spectra of the ethanes from reaction of $C_2D_3H_2^+$ with cyclohexane-d_0 and $C_2H_3D_2^+$ with cyclohexane-d_{12} is taken to indicate that secondary deuterium isotope effects are not important. It is of interest to note that the data of Ausloos, *et al.*,[8] also show that secondary deuterium isotope effects are unimportant in the hydride abstraction reaction of ethyl ion in the gas phase. We conclude therefore that hydrogen atoms in ethyl ion are completely randomized prior to hydride transfer even at low vibrational energies and lifetimes very much shorter than those observable by nmr spectroscopy.

Although the ground-state structure of the ethyl ion cannot be ascertained from these data, it is possible to estimate the activation energy for intramolecular hydride transfer. From the observed randomization of hydrogens in ethyl ion, it follows that the rate of the intramolecular hydride shift must be rapid with respect to the rate of intermolecular hydride transfer. Intermolecular hydride transfer may be assumed to occur on the first collision of ethyl ion and cyclohexane as it does in the gas phase.[12] For the ethanes formed in SO_2 solution the rate of intermolecular hydride transfer is limited by the rate of diffusion which is approximately 4×10^9 l./(mol sec).[13] At a cyclohexane concentration of 0.1 *M*, the pseudounimolecular rate constant is 4×10^8 sec^{-1}. For the hydrogen atoms to become completely randomized prior to hydride transfer, the unimolecular rate constant for 1,2-hydride shift in ethyl ion must be at least an order of magnitude greater than the rate of hydride transfer. With a normal frequency factor of $10^{13.2}$ sec^{-1} for 1,2-hydride shift and requiring the unimolecular rate constant for randomization to be greater than 4×10^9 sec^{-1}, one calculates the maximum permissible Arrhenius activation energy to 3.5 kcal/mol. However, ethyl ions formed in neat cyclohexane undergo hydride transfer at a rate determined by the collision frequency in the liquid, which corresponds to a pseudounimolecular rate constant of 6×10^{10} sec^{-1} [13] and an upper bound on the Arrhenius activation energy of 1.9 kcal/mol. Although this estimate does not identify the ground-state structure for the ethyl ion, it does indicate that the two structures must be very close in terms of stability as suggested by Hariharan, Lathan, and Pople.[5]

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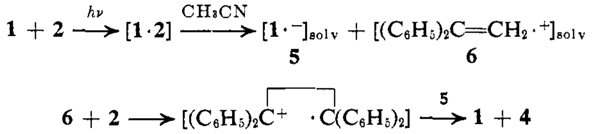
Radical Ions in Photochemistry. I. The 1,1-Diphenylethylene Cation Radical[1]

Sir:

As part of our effort to define the scope and limitations of the photocycloaddition of carbonyl compounds to olefins, our attention was attracted by the recent finding that aromatic esters, substituted with electron-withdrawing groups, for example methyl *p*-cyanobenzoate (**1**), can undergo this reaction.[2] The mechanism first proposed[2a] involved reaction of the n,π^* triplet of **1** in the usual sense.[3] The same authors[2b] later considered an exciplex mechanism with the electron-deficient ester acting as the acceptor.[4]

When we irradiated solutions of **1** and 1,1-diphenylethylene (**2**) in benzene-d_6 and in acetonitrile-d_3 under comparable conditions,[5] the rate of formation of 2-methoxy-2-(*p*-cyanophenyl)-3,3-diphenyloxetane (**3**) decreased slightly with increasing solvent polarity whereas **2** was consumed about ten times faster in the nitrile solution.[6] A new product was isolated in 70% yield (column chromatography on silica gel) from a preparative run in acetonitrile and identified as 1,1,4-triphenyl-1,2,3,4-tetrahydronaphthalene (**4**) by ^{1}H and ^{13}C nmr, mass spectrum, and elemental analysis. A confirmation of this structure was accomplished by synthesis *via* a different route.[7]

Exciplexes are known to be sensitive to solvent polarity: in polar solvents they dissociate into the radical ions.[8,9] This encourages us to propose a mechanism for the formation of **4** in which electron transfer to **1** from **2** occurs as a key step. The polar solvent, acetonitrile, then allows the radical ions to dissociate which enables electrophilic attack by the cation radical **6** on the ground-state olefin **2**. Ring closure, back-electron transfer from the anion radical **5**, and aromatization conclude the mechanistic sequence. Formation of the oxetane **3** can then be envisioned as a reaction of the exciplex which competes with dissociation.



