J. Am. Chem. Soc. **1988**, *110*, 8261–8263

The unambiguous interpretation of the kinetic parameters and substituent effects require that the cleavage process be irreversible under the reaction conditions. This requirement is apparently met[7] for our system as shown in experiments with $\mathbf{2a}^{\bullet+}$. A sample of single diastereoisomer[8] of **2a** was treated with 1 equiv of **3**. After the reaction was complete, 46% of the starting material was recovered. NMR analysis of this material indicated no detectable isomerization. Also of importance for mechanistic considerations, the observed activation parameters exclude involvement of an electron jump from the nonaminated ring as a kinetically significant step.[9]

The observed activation parameters indicate *significant C–C bond activation upon electron removal*. For comparison, the homolysis[11] of bicumene has $\Delta H^{\ddagger} = 46$ kcal/mol and $\Delta S^{\ddagger} = 14$ eu, and the activation energy is higher than that of $\mathbf{1a}^{\bullet+}$ by ca. 20 kcal/mol (at 300 K). Although the entropies of activation for reactions in solution are difficult to rationalize,[12] the negative $\Delta S^{\ddagger}$ values for $\mathbf{1}^{\bullet+}$ indicate that highly ordered solvation of the transition state is probably involved. This conclusion is supported by the activation parameters for $\mathbf{2}^{\bullet+}$, where steric hindrance to solvation seems to result in higher $\Delta H^{\ddagger}$. Such an interpretation is an apparent contradiction to the results observed for $\mathbf{1a}^{\bullet+}$ in solutions containing varying amounts of methanol (see above). These results indicated that the ground state is slightly more stabilized than the transition state by increased solvent polarity or hydrogen bonding. The contradiction can be reconciled by assuming that in solvation of the transition state the geometrical constraints are of greater importance than a small change in polarity of the medium.

Additional support for the importance of entropy factors is the observation that the differences in rate constants for $\mathbf{1a}$–$\mathbf{g}^{\bullet+}$ are due largely to $\Delta\Delta S^{\ddagger}$. The substituent effect on the reaction rate is, however, rather small. This effect ($\log k_{\mathrm{rel}}$) correlates well ($r = 0.998$) with σ^+ values[13a] yielding ρ^+ of -0.8. This value indicates a small but significant positive charge formation on carbon 2 (Scheme I). There is no correlation ($r < 0.68$) with $\sigma^{\bullet}$ values of Arnold[13b,c] or Creary.[13d] Lack of such correlation excludes formation of an unpolarized radical center on carbon 2. However, the observed ρ^+ is consistent with a polarized radical center,[14] and, in accordance with this observation, the transition state for C–C bond cleavage in $\mathbf{1}^{\bullet+}$ can be described in valence-bond terms as an interacting radical–cation pair ($\mathrm{ArC}^{\bullet}\cdots{}^{+}\mathrm{CAr}' \leftrightarrow \mathrm{ArC}^{+}\cdots{}^{\bullet}\mathrm{CAr}'$).

Acknowledgment. This research was supported by grants from NSF and the Research Corporation. P.M. is a recipient of the Camille and Henry Dreyfus Foundation New Faculty Award.

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[7] Recombination of the radical and cation faster than rotation of fragments and slower than oxidation of radical would not be detected.

[8] Diastereochemically pure **2a** of as yet unconfirmed stereochemistry was used. As little as 3% of the other diastereoisomer would have been easily detected. Meso and dl diastereoisomers of the parent hydrocarbon have essentially identical heats of formation (Kratt, G.; Beckhaus, H.-D.; Lindner, H. J.; Ruchardt, C. *Chem. Ber* **1983**, *116*, 3235).

[9] For example, the oxidation potentials of 4-(*N*,*N*-dimethylamino)toluene and 4-methoxytoluene differ by almost 1 V.[10] The activation energy for such a jump would be at least 23 kcal/mol, much larger than that observed for $\mathbf{1b}^{\bullet+}$ (16.5 kcal/mol at 300 K).

[10] (a) Seo, E. T.; Nelson, R. F.; Fritsch, J. M.; Marcoux, L. S.; Leedy, O. W.; Adams, R. N. *J. Am. Chem. Soc.* **1967**, *89*, 3498. (b) Sankararaman, S.; Haney, W. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 7824.

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[12] See, for example: Bunnett, J. F. In *Techniques of Chemistry*, 4th ed.; Bernasconi, C. F., Ed.; Wiley-Interscience: New York, 1986; Vol. 6, Part I, p 253.

