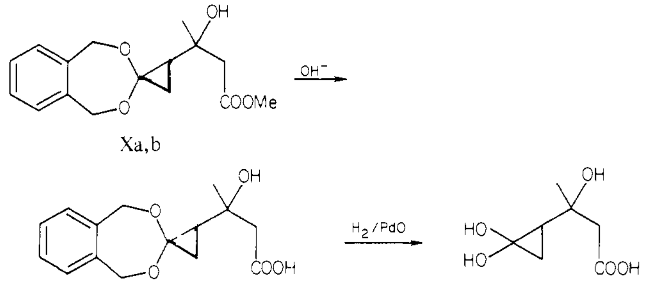
in hydrolysis of the ortho ester IX to the corresponding methyl ester X, an approximately 50:50 mixture of diastereomers Xa[8] and Xb.[8] The latter were separated by chromatography on silica gel and were readily distinguished by their NMR spectra.

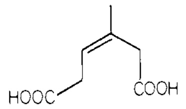
The methyl esters Xa and Xb were hydrolyzed to the corresponding acids XIa,[8] mp 90–91.5 °C, and XIb,[8] mp 105–107 °C, respectively. Each acid was then hydrogenated to remove the protecting *o*-xylylene group. This reaction required careful control because the cyclopropanone hydrate tends to undergo ring opening to the dicarboxylic acid XIII.[11] In the most successful and reproducible regimen, the reduction was carried out at −5 °C (ice–salt bath) with dry PdO, prepared according to Schopf.[12] The catalyst was prereduced in EtOAc for 3 h; then the substrate was added. The disappearance of starting material was monitored at R_f 0.7 on silica gel plates in 60:40 ethyl acetate–hexane. When the reaction was complete, it was worked up by filtration and solvent removal at 0 °C. The diastereomeric cyclomevalonic acids IIIa[8] and IIIb[8] appear to be stable at −15 °C. Complete decomposition to XIII occurred after 24 h at room temperature.



Xa,b

XIa,b

IIIa,b



XIII

Cyclomevalonate IIIa is an active inhibitor of HMG-CoA reductase[13] with $K_i = 10^{-4}$ M. Cyclomevalonate IIIb showed no inhibitory activity.

The lithium derivative VII of the protected cyclopropanone provides a useful link, not available before, in the synthesis of functionalized cyclopropanone hydrates. A second feature of the synthesis is the use of the ortho ester VIII[14] to direct the condensation reaction to the ketone carbonyl group of acetoacetate.[15,16] The ortho acetoacetate VIII is readily available and the ortho ester protecting group is cleanly removed under the mild conditions of silica gel chromatography.

Acknowledgment. This research was generously supported by the National Institute for General Medical Sciences under Grant GM 27667.

Supplementary Material Available: Experimental data for compounds V, VI, Xa,b, and IIIa,b (3 pages). Ordering information is given on any current masthead page.

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(11) The diester corresponding to XIII has been prepared by: Tsuji, J.; Hosaka, S. *J. Am. Chem. Soc.* **1965**, *87*, 4075.

(12) Schopf, C.; Brass, E.; Jacobi, E.; Jorde, W.; Mochik, W.; Neuroth, L.; Salzer, W. *Leibigs Ann. Chem.* **1940**, *544*, 53. In our preparation we omitted the final washings with methanol to remove unreacted $PdCl_2$.

(13) Purified according to: Oureshi, N.; Dugan, R. E.; Nimmannit, S.; Wu, W.-H.; Porter, J. W. *Biochemistry* **1976**, *15*, 4185.

(14) Prepared according to: Banville, J.; Brassard, P. *J. Chem. Soc., Perkin Tran. 1* **1976**, 1852.

(15) Cf.: Rousseau, B.; Beaucourt, J.-P.; Pichat, L. *Tetrahedron Lett.* **1982**, 2183. These authors have, while our work was in progress, developed several mevalonate syntheses making use of a *cis,cis*-1,3,5-cyclohexanetriol protected ortho acetoacetate.[12,13]

(16) Stetter, H.; Steinwacker, K. H. *Chem. Ber.* **1964**, *97*, 1839. Pichat, L.; Beaucort, J. P. Herbert, M. *Radioisotopy* **1971**, *12*, 519.

