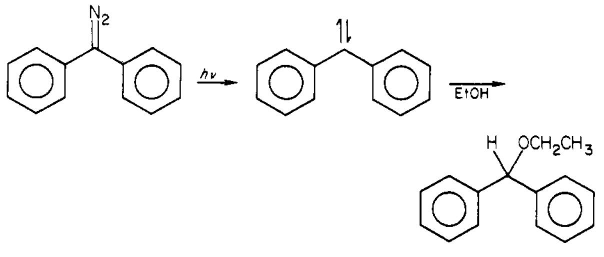
the formation of triplet diphenylcarbene from diphenyldiazomethane in benzene is $\Delta H = -12 \pm 2$ kcal/mol. This is to be contrasted with the endothermic heat of reaction of $\sim$33 kcal/mol for the formation of triplet methylene from diazomethane.[3]

In addition, this technique can be used to study reactions of carbenes. Examination of the photolysis of diphenyldiazomethane in neat ethanol results in the formation of diphenylmethyl ethyl ether (eq 2) with a quantum yield of $\Phi = 0.78$.[6] In neat ethanol, the rate of insertion of the singlet carbene into the O-H bond, $k = 3.5 \times 10^{10}$ mol^{-1} s^{-1},[2d] will be approximately 2 orders of magnitude faster than the intersystem crossing rate of the carbene. Thus, the resulting ether will be formed on the picosecond time scale, satisfying the requirements for the application of photoacoustic calorimetry. We find that the heat of reaction from diphenyldiazomethane to diphenylmethyl ethyl ether is $\Delta H = -54 \pm 2$ kcal/mol. Assuming that the energy of the carbene is solvent independent, this result indicates a heat of reaction of -47 ± 2 kcal/mol for the formation of diphenylmethyl ethyl ether from singlet diphenylcarbene in ethanol.



(2)

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE-8117519). K.S.P. also thanks the Camille and Henry Dreyfus Foundation and the Alfred P. Sloan Foundation for this support.

Registry No. Diphenyldiazomethane, 883-40-9; diphenylcarbene, 3129-17-7; ethanol, 64-17-5.

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(9) (a) Wilkinson, F. In "Organic Molecular Photophysics"; Birks, J. B., Ed.; Wiley: New York, 1975; Vol. 2, p 95. (b) Berlman, I. B. "Handbook of Fluorescence Spectra of Aromatic Molecules", 2nd ed.; Academic Press: New York, 1971. (c) Sharafy, S.; Muszkat, K. A. *J. Am. Chem. Soc.* **1971**, *93*, 4119. (d) Turro, N. J. "Modern Molecular Photochemistry"; Benjamin Cummings: Reading, MA, 1978.

Cation Radical Diels-Alder Reactions of Electron-Rich Dienophiles

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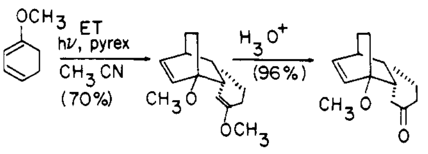
The exceptional reactivity and selectivity of cation radicals of hydrocarbon conjugated dienes as dienophilic components in Diels-Alder cycloadditions is now well documented.[1-5] The concept of cation radicals in general as highly electron deficient and therefore extremely reactive dienophiles is particularly significant in view of the strategic position of the Diels-Alder in organic synthesis and the inherent complementarity of the new Diels-Alder procedure to the classic one. Specifically, electron-rich π systems, which normally are ineffective as Diels-Alder dienophiles, are precisely the systems that are most readily converted to cation radicals. The extension of the cation radical catalyzed Diels-Alder procedure to a variety of electron rich dienophiles would thus qualify it as a significant adjunct to the conventional Diels-Alder synthetic strategy. The feasibility of the proposed extension to electron-rich dienophiles including dienes, alkenes, and styrenes is now reported, and a new and efficient alternative procedure for initiating the cation radical Diels-Alder is described.

