The conclusions on excimer symmetry presented above, which are based on the similarity of the excimer lifetimes, are fully supported by the correlation of the data in Figure 1. In this Figure the data points for excimer $^1D^*_1$ of 1Py(3)1Py, for which a symmetric structure was assumed, have the same linear ΔH vs. ΔS correlation as that of the symmetric excimers of 2Py(3)2Py and *meso*- and *rac*-2DPP (line L1). The ΔH–ΔS data of the second, asymmetric, excimer $^1D^*_2$ of 1Py(3)1Py lie on the same line as those of the asymmetric excimer of 1Py(16)1Py (line L2). It can therefore be concluded that the two straight lines in Figure 1 differentiate the data according to excimer symmetry.

Further, of special interest is the observation that in the case of *meso*-2DPP in methylcyclohexane, which has a positive value for ΔH (Figure 1, point 51), efficient excimer formation occurs ($k_a = 5.6 \times 10^8$ s^{-1} at 25 °C),[6c] the reaction being driven by entropy.[5]

An important general conclusion to be derived from the ΔH–ΔS relationship for excimers presented here is that the formation of weakly stabilized complexes in the excited state (even those with positive ΔH) cannot be ruled out a priori. Their small ΔH values are compensated by a proportionally less negative or even positive value for ΔS. This is especially important in the ongoing discussions on the existence of triplet excimers.[10] Triplet excimers certainly will have small absolute ΔH values, as locally excited triplet states do not lead to a stabilization by exciton interaction.[11,12] In addition, the charge resonance interaction between the states $^3A^*A$ and A^+A^- mostly is weak, due to the relatively large energy difference between the two states, as compared to singlet excimers. Because of the ΔH–ΔS compensation, such weakly stabilized triplet excimers can nevertheless be formed. As an example, for the triplet excimer of 1,3-di(9-phenanthryl)propane in *n*-decane, a ΔH of −11 kJ/mol was found, with a ΔS value of −23 J K^{-1} mol^{-1}.[6f–h]

(10) (a) Nickel, B.; Rodriguez Prieto, M F. *Z. Phys. Chem.* (*Munich*) **1986**, *150*, 31 and references cited therein. (b) Lim, E. C. *Acc. Chem. Res.* **1987**, *20*, 8.

(11) Mc Glynn, S. P.; Armstrong, A. T.; Azumi, T. In *Modern Quantum Chemistry*; Sinanoglu, O., Ed.; Academic: New York, 1965; Vol. 3.

(12) Weller, A. In *The Exciplex*; Gordon, M.; Ware, W. R., Eds.; Academic: New York, 1975.

A Cis Hydroxyamination Equivalent: Application to the Synthesis of (−)-Acosamine

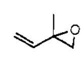
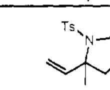
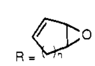
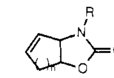
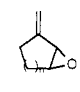
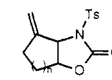
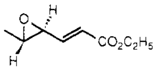
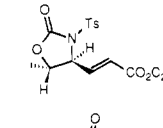
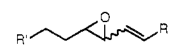
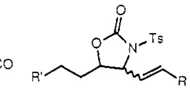
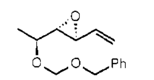
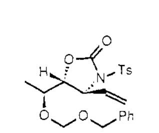
Barry M. Trost* and Anantha R. Sudhakar

Department of Chemistry, University of Wisconsin Madison, Wisconsin 53706

Received January 29, 1987

Diastereoselective introduction of heteroatoms constitutes an important challenge in complex synthesis. Recent interest in amino sugars[1–3] has drawn attention to the process of hydroxyamination.[4]