Photoreactivity of α,β-Unsaturated Carbonyl Compounds. 2. Fast Transients from Irradiation of 2-Cyclohexenones and Amines

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We recently reported results of steady irradiation experiments of 2-cyclohexenone (**1**) in the presence of triethylamine (**2**) that suggested enone dimerization was competitive with adduct formation to the amine.[1] We proposed that an enone excimer or some other dimeric metastable species was the precursor to the cyclobutane dimers (via unimolecular decay) and to the amine adducts via a mechanism first order in each amine and excimer. Evidence that the latter involves electron transfer or at least substantial charge transfer is consistent with CIDNP results.[2] Further support for this mechanism comes from transient decay measured on absorption changes using a Q-switched Nd:YAG laser line at 355 nm as the excitation beam.

A transient absorption change in the region 270–290 nm was reported for various enones in the absence of amines.[3,4] The transient is observed between 260 and 330 nm, a window in the ground-state absorption, as a maximum centered at 280 nm. Table I presents lifetimes at 280 nm for **1** irradiated in the presence of **2**.[5] The observation of *increasing lifetime* with added amine cannot be accounted for by any mechanism where amine simply reacts with or quenches the transient. In the presence of amine, we are likely to be observing a second transient of longer lifetime in fast equlibrium with the original species. The plateau in lifetime reached with added 1,4-diazabicyclo[2.2.2]octane (DABCO) (**4**) and the change in behavior with a given concentration of **2** at higher enone concentration support this.[5] Equation 1 is suggested

$$\mathrm{EN} \rightarrow\ \rightarrow \mathrm{EN}^3 \rightarrow \text{twisted } \pi,\pi^* \text{ (I)} \overset{K[\mathrm{AM}]}{\rightleftharpoons} (\mathrm{EN{\cdot}AM})^* \text{ (II)} \qquad (1)$$

to account for both transients (EN = enone; AM = amine).[6] Equation 2 represents the observed lifetime expressed in terms

$$1/\tau = k_{\mathrm{obsd}} = \alpha k_1 + (1 - \alpha)k_2 \qquad (2)$$

of the decay of I (rate = k_1; α = mole fraction of I) and II (rate = k_2; $(1 - \alpha)$ = mole fraction of II). Since the equilibrium can be represented by $K = [\mathrm{II}]/([\mathrm{I}][\mathrm{AM}])$ and $\alpha = [\mathrm{I}]/([\mathrm{I}] + [\mathrm{II}])$:

$$1/\tau = k_{\mathrm{obsd}} = \left(\frac{1}{1 + K[\mathrm{AM}]}\right)k_1 + \left(\frac{K[\mathrm{AM}]}{1 + K[\mathrm{AM}]}\right)k_2 \qquad (3)$$

This can be simplified to the form of eq 4. At low amine concentration $k_1 >> k_2K[\mathrm{AM}]$ and the lifetime becomes linearly dependent on amine concentration (eq 5) with a slope/intercept

$$k_{\mathrm{obsd}} = \frac{k_1 + k_2K[\mathrm{AM}]}{1 + K[\mathrm{AM}]} \qquad (4)$$

$$\tau_{\mathrm{obsd}} = (1 + K[\mathrm{AM}])/k_1 \qquad (5)$$

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(1) Pienta, N. J.; McKimmey, J. E. *J. Am. Chem. Soc.* **1982**, *104*, 5501-5502.

(2) Back electron transfer from the radical anion of **1** and **7** to the radical cation of DABCO explains observed polarizations: Smith, DW.; Pienta, N.J. *Tetrahedron Lett.* **1984**, 915.

(3) Goldfarb, T. D. *J. Photochem.* **1978**, *8*, 29-38.

(4) Bonneau, R. *J. Am. Chem. Soc.* **1980**, *102*, 3816-3822.

(5) Enone **1** (46.5 mM in acetonitrile) was also irradiated in the presence of triethylamine (**2**), *n*-butylamine (**3**), and DABCO (**4**) and gave the following data ([amine] (mM), lifetime at 280 nm (ns)): For **2** 120, 38.8; 310, 48.5; 550, 67.5. For **3** 67, 33.2; 202, 33; 405, 34.1; 742, 36.8. For **4** 10, 63; 20, 286; 30, 342; 40, 338; 70, 346.