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[14] Many radical reactions show negative ρ^+ values, although rarely of such large magnitude. See, for example: (a) Russell, G. A. In *Free Radicals*; Kochi, J. K., Ed.; John Wiley and Sons: New York, 1973; Vol. 1, p 275. (b) Russell, G. A.; Williamson, R. C., Jr. *J. Am. Chem. Soc.* **1964**, *86*, 2357. (c) Gleicher, G. J. *J. Org. Chem.* **1968**, *33*, 332.

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Are Triplet Exciplexes Involved in [2 + 2] Photocycloaddition of Cyclic Enones to Alkenes?

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In his seminal 1964 paper on photocycloaddition of cyclic enones to alkenes, Corey[1] suggested that the reaction proceeds by interaction of an enone excited state (subsequently identified as a triplet state)[2] with the alkene to give initially an "oriented π-complex"[1] (or exciplex)[3] which leads to a 1,4-biradical and ultimately cyclization and disproportionation products. De Mayo[4] later recognized that any of these intermediates could in principle revert to enone and alkene ground states. In the interim, enone–alkene photocycloaddition (or photoannelation) has become arguably the most frequently utilized photochemical reaction by synthetic organic chemists.[5]

Corey[1] invoked a polar π-complex, with alkene as electron donor and enone as acceptor, to rationalize the regiochemistry in photocycloadditions to cyclohexenone and "relative rate factors" determined from yields of photoadducts of cyclohexenone to alkenes formed under competitive conditions. However, photoproduct yields in multistep processes depend on overall quantum efficiencies (QE) and not on the rate of a single specific step, as demonstrated many years ago by Wagner for the Norrish type II reaction of aromatic ketones.[6] Thus, Corey's data[1] and similar findings[7] in fact provide no insight into alkene reactivity or the nature of the initial intermediate(s) formed from enone triplets and alkenes. In addition, the charge distribution assigned to Corey's exciplex assumed a reactive enone n,π^* triplet state,[1] although the reactive state is known to be a π,π^* state,[8] which for most enones is the lowest triplet.[9] Nonetheless, the exciplex hypothesis has enjoyed general acceptance for nearly 25 years,[5] although Eaton suggested[10] that this mechanism was not entirely satisfactory in rationalizing all available data.[11] We now present kinetic data which is clearly inconsistent with the Corey–de Mayo exciplex hypothesis.

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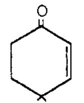
Table I. Rate Constants for Quenching of Enone Triplets by Alkenes[a] and Quantum Yield for Adduct Formation[b]

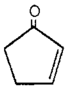
			$k_q \times 10^{-7}$ M^{-1} s^{-1}		$\Phi_{add}{}^c$ $(\Phi_{tc})^d$	
ketone		alkene[e]	MeCN	C_6H_{12}	MeCN	C_6H_{12}
2	+	CAN	200	520	0.04 (0.28)	0.05 (0.67)
		AN	63	180	0.08 (0.95)	0.03 (0.96)
		FN	160	460	0.00 (0.22)	(0.77)
		CH	33	42	0.64 (0.94)	0.42 (0.96)
		TCE	65		0.00 (0.91)	0.00
		CP	15	40	0.56 (0.85)	0.26 (0.87)
		TME		99	0.71	0.29 (0.97)
		DCE	78		0.18 (0.91)	0.15
		DME	3			
3	+	CAN	46	35	0.10 (0.95)	0.07 (0.91)
		AN	15	11	0.14 (0.84)	0.08 (0.29)
		FN		67	0.20	(0.95)
		CH	5.2	0.5	0.16 (0.66)	0.07 (0.12)
		TCE	1.2	2.0	0.00 (0.31)	0.00 (0.41)
		CP	<0.1	0.5	0.21	0.10 (0.14)
		TME	<0.1		0.08	0.03
		DME	0.7			
		DCE			0.07	0.04
4	+	AN	24			
		CP	6		0.21[f] (0.82)	
5	+	AN	130		1.60[g]	
		CH	27		4.16[g]	
		CP	3.8		1.00,[g] 0.048[f] (0.91)	
		DME	26		0.62[g]	

[a] Determined from lifetimes of enone triplet decay at 280 nm on flash excitation at 355 nm as a function of alkene concentration. [b] Adducts determined by GC/MS. Conversion <10%. [c] Quantum yield for photoaddition at 313 nm at 0.50 M alkene. [d] Quantum yields for enone capture at alkene concentrations used in determining Φ_{add}; see text for details. [e] Abbrebiations: CH = cyclohexene, DCE = 1,1-dichloroethylene, DME = 1,1-dimethoxyethylene, TCE = tetrachloroethylene. For others, see text. [f] Quantum yield at 313 nm in neat cyclopentene. [g] Relative quantum yield at 0.75 M alkene.