Table I. Pd-Catalyzed Oxazolidin-2-one Synthesis

entry	vinyl epoxide	isocyanate	product	yield
1		TsNCO		79%
		RNCO		
2	n = 1	R = Ph	n = 1, R = Ph	78%
3	n = 2	R = Ph	n = 2, R = Ph	90%
4	n = 2	R = C_6H_4–OCH_3	n = 2, R = C_6H_4–OCH_3	92%
5	n = 2	R = Ts	n = 2, R = Ts	100%
		TsNCO		
6	n = 1		n = 1	87%
7	n = 2		n = 2	63%
8		TsNCO		60%
		TsNCO		
9	R = H, R' = Ph		R = H, R' = Ph	92%
10	R = CH_3, R' = Ph		R = CH_3, R' = Ph	74%
11	R = H, R' = n-$C_{10}H_{21}$		R = H, R' = n-$C_{10}H_{21}$	94%
12		TsNCO		100%

The ready availability of epoxides in enantiomerically pure form from olefins[5] makes such intermediates particularly useful in achieving a net hydroxyamination of olefins.[6,7] Reaction of vinyl epoxides with nitrogen nucleophiles in the presence of Pd(0) catalysts leads to 1,4-substitution (eq 1, path a).[8] We therefore sought a complementary regiochemistry, i.e., a vicinal hydroxyamination (eq 1, path b), based upon the notion of tethering the nucleophile to the oxygen of the leaving group as in eq 1, path c. The conceptual problems with this approach are (1) the efficacy of trapping the initial zwitterion with isocyanates prior to its unimolecular decomposition and (2) the possibility of O- rather than N-alkylation if the zwitterion can be intercepted by the isocyanate.[9] Indeed, the thermal reaction of vinyl epoxides with

(1) For recent reviews, see: Hauser, F. M.; Ellenberger, S. R. *Chem. Rev.* **1986**, *86*, 35. McGarvey, G. J.; Kimura, M.; Oh, T.; Williams, J. M. *J. Carbohydr. Chem.* **1984**, *3*, 125.

(2) For some very recent references toward daunosamine, see: Hirama, M.; Nishizaki, I.; Shigemoto, T.; Ito, S. *J. Chem. Soc., Chem. Commun.* **1986**, 396. Hauser, F. M.; Ellenberger, S. R.; Glusker, J. P.; Smart, C. J.; Carrell, H. L. *J. Org. Chem.* **1986**, *51*, 50. Waim, A.; Vogel, P. *Tetrahedron Lett.* **1985**, *26*, 5127; Hirama, M.; Shigemoto, T. Ito, S. *Tetrahedron Lett.* **1985**, *26*, 4137. Wovkulich, P. M.; Uskokovic, M. R. *Tetrahedron* **1985**, *41*, 3455. Hanessian, S.; Kloss, J. *Tetrahedron Lett.* **1985**, *26*, 1261. Jager, V.; Muller, I. *Tetrahedron* **1985**, *41*, 3519.

(3) For some very recent references toward acosamine, see: Hirama, M.; Shigemoto, T.; Yamasaki, Y.; Ito, S. *Tetrahedron Lett.* **1985**, *26*, 4133. Brimacombe, J. S.; Hanna, R.; Tucker, L. C. N. *Carbohydr. Res.* **1985**, *136*, 419. Hiyama, T.; Nishide, K.; Kobayashi, K. *Tetrahedron Lett.* **1984**, *25*, 569. Suami, T.; Tadano, K.; Suga, A.; Ueno, Y. *J. Carbohydr. Chem.* **1984**, *3*, 429.

