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Photoreactivity of α,β-Unsaturated Carbonyl Compounds. Competitive 2-Cyclohexenone Dimerization and Adduct Formation with Triethylamine

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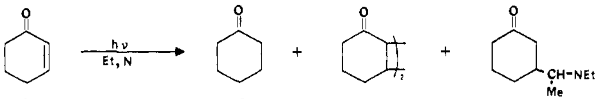
The photoreactions of α,β-unsaturated carbonyl compounds in the presence of amines have been reported to yield 1:1 adducts between amines and carbonyl compounds.[1,2] Enones, enoic acids, and esters yield these products in addition to cyclobutane-type dimers, the corresponding carbonyl compound, and the double-bond isomer, the β,γ-enone. The dimerization is observed almost exclusively with cyclic compounds,[3–9] while double bond isomerization occurs in both cyclic and acyclic cases but is more common in the latter.[10,11] These latter two types of reactions occur in the absence of amines, under a variety of conditions, and are generally thought to be mechanistically understood. Photoreduction of 2-cyclohexenone (**1**) has also been the subject of considerable interest and apparently involves hydrogen atom abstraction from an alcohol[12,13] or a benzylic position.[14] Schuster and co-workers have concluded that this abstraction in alcoholic solvents is accomplished by the β-carbon atom of the enone, a result based on a series of labeling experiments[13] and one consistent with the results of Schaffner et al.[14] Although adduct formation between enones and amines has been reported,[1,2] these photoreactions have not been systematically studied. We herein report on the reactions of cyclohexenone (**1**) with triethylamine.

When **1** was irradiated with amine as solvent or with cosolvent, the products in eq 1 were observed.[15] Structure **3** is meant to represent all of the possible dimerization isomers.[16] No attempt was made to separate these, and their sum will be referred to collectively from this point.



1 **2** **3** **4** (1)

Table I. Irradiation of 0.127 M Cyclohexenone with Various Concentrations of Et_3N in Acetonitrile

	yield, %[a]				
[amine], M	**2**	**3**	**4**	(**2** + **4**)/**3**[b]	Φ_{SM}[c]
7.17[d]	12.0	28.4	43.4	3.90	0.55
5.98	10.3	28.8	39.0	3.42	
5.03	9.8	29.6	32.0	2.82	0.54
4.00	8.4	31.0	27.4	2.31	
3.01	7.4	33.8	19.9	1.62	
1.99	4.0	43.4	15.0	0.88	
0.99	2.8	55.4	9.9	0.46	
0	*e*	86	0	0	0.08[f]

[a] Yields determined by gas chromatographic analysis relative to an internal hydrocarbon standard. Theoretical yields based on starting amount of 1 measured at 20–25% conversion. The yields for product **3** are the actual mole yields multiplied by 2 to account for the fact that two reactant molecules are necessary to form one molecule of **3**. [b] Ratio of moles of (**2** + **4**)/**3** formed: (%**2** + %**4**)/0.5 (%**3**). [c] Quantum yields for disappearance of **1** measured by benzophenone-benzhydrol actinometry (ref 17) for enone conversions to 5–6%. [d] Neat Et_3N, no CH_3CN. [e] None detected. [f] This value agrees with the data of Wagner and Bucheck (ref 9). Extrapolation of their data to this enone concentration gives a value of 0.078.

Table II. Irradiation of Cyclohexenone at Various Concentrations in Et_3N as Solvent[a]

[**1**], mM	(**2** + **4**)/**3**[b]	Φ_{SM}[c]	Φ_{dim}[d]	Φ_{ADD}[e]
2002	*f*	1.02	0.14	0.57
1262	3.75	0.94	0.13	0.53
502	4.15	0.85	0.12	0.48
256	4.17	0.64	0.09	0.36
127	3.90	0.55	0.08	0.31
100	3.76	0.48	0.06	0.27
65.3	3.98	0.38	0.05	0.21
33.8	4.34	*g*		
24.6	4.38	*g*		
17.6	4.34	*g*		
9.5	4.25	*g*		
5.7	3.72	*g*		