Scheme I



1 2 3

Triarylaminium salt catalyzed Diels-Alder cycloadditions of conjugated dienes bearing a directly attached electron-donating oxygen functionality (acetoxy, methoxy) were selected for initial investigation. The unreactivity of 1-acetoxy-1,3-butadiene toward dimerization suggested that the acetoxy group is insufficiently activating to permit cation radical formation in the simple diene system. More surprising was the unreactivity of 1-acetoxy-1,3-cyclohexadiene, which indicates the acetoxy group is actually sharply deactivating toward cation radical formation. In contrast, 1-methoxy-1,3-cyclohexadiene (**1**) instantly decolorizes the catalyst but apparently suffers polymerization, and no Diels-Alder dimer is formed. Similar discouraging results emerged from studies of other oxygenated dienes. Consequently, an alternate procedure for generating the requisite cation radicals, under conditions where polymerization is largely suppressed, was sought. An excellent procedure, modeled upon the well-known method of photosensitized electron transfer,[6,7] fortunately was developed and is illustrated in the Diels-Alder cyclodimerization of **1** (Scheme I): A solution of 7.7 g of **1**[8] dissolved in acetonitrile (140 mL) containing 25 mol % (3.2 g) of 1,4-dicyanobenzene (the electron transfer sensitizer = ET) was irradiated 32 h at room temperature by a 450W Hanovia medium-pressure mercury vapor lamp with Pyrex filter. The GC yield of dimer was determined to be 71%. Evaporation of the solvent, removal of the ET by extraction of the dimer into hexane, and distillation (bp 122-125 °C (2.75 torr)) yielded 3.8 g (50%) of dimer **2** as a 2:1 endo/exo pair. No other diastereomers were present in significant amounts. Hydrolysis of the dimer (methanol:water = 4.5:1, room temperature, 1.75 h, 10 mol % TsOH) gave 96% of ketone **3**. Diels-Alder additions and dimerizations of many of the hydrocarbon dienes previously studied[1,2] were repeated by using the new procedure, giving identical products in very similar proportions but generally more cleanly and often in slightly higher yields.[9] In each case a parallel blank reaction, omitting only ET, established the negligibility of direct photoreactions bypassing ET. Cross additions of **1** and these hydrocarbon dienes, either as diene or dienophile, were unfortunately unsuccessful. Apparently **1** is far more reactive in either Diels-Alder role than such dienes.

In addition to confirming the compatibility of the cation radical Diels-Alder with electron donor functionality, a second major goal of this work was to extend the reaction beyond the diene-diene format. The exploitation of electron-rich alkenes as dienophiles was considered a particularly important target. Not only are a variety of such systems readily available synthetically, but their cross additions to dienes should not be subject to competing Diels-Alder dimerization. Indeed, enol ethers and enamines were

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(1) Bellville, D. J.; Wirth, D.; Bauld, N. L. *J. Am. Chem. Soc.* **1981**, *103*, 718.

(2) Bauld, N. L.; Bellville, D. J. *J. Am. Chem. Soc.* **1982**, *104*, 2665.

(3) Bauld, N. L.; Bellville, D. J.; Gardner, S. A.; Migron, Y.; Cogswell, G. *Tetrahedron Lett.* **1982**, *23*, 825.

(4) Bauld, N. L.; Bellville, D. J.; Pabon, R. A.; Chelsky, R.; Green, G. *J. Am. Chem. Soc.* **1983**, *105*, 2378.

(5) Bauld, N. L.; Bellville, D. J.; Pabon, R.; Gardner, S. A. *J. Am. Chem. Soc.* **1983**, *105*, 3584.

(6) Farid, S.; Shealer, S. E. *J. Chem. Soc., Chem. Commun.* **1973**, 677.

(7) Kuwata, S.; Shigemitsu, Y.; Odaira, Y. *J. Chem. Soc., Chem. Commun.* **1972**, 2.

(8) This actually was 11.0 g of the 70% mixture available commercially. No products were observed to emanate from the minor isomer.

(9) All adducts were collected by preparative GC unless noted otherwise and characterized by GC/MS, high resolution MS, ^{1}H and ^{13}C NMR spectroscopy, and, where appropriate, proton decoupled ^{1}H NMR spectroscopy.