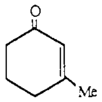
On the basis of triplet state lifetimes measured by using nanosecond flash photolysis, cyclic enones fall into two groups: (1) enones such as **1** whose triplets are very short-lived due to relaxation by twisting around the C=C bond and (2) enones such as **2–5** whose triplets are either planar or less twisted and hence longer lived.[12] The reactive triplet state of **1** is not directly intercepted by alkenes[13] (such as tetramethylethylene (TME), cyclopentene (CP), and acrylonitrile (AN)) but nonetheless affords cycloadducts, possibly by thermal addition to transoid cycloalkenones, as with cyclooctenone.[10,14] However, since alkenes react directly with triplets of enones **2–5**, rate constants k_a were directly obtainable, from the variation in enone triplet lifetime τ_T with alkene concentration, according to the relationship $(\tau_T)^{-1} = (\tau_o)^{-1} + k_a[\text{alkene}]$ (see Table I). The most striking observation is that the largest values of k_a are for electron-deficient alkenes, acrylonitrile (AN), α-chloroacrylonitrile (CAN), and fumaronitrile (FN). No correlation whatsoever is seen between k_a and QE for cycloaddition (Table I), just as for the Norrish II reaction.[6]



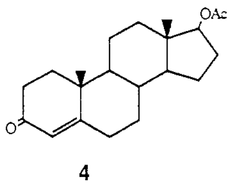
1



2



3



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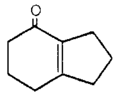

5

These data are totally inconsistent with expectations based on a single polar exciplex structure as described by Corey.[1] A mechanism involving direct formation of triplet biradicals is neither required nor excluded by these data; in this mechanism, QE_{add} would be determined primarily by partitioning of one or more biradicals between cyclization, disproportionation, and reversion to starting materials.[11] However, we cannot exclude the involvement of exciplexes of different polarity depending on the electron donor/acceptor properties of the alkene. Caldwell[15] has presented a strong case, based primarily on measurement of secondary kinetic isotope effects, for triplet exciplex precursors to 1,4-biradicals on interaction of aryl ketone n,π* triplets with alkenes en route to oxetanes and isomerized alkenes. Also, both electron-rich and electron-poor alkenes appear to interact with alkanone n,π* excited states but via two quite distinct geometries.[16] These findings[15,16] cannot be directly extrapolated to the fundamentally different case of photoannelation, where alkenes interact with enone π,π* triplets. The efficiency of triplet capture ϕ_{tc}, which is given by $k_a[\text{alkene}]\tau_T$, is typically much higher than ϕ_{add} (see Table I), demonstrating the importance of reversion from reaction intermediates and/or bimolecular quenching and the danger of drawing mechanistic conclusions from photoproduct yields. Inefficiency may also arise from triplet decay when k_a is small and the enone triplet is short-lived.

We were concerned that electron-deficient alkenes might be quenching enone triplets by triplet energy transfer, complicating the interpretation of the data in Table I, since AN is known to undergo triplet-sensitized photodimerization via a low-energy (ca. 60 kcal/mol) triplet state.[17,18] However, we find that dimers of both AN and CAN, readily produced by benzophenone (BP) sensitization, are produced in at most trace quantities on photoexcitation of **2**, **3**, **5** or cyclohexenone in neat AN or CAN, while photoadducts (identified by GC/MS) are formed in good yields.

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To determine if adducts might be formed in these systems via a route involving triplet energy transfer followed by addition of alkene triplets to ground-state enone, triplet AN was generated by BP sensitization in the presence of **2** (0.2 M) in neat AN under conditions where BP (1.0 M) absorbed >97% of the incident excitation. Only AN dimers were formed under these conditions; no adducts of AN to **2** could be detected. Thus, occurrence of triplet excitation transfer as the electron donor/acceptor properties of the alkene are varied cannot explain our data.

Spectroscopic analysis indicates that photoadducts of enones **2–5** with AN, FN, and CAN are annelation products and not oxetanes,[19] but their regio- and stereochemistry have yet to be established. Such adducts are also formed with cycloheptenone,[20] which does not form adducts with electron-rich alkenes.[1] We believe that widespread acceptance of the exciplex hypothesis[5] has inhibited exploration of the utility of photocycloadditions of enones to electron-poor alkenes in synthetic methodology.[21]

Thus, despite the undeniable heuristic value of the exciplex hypothesis,[5] the intermediacy in enone photoannelations of Corey's "oriented π-complex"[1] is not supported by our kinetic data. A distinction between direct formation of triplet biradicals and the involvement, at least in some cases, of a prior intermediate must await the results of further kinetic studies.