$$\mathbf{1} + \mathbf{2} \xrightarrow{h\nu} [\mathbf{1}\cdot\mathbf{2}] \xrightarrow{CH_3CN} \underset{\mathbf{5}}{[\mathbf{1}\cdot^-]_{solv}} + \underset{\mathbf{6}}{[(C_6H_5)_2C{=}CH_2\cdot^+]_{solv}}$$

$$\mathbf{6} + \mathbf{2} \longrightarrow [(C_6H_5)_2C^+ \quad \cdot C(C_6H_5)_2] \xrightarrow{\mathbf{5}} \mathbf{1} + \mathbf{4}$$

This mechanism is supported by the fact that we observe a transient absorption upon flash photolysis of an acetonitrile solution, 0.1 *M* in both **1** and **2**, which is similar to the reported absorption of the 1,1-diphenylethylene cation radical **6**.[10] This transient cannot be the exciplex[11] because of its lifetime ($\tau_{1/2} \approx 0.5$ msec). Continuous irradiation with a 1-kW xenon–mercury

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(1) Contribution No. 59 from the Photochemistry Unit, Department of Chemistry, The University of Western Ontario.

(2) (a) Y. Shigemitsu, H. Nakai, and Y. Odaira, *Tetrahedron*, **25**, 3039 (1969); (b) Y. Shigemitsu, Y. Katsuhara, and Y. Odaira, *Tetrahedron Lett.*, 2887 (1971).

(3) (a) D. R. Arnold, *Advan. Photochem.*, **6**, 301 (1968); (b) P. J. Wagner and G. S. Hammond, *ibid.*, **5**, 21 (1968).

(4) Aromatic esters such as **1** are known to have a π,π^* configuration in the lowest triplet: D. R. Arnold, J. R. Bolton, and J. A. Pedersen, *J. Amer. Chem. Soc.*, **94**, 2872 (1972).

(5) All irradiations were carried out on argon purged solutions in sealed Pyrex tubes using a 450-W medium-pressure mercury vapor lamp (Hanovia L679A) unless otherwise stated. The rate of reaction was followed by nmr.

(6) In the absence of **1** solutions of **2** in either solvent remained unchanged even upon prolonged irradiation.

(7) 1,1,4,4-Tetraphenyl-1-butene, prepared according to G. Wittig, *Ber.*, **64**, 442 (1931), was cyclized to **4** by refluxing with $AlCl_3$ in CCl_4.

(8) A. Weller, "Nobel Symposium 5, Fast Reactions and Primary Processes in Chemical Kinetics," S. Claesson, Ed., Almqvist and Wiksell, Stockholm, 1967, p 413, and references cited therein.

(9) T. Okada, H. Oohari, and N. Mataga, *Bull. Chem. Soc. Jap.*, **43**, 2750 (1970).

(10) W. H. Hamill, "Radical Ions," E. T. Kaiser and L. Kevan, Ed., Wiley, New York, N. Y., 1968, p 404.

(11) In some cases the exciplex has absorption which coincides with that of the radical ions: R. Potashnik and M. Ottolenghi, *Chem. Phys. Lett.*, **6**, 525 (1970).

high-pressure lamp of the same solution furthermore gives rise to an esr signal ($g = 2.005$). However, further studies using the combined esr and optical flash technique[12] are needed for a definitive assignment.

A radical-chain mechanism, found recently for the sensitized dimerization of 1,1-bis(*p*-dimethylaminophenyl)ethylene[13] is unlikely on the basis of the quantum yield for formation of **4** which is less than 10^{-1}.

The same products, **3** and **4**, are formed when the acetonitrile solution is irradiated at 254 nm (low-pressure mercury vapor lamp). At this wavelength olefin **2** absorbs most of the light ($\epsilon(\mathbf{1}):\epsilon(\mathbf{2}) = 1:3$), whereas, upon irradiation with the medium-pressure mercury vapor lamp through Pyrex mostly **1** is excited ($\epsilon(\mathbf{1}):\epsilon(\mathbf{2}) = 7:1$ at 302 nm and 1:1 at 313 nm). The absorption spectrum, at long wavelengths, shows no evidence for complex formation between ground state molecules; however, a weak complex might not be detected.[14]

Formation of **4** is not restricted to sensitization by **1**; methyl *o*-cyanobenzoate or dimethyl terephthalate can also be used.[15] A thorough investigation of the efficiency of the reaction under various conditions is in progress.