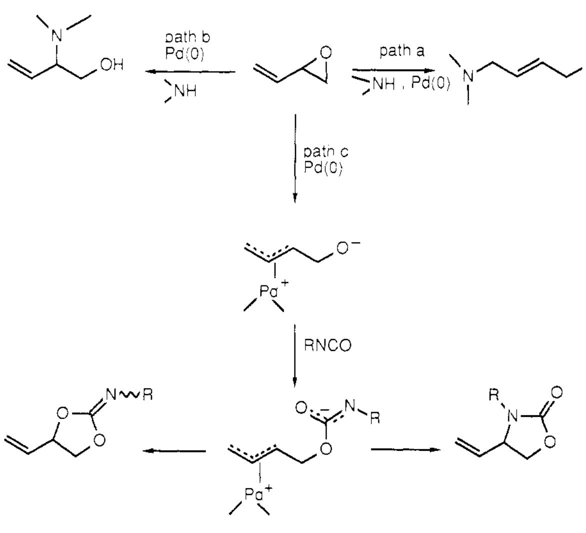
(4) Sammes, P. G.; Thetford, D. *Tetrahedron Lett.* **1986**, *27*, 2275. Caron, M.; Sharpless, K. B. *J. Org. Chem.* **1985**, 50, 1557. Trost, B. M.; Shibata, T. *J. Am. Chem. Soc.* **1982**, *104*, 3225. Herranz, E.; Sharpless, K. B. *J. Org. Chem.* **1978**, *43*, 2544. Kretchmer, R. A.; Daly, P. J. *J. Org. Chem.* **1976**, *41*, 192.

(5) Sharpless, K. B.; Behrens, C. H.; Katsuki, T.; Lee, A. W. M.; Martin, V. S.; Takatani, M.; Viti, S. M. Walker, F. J.; Woodard, S. S. *Pure Appl. Chem.* **1983**, *55*, 589.

(6) (a) For alternative approaches, see: Fujiwara, M.; Baba, A.; Tomohisa, Y.; Matsuda, H. *Chem. Lett.* **1986**, 1963. Mereyala, H. B.; Frei, B. *Helv. Chim. Acta* **1986**, *69*, 415. Julina, R.; Herzig, T.; Bernet, B.; Vasella, A. *Helv. Chim. Acta* **1986**, *69*, 368. Baba, A.; Fujiwara, M.; Matsuda, H. *Tetrahedron Lett.* **1986**, *27*, 77. Farooqi, J. A.; Ahmad, M. *Chem. Ind.* (*London*) **1985**, 598. Baba, A.; Shibata, I.; Masuda, K.; Matsuda, H. *Synthesis* **1985**, 1144 and references therein. (b) For a review, see: Dyen, M. E.; Swern, D. *Chem. Rev.* **1967**, *67*, 197. Also see: Roush, W. R.; Adam, M. A. *J. Org. Chem.* **1985**, *50*, 3752. (c) For reactions of chlorosulfonyl isocyanate, see: Lorincz, T.; Erden, I.; Nader, R.; de Meijere, A. *Synth. Commun.* **1986**, *16*, 123. Murthy, K. S. K.; Dhar, D. N. *Synth. Commun.* **1984**, *14*, 7, 687.

(7) A tin iodide–phosphine oxide reaction of vinyl epoxides proceeds in poor yields and, in the case of the monoepoxide of isoprene, with opposite regioselectivity. See: Shibata, I.; Baba, A.; Iwasaki, H.; Matsuda, H. *J. Org. Chem.* **1986**, *51*, 2177.

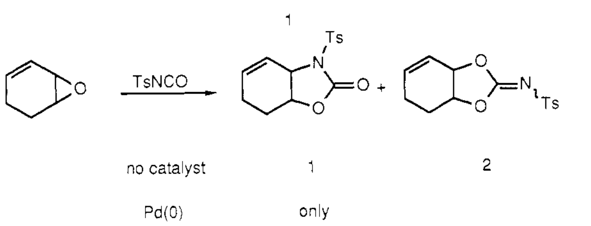
(8) Trost, B. M.; Molander, G. *J. Am. Chem. Soc.* **1981**, *103*, 5969. Trost, B. M.; Romero, A. G. *J. Org. Chem.* **1986**, *51*.