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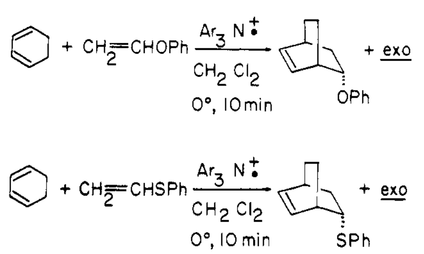
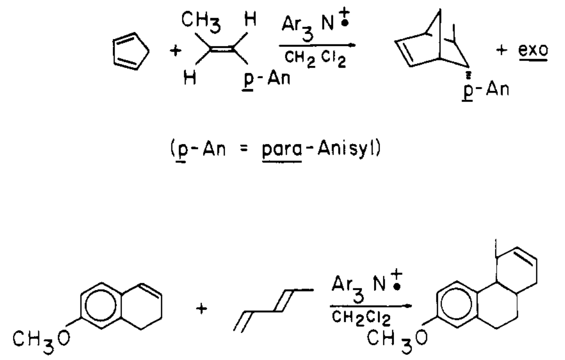
Scheme II



Scheme III



found to decolorize the aminium catalyst instantly, but Diels–Alder adducts were not formed, either in this procedure or in the new photosensitized one. It was noted that these cycloadditions require removal of the oxygen or nitrogen function from conjugation concomitantly with the generation of a relatively less stable cyclohexene type cation radical site in the adduct. They may thus be significantly slower than, for example, the diene–diene cation radical Diels–Alder. It was further reasoned that phenyl vinyl ethers might be more appropriate dienophiles since a more favorable cation radical locus, the phenoxy ring, would then exist in the adduct. In fact, though such vinyl type monomers are extremely susceptible to polymerization, phenyl vinyl ether itself adds to 1,3-cyclohexadiene (Scheme II) to afford a 75% yield of a 1.3:1.0 endo/exo mixture of adducts under optimum reaction conditions (20 mol % aminium salt on the basis of the diene, 9:1 ratio of the vinyl ether to cyclohexadiene, 0.1–0.3 M, 0 °C, 10 min). Phenyl vinyl sulfide (Scheme II) affords a 68% yield of the analogous Diels–Alder adducts (endo:exo = 15.0:1.0; 80 mol % catalyst, 9:1 ratio of sulfide/diene, 0 °C, 10 min). These reactions work modestly (10–30%) at 1:1 reactant ratios, but competing polymerization of the electron-rich alkene makes use of an alkene excess desirable.[10] It is appropriate to emphasize here that, in general, increasing alkyl substitution dramatically decreases polymerization and enhances yields and stereoselection in the cation radical Diels–Alder.

Electron-rich styrenes are also effective cation radical Diels–Alder dienophiles (Scheme III). The examples cited were selected, in part, to reveal the rather wide variety of dienic structures that can be elected in cross cation radical Diels–Alder reactions, generally. The cyclopentadiene–anethole adduct was obtained in 74% yield (3:1 endo/exo; 10% catalyst, 1.5:1 reactant ratio; GC collected in 52% yield). The anisyl ring, it is noted, can be incorporated into synthetic strategies by Birch reduction/hydrolysis to a cyclohexenone unit. The second example adumbrates possible applications to a steroidal hormone synthesis (yield 69%; 10% catalyst, 1:9 dienophile/diene ratio). Regioselection is complete here.

Research in progress promises to further define and extend the scope of the cation radical Diels–Alder reaction.

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[10] The phenyl vinyl sulfide addition to cyclohexadiene occurs in 31% yield at 1:1 reactant ratios. Photosensitized electron transfer catalysis is efficient, resulting in a 35% conversion of the 1:1 reactant mixture to Diels–Alder adducts in only 16 h. Unfortunately, competing photochemistry of cyclohexadiene gives rise to 13% of two isomeric cyclobutane photoadducts. This photochemistry, however, should be susceptible of control by use of appropriate light filters and, in any case, is not encountered with acyclic dienes. At 1:1 reactant ratios, the phenyl vinyl ether reaction is not efficient even using the photochemical procedure as a result of excessive cyclohexadiene dimerization.

