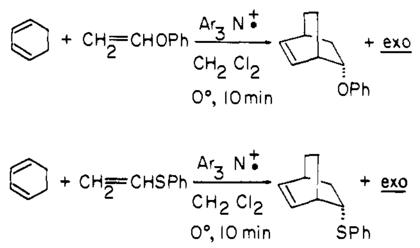
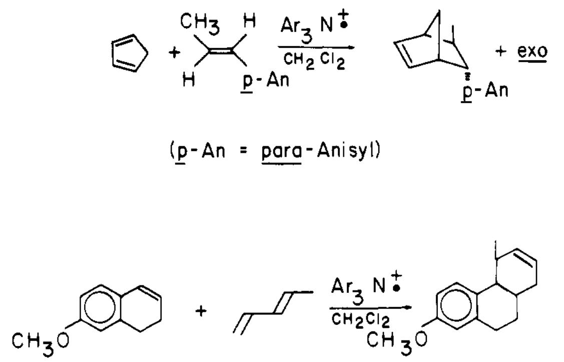
Scheme II



Scheme III



(p-An = para-Anisyl)

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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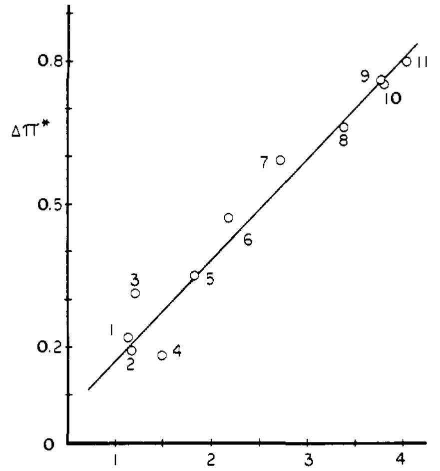

Figure 1. $\Delta\pi^*$ ($\pi^*_{\text{polar solute}} - \pi^*_{\text{model solute}}$) vs. the coefficient s, where $\pi^*(\text{solutes}) = -0.0122 - 0.2031s$. The points represent (1) Et_3N (π^* = 0.14)/Et_3CH (−0.08);[7] (2) anisole (0.73)/toluene (0.54); (3) Bu_2O (0.24)/octane (−0.08);[7] (4) pyridine (0.87)/benzene (0.59); (5) Et_2O (0.27)/butane (−0.08);[7] (6) nitrobenzene (1.01)/toluene (0.54); (7) benzene (0.59)/cyclohexane (0.00); (8) 5-nonanone (0.58)[7]/nonane (−0.08);[7] (9) butanone (0.67)/butane (−0.08);[7] (10) cyclohexanone (0.67)/cyclohexane (0.00); (11) acetone (0.72)/propane (−0.08).[7]

and ΔH_v (or ΔH_{subl}) of the solutes need not be known. We have correlated ΔH_p values (eq 2, typical uncertainty ±0.1 kcal/mol) in 14 solvents (1,2-dichloroethane, carbon tetrachloride, *tert*-butyl alcohol, methanol, DMF, Me_2SO, triethylamine, benzene, toluene, mesitylene, *n*-butyl ether, ethyl acetate, cyclohexane, and heptane) for a variety of ethers, ketones, and other dipolar and polarizable solutes, with π^* of the solvents (kcal/mol):

$$\Delta H_p(\text{anisole vs. toluene}) = -1.332 - 1.160\pi^*,\ r = 0.925,\ \text{sd} = 0.109$$

$$\Delta H_p(\text{Et}_3\text{N vs. Et}_3\text{CH}) = 0.115 - 1.130\pi^*,\ r = 0.971,\ \text{sd} = 0.086$$

$$\Delta H_p(\text{Bu}_2\text{O vs. octane}) = -0.781 - 1.202\pi^*,\ r = 0.821,\ \text{sd} = 0.199$$

$$\Delta H_p(\text{pyridine vs. benzene}) = -0.580 - 1.485\pi^*,\ r = 0.952,\ \text{sd} = 0.124$$

$$\Delta H_p(\text{Et}_2\text{O vs. butane}) = -0.912 - 1.813\pi^*,\ r = 0.895,\ \text{sd} = 0.223$$