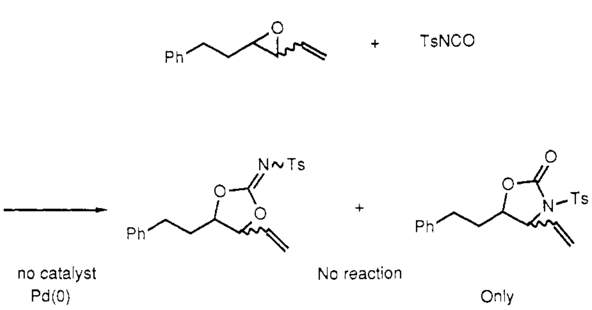
(1)

chlorosulfonyl isocyanate proceeds by intramolecular O- rather than N-alkylation.[6] An additional concern arises from the poor nucleophilic properties of amides in palladium-catalyzed reactions.[10]

To test the feasibility of a palladium-mediated vicinal hydroxyamination, we examined the reactions of *p*-toluenesulfonyl isocyanate (**1**) and the monoepoxides of cyclohexadiene (**2**) and 6-phenyl-1,3-hexadiene (**3**). A thermal reaction does proceed with vinyl epoxide **2** but *not* with **3**. However, the major product in the thermal reaction of **2** is the O-alkylated product **4**. In contrast to these results, both vinyl epoxides react smoothly in the presence of 1–3 mol % Pd(0) derived from $(dba)_3Pd_2CHCl_3$ (**7**)[11a] and 6–18 mol % triisopropyl phosphite (**8**) in THF at room temperature to give only the *N*-*p*-toluenesulfonyl-2-oxazolidones **5** and **6**.[11b] Table I illustrates the generality of this reaction.



(2)



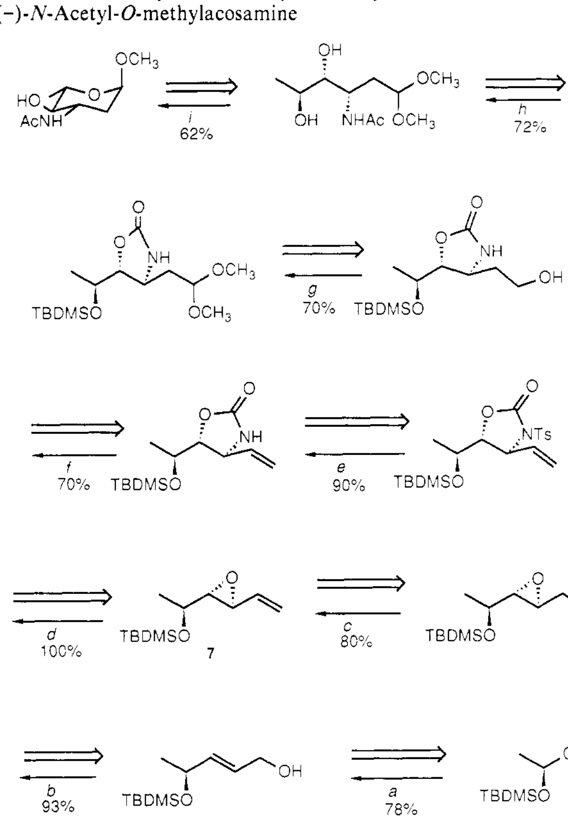
(3)

The choice of isocyanate is important. As shown in entries 2, 3, and 4, phenyl and *p*-anisyl isocyanate react equally well but benzyl isocyanate fails to participate presumably because it fails to intercept the zwitterion because of its poor electrophilicity. The *p*-toluenesulfonyl isocyanate reacts significantly faster than the aryl isocyanates—a fact that might suggest opening of the epoxide is also facilitated by coordination with the isocyanate. The choice of ligand is also important. Triarylphosphines lead to poor catalyst lifetime compared to triisopropyl phosphite, presumably because of their higher basicity leading to reactions with the isocyanates.

