel[4] has pointed out that Zimmerman and Swenton's data suggest but do not demand that a triplet state is involved in the rearrangement. Implicit in this criticism is the possible danger of extrapolating from spectroscopic results obtained at very low temperatures to reactions at higher temperatures. We now report the results of a study which allow unambiguous characterization of a dienone excited state.

It is well established that a characteristic reaction of ketone triplet n,π^* excited states is inter- or intramolecular hydrogen abstraction leading to alcohol or pinacol.[5,6] We have shown that photochemical hydrogen abstraction accompanied by loss of a CCl_3 group to form *p*-cresol occurs on photolysis of dienone **1** in ethyl ether and isopropyl alcohol and, to a lesser extent, in hexane and cumene.[7,8] The reaction depends

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[1] (a) The authors wish to express their appreciation to the U. S. Army Research Office (Durham) for generous support. (b) Part X of a series on the photochemistry of unsaturated ketones in solution. Part IX: D. I. Schuster and A. C. Fabian, *Tetrahedron Letters*, 4093 (1966).

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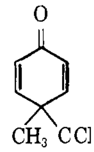
on the hydrogen-donating properties of the solvent (it does not take place in benzene, methanol, or water) and is sensitized by benzophenone and quenched by piperylene. The quantum yield for formation of *p*-cresol in ethyl ether is 0.7 at 3660 A. The efficiency of intersystem crossing to the triplet state, Φ_{ST}, determined at 3660 A by the counting method of Lamola and Hammond,[9] is 0.73 in benzene. Thus k_d, the rate of decay of the triplet state to the ground state, is negligible in comparison with the rate of reaction of triplet to give *p*-cresol. From a Stern–Volmer plot of Φ_0/Φ *vs.* [piperylene], the rate of hydrogen abstraction from ether by the triplet state, k_a, can be calculated using

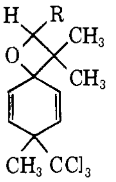
$$\Phi_0/\Phi = 1 + \frac{k_q[Q]}{k_a[RH]} \qquad (1)$$

Using 5×10^9 l. mole^{-1} sec^{-1} for the rate constant of diffusion-controlled quenching in benzene[10] and the intrinsic viscosities of ether and benzene, k_q in ethyl ether is calculated to be 1.3×10^{10} l. mole^{-1} sec^{-1}. The slope of the Stern–Volmer plot is 3.5, and [ethyl ether] = 9.65 *M*, leading to a value of $k_a = 4 \times 10^8$ l. mole^{-1} sec^{-1}. Other rate constants (l. mole^{-1} sec^{-1}) for hydrogen abstraction are $1\text{–}2 \times 10^6$ for benzophenone triplet in benzhydrol,[5] isopropyl alcohol,[11] and methyl 2-octyl ether,[12] 3×10^3 for a tetrahydrophenanthrone triplet in isopropyl alcohol,[13] and 5.2×10^6 for pyruvic acid triplet in isopropyl alcohol.[14] The unusually high reactivity of the triplet of **1** in intermolecular hydrogen abstraction, to be considered in detail in a later paper, is comparable to that observed[10] for triplet n,π* excited states of some aliphatic ketones in intramolecular hydrogen abstraction from a γ-carbon atom.

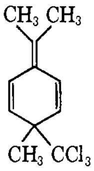
The formation of oxetanes on irradiation of ketones in the presence of olefins is also considered to be a reaction characteristic of triplet n–π* excited states.[15,16] Irradiation of **1** (Pyrex filter) at low temperatures in 2-methyl-2-butene or isobutylene gave materials whose spectra are characteristic of oxetanes.[16] The nmr spectrum of **2a** featured an AB quartet centered at 4.5 ppm (J_{AB} = 7 Hz), and that of **2b** showed a singlet at 4.2 ppm. The other nmr resonances were consistent with these structures, as were broad bands at 1020 and 1040 cm^{-1} in the infrared.[16] While stable at low temperatures, both solid oxetanes decomposed on standing at room temperature or attempted chromatography to give the same solid, assigned structure **3**: mol wt 250, three chlorines (mass spectroscopy); nmr, quartet (4 H) centered at 6.22 ppm (*J* = 10.5 Hz), singlet (6 H) at 1.88 ppm, and singlet (3 H) at 1.47 ppm; ultraviolet (hexane), λ_{max} 269 mμ (ε 18,900).[17] The triene undergoes a further rearrangement thermally to an aromatic compound **4**: nmr, AB quartet (J_{AB} = 8 Hz) at 7.3 ppm (4 H), singlets at 2.3 (3 H) and 1.8 ppm (6 H), and appropriate infrared bands. This 1,5 rearrangement of a trichloromethyl group has been observed previously.[18]