Taft–Kamlet π^* Solvatochromic Polarity Parameters of Solid Compounds

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Although numerous solvent "polarity" parameters have been proposed,[1,2] the Taft–Kamlet solvatochromic parameters[2] (π^*, α, β, etc.) are unique in providing insights into the nature of solvent–solute interactions. Because π^* (dipolarity–polarizability), α (H-bond donation), β (H-bond acceptor), and the Hildebrand solubility parameter δ_H[3] (solvent cohesive energy) can be involved in varying proportions in overall solvation behavior, a much wider variety of data can be correlated than with any single or dual parameter scheme. Solvatochromic parameters for each solvent are assigned on the basis of $p \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ spectral shifts of a series of solutes, and in this way, consistent parameters have been derived, free from experimental or actual idiosyncrasies.

The behavior of a solute in a solvent having particular solvatochromic parameters depends on the ability of the solute to undergo the same types of interactions (dipole–dipole, dipole-induced dipole, etc.) of which solvents are capable. If we were seeking a solvent capable of strong interactions with dipolar, H-bond donor solute trifluoroethanol ($\pi^* = 0.73$, $\alpha = 1.35$), we might choose the highly dipolar, H-bond acceptor dimethyl sulfoxide ($\pi^* = 1.00$, $\beta = 0.76$). But a great majority of interesting and important solutes are solids, on which measurements of solvatochromic parameters can not presently be made. On the basis of our quantitative studies of the relationship of enthalpies of interaction and the dipolarity–polarizability (π^*) of both solvent and solute, *we now propose a method by which π^* values of solid compounds can be determined from calorimetric heats of solution.*

We have for some time measured heats of solution (ΔH_s) of polar and nonpolar solutes in a variety of solvents[4,5] and have combined these with heats of vaporization (ΔH_v) to give the enthalpies of transfer from vapor to solvents.

$$\Delta H(\mathrm{v} \rightarrow \mathrm{S}) = \Delta H_s - \Delta H_v \qquad (1)$$

Polar interactions of a solute with a solvent can be estimated from the value of $\Delta H(\mathrm{v} \rightarrow \mathrm{S})$ compared with $\Delta H(\mathrm{v} \rightarrow \mathrm{S})$ of a nonpolar model compound.[5]

$$\Delta H_p = \Delta H(\mathrm{v} \rightarrow \mathrm{S})(\text{polar solute}) - \Delta H(\mathrm{v} \rightarrow \mathrm{S})(\text{model solute}) \qquad (2)$$

Alternatively, a variation[5] of the "pure base" method[6] can be used,

$$\Delta H_p = [\Delta H_s(\text{polar solute}) - \Delta H_s(\text{model solute})]_{\text{polar solvent}} - [\Delta H_s(\text{polar solute}) - \Delta H_s(\text{model solute})]_{\text{ref solvent}} \qquad (3)$$

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[1] Reichert, C. "Solvent Effects in Organic Chemistry"; Verlag Chemie: Weinheim, 1979.

[2] Kamlet, M. J.; Abboud, J. L. M.; Taft, R. W. *Progr. Phys. Org. Chem.* **1981**, *13*, 485.

[3] Abraham, M. H.; Kamlet, M. J.; Taft, R. W. *J. Chem. Soc., Perkin Trans. 2* **1982**, 923.

[4] Saluja, P. P. S.; Young, T. M.; Rodewald, R. F.; Fuchs, F. H.; Kohli, D.; Fuchs, R. *J. Am. Chem. Soc.* **1977**, *99*, 2949. Saluja, P. P. S.; Peacock, L. A.; Fuchs, R. *Ibid.* **1979**, *101*, 1958.

[5] Fuchs, R.; Peacock, L. A.; Stephenson, W. K. *Can J. Chem.* **1982**, *60*, 1953.