The diastereoselectivity of the reaction using tosyl isocyanate is excellent. For both entries 8 and 12, diastereomerically and, in the latter case, enantiomerically pure products result. Equations 4–6 illustrate the ease with which the derived 2-oxazolidones may be manipulated.[12,13]

The potential of this approach in a synthetic application culminated in a synthesis of (−)-acosamine, conveniently isolated as its *N*-acetyl-*O*-methyl glucoside, mp 159–160 °C, $[\alpha]^{20}_D$ −148° (*c* 0.05, CH_3OH) [lit.[14] mp 160–161 °C, $[\alpha]^{20}_D$ −146 (*c* 0.52,

Scheme I. Retrosynthetic Analysis and Synthesis of (−)-*N*-Acetyl-*O*-methylacosamine



[a](i) $(CH_3O)_2P(O)CH_2CO_2CH_3$, $(i\text{-}C_3H_7)_2NC_2H_5$, LiCl, CH_3CN, room temperature (cf. ref 15 and 16); (ii) DIBAL-H, $PhCH_3$, hexane, ether, −78 °C. [b](i) $t\text{-}C_4H_9OH$, 5 mol % $Ti(OC_3H_7\text{-}i)_4$, 7 mol % (+)-DET, $PhCH_3$, CH_2Cl_2, −12 °C (cf. ref 17). [c](i) $(COCl)_2$, Me_2SO, CH_2Cl_2, $(C_2H_5)_3N$, −65 °C; (ii) Ph_3PCH_3Br, $KOC_4H_9\text{-}t$, THF, −78 °C to room temperature. [d]TsNCO, 1 mol % $(dba)_3Pd_2$ $CHCl_3$, 6 mol % $(i\text{-}C_3H_7O)_3P$, THF, room temperature. [e]Na^+, $C_{10}H_8^-$, DME, −78 °C. [f]$[(CH_3)_2CHCH(CH_3)]_2BH$, THF then $NaHCO_3$, H_2O_2. [g](i) PCC, Celite, CH_2Cl_2, room temperature (cf. ref 18); (ii) $(CH_3O)_3CH$, CH_3OH, PPTS, reflux. [h](i) NaOH, C_2H_5OH, H_2O, reflux; (ii) Ac_2O, CH_3OH, room temperature. [i]CH_3OH, HCl, reflux.

(9) In our previous study with carbon dioxide as a trap, this regioselectivity problem does not arise. See: Trost, B. M.; Angle, S. R. *J. Am. Chem. Soc.* **1985**, *107*, 6123. Also see: Fujinami, T.; Suzuki, T.; Kamiya, M.; Fukuzawa, S.; Sakai, S. *Chem. Lett.* **1985**, 199.

(10) However, see: Bystrom, S. E.; Aslanian, R.; Backvall, J. E. *Tetrahedron Lett.* **1985**, *26*, 1749. Inoue, Y.; Taguchi, M.; Hashimoto, H. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2721.

(11) (a) Dba = dibenzylideneacetone. (b) All new compounds have been satisfactorily characterized by spectral analysis and elemental composition established by either high-resolution mass spectrometry or combustion analysis.

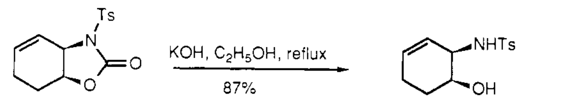
(12) Adams, C. E.; Walker, F. J.; Sharpless, K. B. *J. Org. Chem.* **1982**, *47*, 2765. For photolytic reductive cleavage, see: Hamada, T.; Nishida, A.; Yonemitsu, O. *J. Am. Chem. Soc.* **1986**, *108*, 141.

(13) Kronenthal, D. R.; Han, C. Y.; Taylor, M. K. *J. Org. Chem.* **1982**, *47*, 2765.

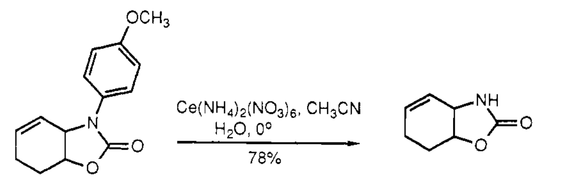
(14) Lee, W. H.; Yu, H. Y.; Christensen, J. E.; Goodman, L.; Henry, D. W. *J. Med. Chem.* **1975**, *18*, 768.