(6) The assignment of I as a twisted π,π* state of the enone was made by Bonneau[4] and still best explains all data in the absence of amine: Structure II represents some exciplex of this state with amine.

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Table I. Irradiation of 33.5 mM **1** with **2** in Acetonitrile[a]

[**2**], mM	τ, ns[b]	[**2**], mM	τ, ns[b]
0	36.7	323	64.3
36	39.9	467	70.3
72	41.1	682	110.0
108	42.3	1041	154.0
180	49.8		

[a] Deoxygenated with N_2, irradiated at 355 nm, monitored at 280 nm. [b] Average of five transients. Standard deviations ≤3–5%. The uncertainty increases to the upper limit in the last three entries where the OD of the microsecond transient becomes greater than the OD of the nanosecond counterpart (ref 9).

Table II. Lifetimes of Substituted Cyclohexenones in Acetonitrile and Equilibria for Transient Complexation with **2**

cyclohexenone	τ, ns[a]	K, M^{-1} [b]
1	35.8 ± 1.4	1.78 ± 0.26
2-methyl (**5**)	56.0	c
3-methyl (**6**)	55.9	0.12
4,4-dimethyl (**7**)	29.7	0.39
5,5-dimethyl (**8**)	44.6	4.6
3,5,5-trimethyl (**9**)	84.0	0.28

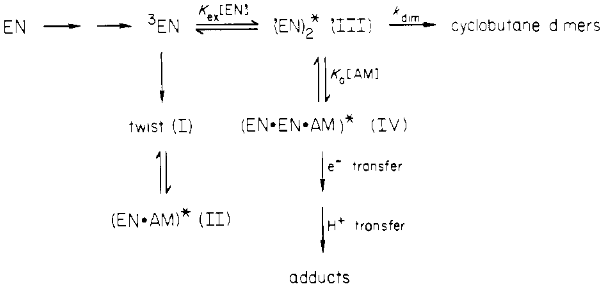
[a] Determined on enone 30–50 mM in acetonitrile, irradiated at 355 nm, monitored at 280 nm. Standard deviations are all 3–6%. [b] Calculated by plotting τ vs. [**2**] and dividing the slope by the intercept. See derivation in text. [c] The best-fit line predicts $K \approx 0$, but the experimental uncertainty sets the limit at $K < 0.01$.

ratio = K. A plot of the first seven entries in Table I gives an excellent fit (slope = 76.6; intercept = 36.2; $r = 0.99$; $K = 2.1$ M^{-1}). Similar treatment gives $K = 8.7 \times 10^{-2}$ for **3**, $K = 3.9 \times 10^{2}$ for **4**, and an average $K = 1.78 \pm 0.26$ for **2**.[7] The efficiency of complex II formation appears to be related to the donor ability of the amine.[8] The lifetimes and equlibria for various substituted cyclohexenones are listed in Table II and imply complexation is also limited by steric factors when methyl groups are directly attached to the chromophore.

No new transients at wavelengths different from the 260–330-nm region are observed in the presence of amines. However, the transient at 280 nm has two additional slow decay components that become measureable even at the lowest concentration in Table I. They give lifetimes of 2.7 ± 0.2 and 51 ± 4 μs and are invariant with amine concentration over the range studied. Thus, the decay data between 0 and 500 ns was best fit to the nanosecond and the 2-μs exponentials, while analysis between 0.2 and 40 μs gave the 2-μs exponentials. The common, microsecond rate determined from each of the two regions of the same decay curve were in excellent agreement. No satisfactory second-order fits were obtained. Replicate runs at half dose gave identical first-order rates with no better evidence for second-order fits. The relative contribution to the optical density of the microsecond transient increases while the nanosecond portion decreases as amine concentration is increased.[9] Similar data are obtained for the substituted enones irradiated in the presence of **2**: **6**, 10.3 and 226 μs; **7**, 1.65 and 26.6 μs. A single additional component with a lifetime of 2.30 ± 0.50 μs is observed when **1** is irradiated in the presence of **4**. Again these slower components grow at the expense of the nanosecond ones as amine concentration increases.