[a] Yields determined by gas chromatographic analysis relative to an internal hydrocarbon standard. Theoretical yields are based on starting amount of **1** measured at 20–25% conversion. The yields for product **3** are the actual mole yields multiplied by 2 to account for the fact that two reactant molecules are necessary to form one molecule of **3**. [b] Average ratio exclusive of first entry: 4.09 ± 0.28. Ratio based on number of moles formed: (**2** + **4**)/**3** = (%**2** + %**4**)/0.5(%**3**). [c] Quantum yields for disappearance of **1** measured by benzophenone-benzhydrol actinometry (ref 17) for enone conversions to 5–6%. [d] Quantum yield for appearance of **3**. [e] Quantum yield for appearance of the sum of **2** and **4**. [f] New unidentified products in the dimer region of the GC were observed and when included give a ratio of 1.77. [g] Concentration at which sample does not absorb all incident light under conditions employed.

Tables I and II present yield values at 20–25% conversion as a function of amine and enone concentration, respectively. Yields for product **3** are the actual mole yields multiplied by 2 to account for the fact that two reactant molecules are necessary to form one molecule of **3**. From the data in Table I a plot of the ratio of (**2** + **4**)/**3** vs. amine concentration is found to be linear (slope = 0.57 M^{-1}, intercept = −0.080, r = 0.997). In Table II yields were omitted since all entries are the same (**2**, 10.8 ± 0.9%; **3**, 27.4 ± 1.4%; **4**, 45.4 ± 3.9% at 20–25% conversion) within experimental error and are independent of the concentration of **1**. Mass balances

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(15) Degassed solutions of **1** were irradiated in 1.0-cm i.d. Pyrex vessels suspended in a Rayonet type reactor equipped with 16-F15T8 BL (blacklight) lamps whose output is centered at 350 nm. Reactions were monitored spectrophotometrically and by gas chromatography with appropriate corrections for detector response. Products **2** and **4** were isolated and identified by spectroscopic means. Product **4**, which occurs as a poorly resolved pair of diastereomers on the GC, was characterized by proton decoupled ^{13}C NMR. Isolated adduct **4** was reacted with D_2O and K_2CO_3 and found to exchange four protons. Two minor products (2% and 0.5% at 20% conversion) were observed but not identified. Control experiments indicated that **2**–**4** were not consumed under irradiation conditions and that no ground-state reactions affected the reported results.

(16) The dimers are observed as two poorly resolved peaks in the GC analysis. Their retention times and mass spectra were identical when the mixtures were compared to authentic samples prepared as in ref 5 and 9. Ratios nearly identical with those reported in ref 5 and 9 were observed when identical conditions had been used.

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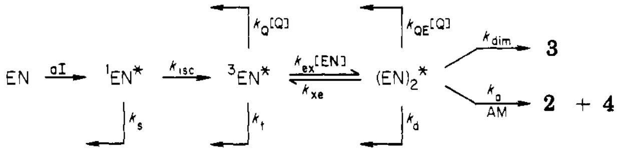
(generally 80–90%) were considerably better than those reported by Cookson and Hudec,[1] where their diminished yields may be the result of photolysis of the products under the conditions employed. Quenching of the reactivity of 0.13 M **1** in Et_3N as solvent was observed with added naphthalene (**5**) or piperylene (**6**) but not with fluorene.[18,19] In all cases the ratio of products (**2** + **4**)/**3** was identical with those in Tables I and II.

These data exclude any kinetic scheme where a ground-state enone competes with an amine molecule for an enone excited state (or two different states) to produce **3** or **4**. All such mechanisms require dependence of product ratios on enone concentration. Equation 2 represents a mechanistic scheme consistent with our observations, where EN is enone **1**, AM is amine, Q is quencher, and k_s, k_t, and k_d represent the sum of all first-order decay rates for the singlet, triplet, and excimer. The product ratio (**2** + **4**)/**3** depends only on the ratio $k_a[AM]/k_{dim}$, and the plot of product ratios vs. amine concentration (Table I) has a slope $k_a/k_{dim} = 0.57$. Excimer formation has been represented as a reversible step.[2,20] The kinetic expression in eq 3 relates quantum yields and enone concentration, where τ_{ex} is the excimer lifetime. A plot of $1/\Phi_{dim}$ vs. $1/[EN]$ gives the relationship in eq 4 from the ratio of the slope to intercept. The data in Table II yields a slope to intercept ratio of 0.11 while in the absence of amine that number is 2.7.[9] Since the bracketed term in eq 4 must be larger than 1, k_t/k_{ex} must be less than or equal to 0.11. Thus, in the absence of amine the excimer–triplet equilibrium allows triplet decay 73% of the time, while with apparent facile reaction between excimer and amine, triplet decay accounts for only 10% of all triplet pathways. The difference in excimer lifetimes is an additional term in the presence of amine (eq 5 and 6). Since $k_a/k_{dim} = 0.57$, the ratio $k_a[AM]/k_{dim} = 4.1$ in neat amine, and the extra term in the latter equation accounts for a substantially shorter excimer lifetime.