(15) For protected lactaldehydes, see: Banfi, L.; Bernardi, A.; Columbo, L.; Gennari, C.; Scolastico, C. *J. Org. Chem.* **1984**, *49*, 3784. A conference report describes the TBDMS ether used here. See: Hirami, M.; Shigemoto, T.; Nishizaki, I.; Yamazaki, Y.; Ito, S. *Chem. Abstr.* **1985**, *105*, 172917g.

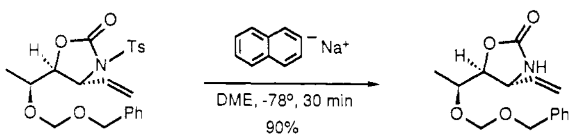
(16) For phosphonate conditions, see: Blanchette, M. A.; Choy, W.; Davis, J. T.; Essenfeld, A. P.; Masamune, S.; Roush, W. R.; Sakai, T. *Tetrahedron Lett.* **1984**, *25*, 2183.



(4)



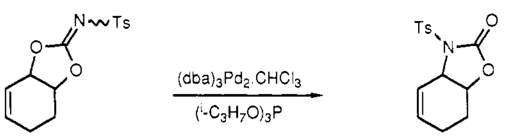
(5)



(6)

$CH_3OH)$], as outlined in Scheme I. The key conversion of the enantiomerically pure vinyl epoxide **7** to the 2-oxazolidone proceeds with complete retention of configuration.

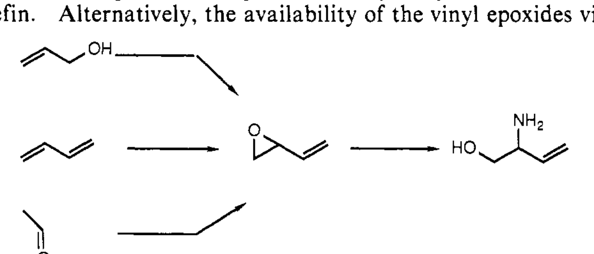
This metal-catalyzed facile (0 °C to room temperature) opening of vinyl epoxides with retention of configuration makes amino alcohol derivatives of defined stereochemistry readily available. The reaction course most simply may be interpreted in terms of path c of eq 1; however, the question of O vs. N alkylation in a kinetic sense is not established. We have determined that products of O-alkylation do rearrange to the products of N-cyclization in the presence of the Pd(0) catalyst (eq 7). Thus, it is possible



(7)

that the kinetic products of cyclization in the Pd(0) opening of vinyl epoxides with isocyanates are the imino carbonates which subsequently rearrange to the presumed thermodynamically more stable 2-oxazolidones. Further work on the mechanism and scope of the reaction is in progress.

Synthetically, the availability of vinyl epoxides from olefins makes this sequence the equivalent of hydroxyamination of an olefin. Alternatively, the availability of the vinyl epoxides via



a sulfur ylide addition[19] to carbonyl partners makes this sequence equivalent to a regiocontrolled addition of an allylamine anion to a carbonyl group.

Acknowledgment. We thank the National Science Foundation and the National Institutes of Health, General Medical Sciences, for their generous support of our programs.

(17) For catalytic epoxidation conditions, see: Hanson, R. M.; Sharpless, K. B. *J. Org. Chem.* **1986**, *51*, 1922. Epoxidation with MCPBA gives a 1:1.8 mixture of the desired epoxide and its diastereomer. For an alternative approach for diastereoselective epoxidation, see: Hasan, I.; Kishi, Y. *Tetrahedron Lett.* **1980**, *21*, 4229.

(18) For oxidation conditions, see: Herscovici, J.; Antonakis, K. *J. Chem. Soc., Chem. Commun.* **1980**, 561.

(19) Rosenberger, M.; Newkom, C.; Aig, E. R. *J. Am. Chem. Soc.* **1983**, *105*, 3656.