Upon irradiation of **1** and **2** in methanol and 2-propanol we found formation of 2,2-diphenylethyl methyl ether (**7**) and 2,2-diphenylethyl isopropyl ether (**8**), respectively, arising from nucleophilic attack of the alcohol on **6**. In both solvents formation of **4** was completely suppressed. The structures of **7** and **8** (after isolation by chromatography on silica gel) were proven by nmr, using spin decoupling and, in the case of **7**, by comparison with an authentic sample.[16]

Proton transfer from the solvent to an excited state of **2** cannot be important in these reactions because formation of the most stable carbonium ion, at the carbon atom bearing the phenyl groups, would lead to other products.[17] If a radical process were involved a carbon–hydrogen bond of the alcohol would be broken rather than the oxygen–hydrogen bond which has the higher bond dissociation energy. Irradiation of **2** in 2-propanol has been reported to yield the three possible coupling products of 1,1-diphenylethyl- and dimethylcarbinol radicals.[18] None of these products was formed in detectable amounts when **1** was present; this means that in our experiments either practically all the light is absorbed by the ester **1** (as stated above) forming the exciplex or that excited **2** leads to formation of **6** in the presence of **1** at a rate faster than hydrogen abstraction from the solvent.

Very little oxetane **3** was formed in the methanol experiment, whereas irradiation in 2-propanol produced appreciable amounts of **3** (**3**:**8** = 1:3.2) besides small quantities of unidentified products. This sensitivity of product distribution to solvent polarity convinces us that the cation radical of 1,1-diphenylethylene (**6**) is the reactive species in reactions leading to **4**, **7**, and **8** and its formation by dissociation of the exciplex is the product-determining step. The solvent polarity, as expressed by the Kirkwood–Onsager parameter (Ω),[19] increases in the order 2-propanol < acetonitrile < methanol. The relative yield of **3** decreases in the same order, whereas the yield of the products arising from **6** increases.

In conclusion we wish to point out that this reaction provides a convenient procedure to achieve anti-Markovnikov addition of alcohols to olefins which can presumably be extended to other systems. Furthermore, the addition of other nucleophiles to photochemically generated cation radicals would make this type of reaction of more general synthetic utility.

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(20) Alfred P. Sloan Fellow, 1972–1974.

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Synthesis and Absolute Configuration of (+)-5-(4′,5′-Dihydroxypentyl)uracil from *Bacillus subtilis* Phage SP-15 Deoxyribonucleic Acid

Sir:

In the following we report the synthesis of (+)-5-(4′,5′-dihydroxypentyl)uracil, the modified base which replaces thymine in bacteriophage SP-15 deoxyribonucleic acid (DNA) of *Bacillus subtilis*.[1] The synthesis allows one to assign an *S* configuration to this compound, which is the sole DNA base known so far to contain a chiral side chain. We also describe a C_1-homologation sequence which can be carried out under the presence of acid-labile functionalities.

(*S*)-(−)-Malic acid was methylated with hydrogen chloride in methanol to give the dimethyl ester **1**, which was reduced to 1,2,4-butanetriol (**2**)[2] with lithium alminum hydride in tetrahydrofuran (50%). Treatment of triol **2** with acetone and *p*-toluenesulfonic acid (Scheme I) gave a single acetonide (95%), to which the five-membered structure **3** was assigned from nmr: 2′-H at 3.75 ppm (t, $J = 6.0$ Hz), 3′-H at 1.81 ppm (d of t, $J = 5.5$ and 6.0 Hz). Namely, the triplet nature of the 3.75-ppm signal can only be accounted for by a freely rotating primary alcohol group attached to a methylene (C-3′).

The triol acetonide **3** was brominated to **4** (77%) under mild neutral conditions by the addition of triphenylphosphine (1 mol equiv) in dichloromethane to a mixture of acetonide **3** and carbon tetrabromide[3] (1:1.5 equiv) in the same solvent; triphenylphosphine

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