(2)

$$\Phi_{dim}^{-1} = \Phi_{isc}^{-1}\frac{1}{k_{dim}\tau_{ex}}\left[\frac{k_t}{k_{ex}[EN]} + (1 - k_{xe}\tau_{ex})\right] \quad (3)$$

$$\text{slope/intercept} = k_t/k_{ex}[1/(1 - k_{xe}\tau_{ex})] \quad (4)$$

$$\text{without amine:} \quad \tau_{ex} = 1/(k_{xe} + k_{dim} + k_d) \quad (5)$$

$$\text{with amine:} \quad \tau_{ex} = 1/(k_{xe} + k_{dim} + k_d + k_a[AM]) \quad (6)$$

Our conclusion is that, at least in the concentration range studied, dimer **3**, adduct **4**, and reduced material **2** arise from competitive reaction from the triplet excimer. Little, if any, product arises by direct interception of the singlet or triplet enone. The structure of adduct **4** is itself inconsistent with a scheme involving hydrogen atom abstraction by the β carbon of the excited state followed by combination of the radicals. We favor a mechanism involving electron transfer to give a radical anion–radical cation pair which decays ultimately to give **2** and **4**. Data from a series of enones and tertiary amines will be presented separately in support of this scheme.

Acknowledgment. We acknowledge helpful discussions with Professor Peter Wagner, the assistance of Professor Jim Hinton in obtaining NMR data, and Research Corp. for financial support.

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[19] A plot of [**5**] (0–1.5 M **5** with 0.13 M **1** in Et_3N) vs. Φ_0/Φ_Q (where Φ_0 and Φ_Q are quantum yields for disappearance of **1** in the absence and presence of quencher, respectively) is linear (slope = 2.2 M^{-1}; intercept = 0.94; $r = 0.998$) as is the plot of [**6**] (0–2.0 M **6** with 0.13 M **1** in Et_3N) vs. Φ_0/Φ_Q (slope = 1.9 M^{-1}; intercept = 0.90; $r = 0.993$). Conversion were carried to 5–6%. The linearity suggests only one intermediate or state is being quenched but from available data it is not certain which.

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Liposomal Membranes. 13. Transport of an Amino Acid across Liposomal Bilayers As Mediated by a Photoresponsive Carrier

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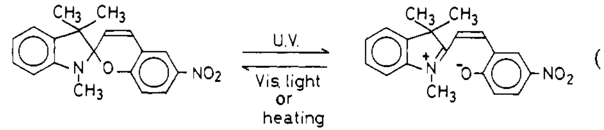
Azobenzene, stilbene, spiropyran, and rhodopsin are photoresponsive compounds that undergo a conformational change upon photoirradiation.[1-7] Hence, they have been utilized as a trigger or switch to photochemically control various phenomena such as substrate binding of crown ethers[2] or cyclodextrins,[3] activity of enzymes,[4] permeation of metal ions into liposomal membranes,[5,6] and morphology of synthetic bilayers.[7] In biological systems, of course, such a photoregulated process is well recognized as a primary stage in the photosynthesis and vision systems.[8] On the other hand, the transport of amino acids across cell membranes is really present in biological systems, where the carrier mechanism is generally preferred over the trans membrane channel mechanism.[9] In this communication, we show the first example of the photocontrolled transport of an amino acid across lipid membranes using the photospiran **1** embedded in liposomal bilayers of egg phosphatidylcholine (egg PC).

Upon UV irradiation in apolar organic solvents, the photospiran **1**, 1′,3′-dihydro-1′,3′,3′-trimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2′-[2*H*]indole], is easily converted to the colored and ring-opened form (**2**) bearing a merocyanine dye skeleton (eq 1).[1] Both the



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