Return Electron Transfer within Geminate Radical Ion Pairs. Observation of the Marcus Inverted Region

Ian R. Gould,* Deniz Ege, Susan L. Mattes, and Samir Farid*

Corporate Research Laboratories, Eastman Kodak Company Rochester, New York 14650

Received December 30, 1986

In recent years the physical and chemical properties of photoinduced electron-transfer reactions have been extensively studied,[1] with particular emphasis on maximizing the efficiency of charge separation.[2] However, energy-wasting return electron transfer, especially within the primary geminate radical ion pair for singlet-state reactions, often results in low quantum yields for free-ion formation.[1,2] Detailed studies of the mechanisms and kinetics of product formation for several photosensitized electron-transfer reactions suggest that a relationship exists between the thermodynamics and the kinetics of the return electron transfer process.[1a,3] In this work we summarize the results of laser flash photolysis studies which were specifically designed to study this relationship. The results provide a clear example of the Marcus "inverted region" in these processes.[4]

Experiments were performed in degassed acetonitrile at room temperature using 9,10-dicyanoanthracene (DCA) and 2,6,9,10-tetracyanoanthracene (TCA) as the excited-state sensitizers and electron acceptors and naphthalene derivatives, diphenylacetylene, and biphenyl as the electron donors (Table I). Absolute quantum yields for formation of free radical ions (Φ_{sep}) were determined by using conventional laser flash photolysis. In each case, the excited acceptor was efficiently quenched by the electron donors; otherwise, minor corrections for incomplete interception were made. 4,4′-Dimethoxystilbene (DMS, 5×10^{-4} M) was added to scavenge the radical cations which escaped the radical ion pair. The low concentration of DMS ensured that interception of the excited acceptor or of the geminate pair by DMS was insignificant. The same transient species, the DMS radical cation, was monitored irrespective of the donor/acceptor pair. The relative amounts of DMS radical cation observed for the different donor/acceptor pairs gave the relative quantum yields for free-ion formation (Φ_{sep}) directly (Table I). The relative yields were converted to absolute yields by using the benzophenone triplet state as an actinometer.[5a,b,6]

A highly simplified mechanism which, however, includes the important processes required to understand the data is shown in Scheme I. Electron transfer from the donors to the excited-state acceptors is exothermic, and so other quenching mechanisms are not expected to be important. Weak exciplex emission can be detected for several of the donor/acceptor pairs, but the only process of significance for these exciplexes is geminate ion pair formation.[5d,e]

(1) (a) Mattes, S. L.; Farid, S. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1983; Vol. 6, p 233. (b) Davidson, R. S. In *Advances in Physical Organic Chemistry*; Gold, V., Bethell, D., Eds.; Academic: London, 1983; Vol. 19, p 130. (c) Mattes, S. L.; Farid, S. *Science (Washington, DC)* **1984**, *226*, 917. (d) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401.

(2) See, for example: Fox, M. A. In *Advances in Photochemistry*; Volman, D. H., Gollnick, K., Hammond, G. S., Eds.; Wiley: New York, 1986; Vol. 13, p 237.

(3) (a) Mattes, S. L.; Farid, S. *J. Chem. Soc., Chem. Commun.* **1980**, 126. (b) Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1983**, *105*, 1386. (c) Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1986**, *108*, 7356.

(4) (a) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966. (b) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.

(5) (a) Details of these experiments will be reported in a full publication. (b) A similar value of Φ_{sep} for the dicyanoanthracene/diphenylacetylene pair is obtained from steady-state product analysis experiments in which diphenylacetylene is used as a cosensitizer for the decomposition of benzyltrimethylsilane (ref 5c). (c) Mattes, S.; Farid, S., unpublished results. (d) Gould, I. R.; Kennedy, T. J.; Farid, S., unpublished results. (e) Weller, A. *Z. Phys. Chem. (Wiesbaden)* **1982**, *130*, 129.

(6) The values of Φ_{sep} were observed to be concentration dependent (ref 5a). The data in Table I are extrapolated to zero concentration.

0002-7863/87/1509-3794$01.50/0