1



2a, R = CH_3
b, R = H



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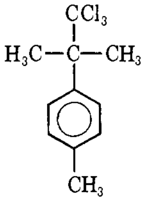

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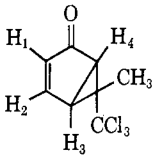

5

In benzene, **1** undergoes the familiar rearrangement[2,3] to lumiproduct **5**,[8,19] with Φ = 0.75 for formation of **5** at 3660 A. The formation of lumiproduct **5** was shown to be sensitized by benzophenone and quenched by piperylene concomitant with *trans–cis* isomerization. Quenching by cyclohexadiene leads to formation of cyclohexadiene dimers, which were isolated and characterized.[20] A kinetic study of formation of **5** in benzene using piperylene as quencher gives values of Φ_0/Φ which fit eq 2. As above, k_d is apparently negligible according to quantum yield data.

$$\Phi_0/\Phi = 1 + \frac{k_q[Q]}{k_r} \qquad (2)$$

From the observed slope of 7.2 for the Stern–Volmer plot, and using $k_q = 5 \times 10^9$ l. mole^{-1} sec^{-1},[10] the value for the unimolecular rate constant for lumiproduct formation from the triplet state, k_r, is found to be 7×10^8 sec^{-1}.

Irradiation of **1** in ether–benzene mixtures gave an increase in *p*-cresol and decrease in lumiproduct yields with increasing ether concentration. The rate of lumiproduct formation remains unchanged on going from room temperature to Dry Ice temperatures. From studies at 30 and −80° an activation energy of about 4 kcal mole^{-1} is determined for hydrogen abstraction by dienone **1** in ethyl ether.[21] This value is of the order of magnitude expected for a hydrogen-abstraction reaction.[6]

Finally, the phosphorescence emission spectrum of **1** in 4:1 methanol–ethanol at 77°K[22] is similar in pattern to those reported for 4,4-diphenylcyclohexa-

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(17) The ultraviolet spectrum is characteristic of cross-conjugated trienes: H. Hart, P. M. Collins, and A. J. Waring, *J. Am. Chem. Soc.*, **88**, 1005 (1966).

(18) M. S. Newman and L. L. Wood, Jr., *ibid.*, **81**, 6450 (1959), and references therein.

(19) The compound described earlier[8] as lumiproduct **5** is now known to be a rapidly formed transformation product of the true lumiproduct. The latter material, mp 74–76°, is assigned structure **5** on the basis of spectral data [infrared (CCl_4): 3030, 1725, 1020 cm^{-1}; λ_{max}^{MeOH} 216 mμ (ε 5600), 253 (3200), 346 (124), 334 (127); nmr ($CDCl_3$): 7.50 ppm (1H), J_{24} = 0.6, J_{23} = 2.8, J_{12} = 5.5 Hz; 6.07 ppm (1 H), J_{14} = 0.9, J_{12} = 5.5 Hz; 3.20 ppm (1 H), J_{23} = 2.8, J_{34} = 5.5 Hz; 2.65 ppm (1 H), J_{24}, J_{14} = 0.7–0.9, J_{34} = 5.6 Hz; 1.55 ppm (3 H) singlet] and chemical transformations (to be reported fully later). The further isomerization of **5** is known not to be a simple epimerization, so that arguments about the stereospecificity of lumiproduct formation[8] are still valid. The stereochemistry of **5** is currently being elucidated.

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(21) The calculation took into account the change in coefficient of viscosity of ethyl ether with temperature.

(22) We are deeply grateful to Dr. Donald Arnold and Mrs. Lynn Gillis for these spectra, obtained at the Union Carbide Research Institute, Eastview, N. Y., and for discussions regarding interpretation.

dienone and benzophenone.[3] The triplet energy of **1**, corresponding to the 0–0 band in the emission spectrum, is 67.2 kcal/mole, and the well-resolved band separation is 1680 cm^{-1}.

The chemical and spectroscopic properties determined for the excited state of **1** which leads to *p*-cresol (by abstraction–fragmentation) and lumiproduct **5** (by rearrangement) are those of a classic n,π* triplet state. The results strongly indicate that these reactions are competitive processes proceeding from a single diradical-like ^{3}(n,π*) excited state.