Acknowledgment. The National Science Foundation (CHE-8320154) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, are thanked for grants in support of the research at NYU. N.J.T. thanks NSF and AFOSR for generous support of the research at Columbia.

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(19) In particular, GC/MS, NMR, and FT-IR spectra of separated products as well as product mixtures show, respectively, the proper mass and molecular fragmentation patterns characteristic of [2 + 2] cycloadducts, the absence of vinyl hydrogens, and the presence of the carbonyl moiety. Full details will be given in the full paper to be published later.

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Phosphine Complexes of Yttrium(III). Synthesis, Reactivity, and Fluxional Behavior of YCl[N(SiMe$_2$CH$_2$PMe$_2$)$_2$]$_2$

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There are no phosphine coordination compounds of the group 3 element yttrium.[1] In fact, if one looks to the lanthanoid metals, to which yttrium is often compared because of its similar physiochemical properties,[2] a conclusion easily reached is that phosphine ligands are not well suited[3] for complexes of these elements. Arguments based on *hard* and *soft*, that is, mismatching of donors and acceptors, undoubtedly have some merit since the prototypical ligands for these hard metal centers are oxygen- and nitrogen-based.[1] Given the fact that the phosphine donor has played a pivotal role in the development of the coordination chemistry of the transition elements,[4] we set out to prepare phosphine complexes of the early transition elements and the lanthanoid metals. We were confident that new chemistry and reactivity patterns would emerge simply because the choice of ligands around a metal is one of the most important factors in tuning a metal's chemical behavior.

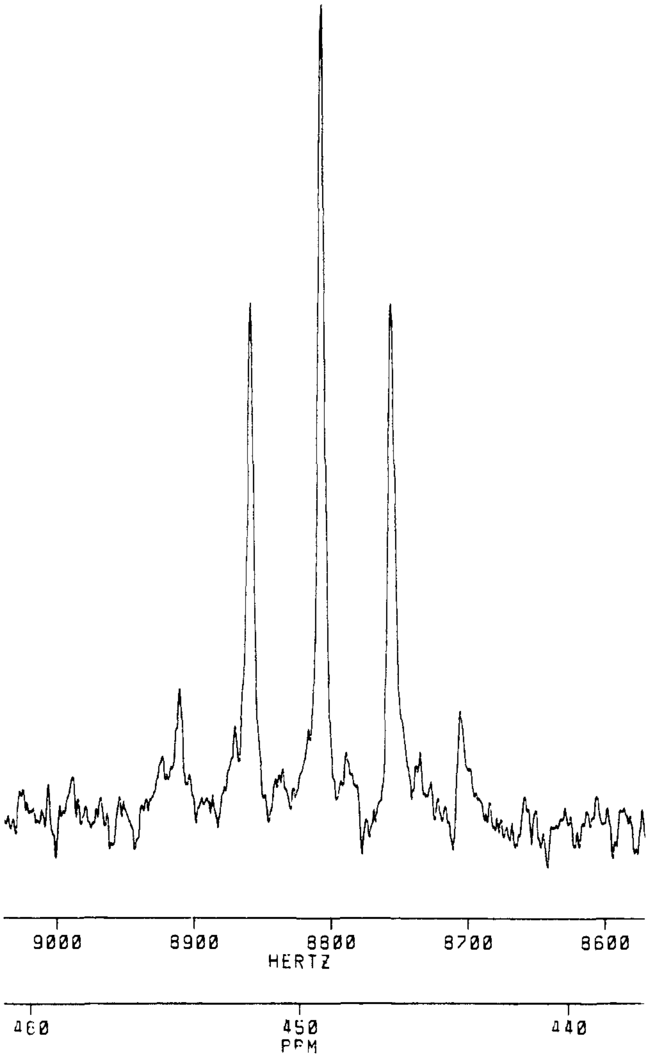

Figure 1. ^{89}Y NMR spectrum of 0.3 M YCl[N(SiMe$_2$CH$_2$PMe$_2$)$_2$]$_2$ (in C$_7$D$_8$–THF; (70:30) relative to aqueous YCl$_3$ at 0 ppm. The spectrum was obtained with a 20-ms pulse and a 2-s acquisition time over a total time of 10 h.

An already proven protocol for the introduction of phosphine ligands onto the group 4 metals, Zr(IV) and Hf(IV), is the use of a chelating array containing the disilylamido donor flanked by two phosphine ligands as shown in the bis(ligand) complexes[5] **1** and the monoligand derivatives[6] **2**. Our strategy for the design of this ligand type was to take advantage of the ability of the amide donor to anchor the chelate array on Zr(IV) and Hf(IV) and force

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