$$\Delta H_p(\text{nitrobenzene vs. toluene}) = -2.470 - 2.174\pi^*,\ r = 0.899,\ \text{sd} = 0.273$$

$$\Delta H_p(\text{benzene vs. } c\text{-C}_6\text{H}_{12}) = 0.514 - 2.718\pi^*,\ r = 0.962,\ \text{sd} = 0.174$$

$$\Delta H_p(\text{5-nonanone vs. nonane}) = -1.113 - 3.378\pi^*,\ r = 0.961,\ \text{sd} = 0.280$$

$$\Delta H_p(\text{cyclohexanone vs. } c\text{-C}_6\text{H}_{12}) = -1.544 - 3.756\pi^*,\ r = 0.957,\ \text{sd} = 0.296$$

$$\Delta H_p(\text{butanone vs. butane}) = -1.380 - 3.895\pi^*,\ r = 0.900,\ \text{sd} = 0.383$$

$$\Delta H_p(\text{acetone vs. propane}) = 1.386 - 4.030\pi^*,\ r = 0.959,\ \text{sd} = 0.308$$

The numerical coefficient of π^*(solvents) (s) tends to increase with the "polarity" of the solute, but the most dipolar solute, nitrobenzene (greatest μ), and the least dipolar, benzene, have similar values of s (Figure 1). The correlation with s becomes very good if the measure of "polarity" is taken to be $\Delta\pi^*$, where

$$\Delta\pi^* = \pi^*(\text{polar solute}) - \pi^*(\text{model solute}) \qquad (4)$$

This is appropriate because the model compounds are not equally "nonpolar" (noninteractive).

If the s coefficients for the above relationships are correlated with $\Delta\pi^*$, the relationship is

$$\Delta\pi^*(\text{solutes}) = -0.0122 - 0.2031s,\ r = 0.978,\ \text{sd} = 0.035,\ n = 11 \qquad (5)$$

For a polar solute in a series of solvents the second term in eq 3, $[\Delta H_s(\text{polar solute}) - \Delta H_s(\text{model solute})]_{\text{ref solvent}}$, is a constant, so

$$[\Delta H_s(\text{polar solute}) - \Delta H_s(\text{model solute})]_{\text{polar solvent}} = \Delta H_p - k \qquad (6)$$

Correlation of the left-hand side of eq 6 with π^*(solvents) yields a different intercept than does eq 3, but the value of s is the same. One can therefore determine ΔH_s of a solid polar compound and the model compound in a series of solvents, correlate the difference in ΔH_s with the π^* values of the solvents, and obtain the value of s. Equation 5 provides the value of $\Delta\pi^*$(solutes) corresponding with that value of s. If a value of π^* of the (usually hydrocarbon) model is known or can be reasonably estimated, π^* of the polar solute can be calculated (eq 4).

Acknowledgment. We thank Dr. Mortimer J. Kamlet for helpful discussions. This study was supported by the Robert A. Welch Foundation (Grant E-136).

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(7) Estimated values of π^*. All alkanes have been assigned the value (−0.08) found experimentally for hexane and heptane.[2] π^* for ketones[2] decreases with increasing size and hindrance to the carbonyl group. A value slightly smaller than that for 3-heptanone (0.59) has been estimated for 5-nonanone (0.58).

Photoaffinity Labeling of Bacteriorhodopsin with 3-([1-^{14}C]Diazoacetoxy)-*trans*-retinal

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Purple membrane[1] is a light-energy transducer that uses bacteriorhodopsin to pump protons across the cell membrane[2] to generate ATP. Bacteriorhodopsin folds into seven α-helical segments spanning the cell membrane.[3] The primary sequence of the apoprotein (opsin)[4,5] and the attachment site of the chromophore (retinal) to lysine-216[6–8] through a protonated Schiff base linkage[9,10] have been established.

Bacteriorhodopson (bR) has two modifications:[2] (i) the light-adapted form (bR^{LA}), $\lambda_{\max}$ 570 nm, containing *trans*-retinal, which is responsible for the proton pump inducing photocycle; and

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