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Electrolytic Generation of Solvated Electrons and Reduction of the Benzene Ring in Ethanol Containing Hexamethylphosphoramide

Sir:

Until now, electrolytic generation of solvated electrons could be achieved only in solvents of low proton donor capability such as liquid ammonia[1,2] or certain amines,[3–5] a fact which imposed severe restrictions on the choice of solvent and reaction conditions. Attempts, described below, to generate solvated electrons electrolytically in a solvent of relatively high proton donor capability such as ethanol were doomed to failure due to hydrogen evolution at a potential far below that required for release of electrons into the solvent. The recently published discovery[6] that hexamethylphosphoramide (HMPA), $[(CH_3)_2N]_3PO$, is capable of dissolving alkali metals prompted us to investigate whether electrolytic generation of solvated electrons in a solution of ethanol containing HMPA was possible.

We found that release of electrons into ethanol–HMPA solutions could be achieved and that the solvated electrons can add to the benzene ring. When a solution of HMPA, 0.3 *M* in LiCl, is electrolyzed, dark blue globules, characteristic of solvated lithium, form at the cathode surface at a potential of −2.3 v (*vs.* Ag wire) and the solution in the cathode compartment becomes deep blue, visual evidence that the reaction $Li_s^+ + e^- \rightarrow Li_s^+ \cdots e_s^-$ is taking place.[7] In the presence of ethanol the intensity of the color is lower, depending on the amount of alcohol present. However, in the presence of both alcohol and benzene the solution remains colorless during electrolysis, with only a small amount of blue color visible at the cathode surface. Proof that electrolytic reduction of the benzene ring in ethanol–HMPA solution is possible was obtained by electrolysis of tetralin in a solution composed of 67 mole % ethanol and 33 mole % HMPA, 0.3 *M* in LiCl. The electrolysis was carried out at a cathode potential of −2.5 v (*vs.* Ag wire) in an apparatus described previously.[4] A carbon electrode served as an anode and an aluminum electrode as the cathode. After completion of the electrolysis, analysis of the recovered product by mass spectrometric and glpc methods showed that it consisted of (volume %) tetralin (80), hexalin (2), octalin (1), and decalin (17), and that tetralin had been hydrogenated at a current efficiency of 54%. When the electrolysis of tetralin is carried out under the same conditions but in the absence of HMPA, copious hydrogen evolution takes place and the cathode potential during electrolysis becomes now −1.5 v (*vs.* Ag wire), *i.e.*, 0.8 v more anodic than that at which release of electrons was observed into HMPA or ethanol–HMPA solution. Under these conditions not even traces of reduced tetralin could be detected in the recovered material. It is remarkable that the strong hydrogen evolution that occurs during electrolysis of ethanol at −1.5 v is drastically reduced in the presence of as little as 33 mole % HMPA. This suggests adsorption of the aprotic but highly polar[8] HMPA at the electrode surface to the near exclusion of ethanol. In the presence of HMPA, the charge-transfer process is release of electrons into the solvent and not hydrogen evolution. The high percentage of decalin in the reaction product is probably due to the high proton availability in the solution containing 67 mole % ethanol, since electrolytic reduction of tetralin in ethanol–HMPA containing only 25 mole % ethanol gave hexalin as the main product. Tetralin is not reduced when the electrolysis is carried out in HMPA in the absence of ethanol. Under these conditions, the catholyte becomes dark green during electrolysis. Mass spectrometric analysis of the recovered reaction product indicates the presence of considerable amounts of mono- and dimethyltetralin and small amounts of dimers of these methyltetralins, in addition to unchanged starting material, tetralin.

On the basis of these results and previous work on the reduction of the benzene ring in ethylenediamine,[4] we believe that electrochemical reduction of the benzene ring in ethanol–HMPA involves addition of the solvated electron, e_s^-, to the solvated benzene ring, B_s,

$$\begin{tikzcd} S + e^- \arrow[r] & e_s^- \\ B_s + e_s^- \arrow[r] & S + B_s^- \arrow[ul, bend right] \end{tikzcd}$$

where S indicates the solvent molecules required to solvate an electron. Subsequent protonation of the benzene anion, B_s^-, and further addition of electron and proton complete the hydrogenation of a double bond, as has been pointed out previously.[9] Apparently, the cathode in ethanol–HMPA solution containing alkali halide functions in the same way as in liquid ammonia[2] and amines,[4] *i.e.*, as an electron electrode.

The present results demonstrate for the first time that electrolytic generation of solvated electrons in a solvent of relatively high proton donor capability is

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