Attempts to further characterize I were not very fruitful. The lifetime of 1 in acetonitrile is invariant with its concentration, although the transient's optical density changes linearly over the range measured.[10] These observations are consistent with previous observations.[4] Attempts to fit the growth of the 280-nm transient peak proved unsuccessful, since we were in the time frame of the flash itself. Quenching experiments were conducted with naphthalene by observing the rise in naphthalene triplet at 414 nm and gave an extrapolated lifetime of about 20 ns at zero quencher concentration.[11] Although the experimental uncertainty makes it difficult to unequivocally state that this is a different species than the one with the 36-ns lifetime, naphthalene appears to be undergoing energy transfer from a species shorter lived than I, a likely candidate being an enone triplet. Both piperylene and cyclohexene give nonlinear quenching plots and undergo efficient product formation under steady irradiation conditions.[12]

The conclusions from these data require a complicated scheme, but one that supports our earlier suggestions:[1]



Apparently, I and II lead to very little, if any, product formation. At high amine concentration ([2] > 1 M), the composite contribution of I and II decreases as the K_a[AM] term dominates and syphons intermediates to the adduct-forming path. The microsecond transients could then correspond to the terplex, IV, or the radical-ions or radical pairs that follow in the scheme. The single component in the presence of DABCO is consistent with its radical ion being reluctant to transfer a proton.

Despite the host of intermediates invoked, we have no evidence to support the presence of a simple enone–amine exciplex as an important contributor in product formation, as ketone–amine work might suggest. The generality of this complex scheme is being pursued by study of additional α,β-unsaturated carbonyl chromophores.

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Registry No. 1, 930-68-7; **2**, 121-44-8; **3**, 109-73-9; **4**, 280-57-9; **5**, 1121-18-2; **6**, 1193-18-6; **7**, 1073-13-8; **8**, 4694-17-1; **9**, 78-59-1.

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(7) Five replicate runs on different samples for **2**; a single set of data for each 3 and 4.

(8) The equilibrium constants parallel amine donor numbers (Gutmann, V.; *Chimia*, **1977**, *31*, 1) and ionization potentials ("Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions", *Natl. Bur. Stand.* (*U.S.*) *Circ.* **1964**, No. 500).

(9) At [2] ≈ 1.0 M the nanosecond transient portion is only ≈5% of the total OD. In neat amine (7.17 M) no nanosecond transient can be observed or extracted from the decay. Without molar absorptivities of the individual transient components, quantitative evaluation of these ratios is indeterminate. The low resolution and narrow wavelength range of the transients preclude spectral assignment at this time.

(10) The first entry represents the lower detection limit under conditions employed ([**1**] (mM), τ (ns)): 3.62, 34.5; 33.1, 37.2; 36.5, 35.3; 40.0, 35.9; 43.4, 35.8.

(11) A plot of naphthalene concentration vs. $1/\tau$ (46.9 mM, 8.50×10^7 s^{-1}; 23.4 mM, 7.01×10^7 s^{-1}; 11.7 mM, 5.87×10^7 s^{-1}) gives $r = 0.993$, slope = 7.31×10^8 s^{-1} M^{-1}, intercept = 5.13×10^7 s^{-1} at [**1**] = 46.5 mM. At [**1**] = 46.5 mM and [naphthalene] = 11.7 mM the lifetimes were remeasured with added **2** ([**2**] (mM), τ (ns)): 17.9, 16.8; 89.6, 17.2; 305, 15.8. The amount of triplet, measured by its peak optical density, appears to decrease only slightly with added amine. A better agreement between transient lifetimes from direct measurement and naphthalene quenching has been obtained in cyclohexane by R. Bonneau, D. I. Schuster, and co-workers. A preliminary report is given in the 1981 IUPAC Photochemistry Meeting abstracts, p 314–315. We appreciate the private communication of additional results by Professors Schuster and Bonneau. The following communication, from these groups, presents convincing data supporting our suggestion that the 280-nm transients are not quenched by naphthalene.

(12) Pienta, N. J.; McKimmey, J. E.; Smith, D. W., unpublished results.