Fortunately the insertion reactions of diazocyclopentadienes provide an easy route to these compounds.

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Figure 1. The dependence of Φ_D on the concentration of ethyl iodide.

Effect of Ethyl Iodide on the Photodimerization of Acenaphthylene[1]

Sir:

Heavy-atom solvents have been shown to produce large increases in the quantum yields of dimerization and cycloaddition of acenaphthylene. These effects have been attributed to an increase in the rate of intersystem crossing resulting from spin–orbit coupling induced by the heavy-atom solvent.[2–6] Most of the work to date has involved heavy-atom solvents containing bromine. In all cases, the magnitudes of the quantum yields of dimerization and cycloaddition have been limited solely by the amount of bound bromine present in the solvent. However, the proposed mechanism for these reactions predicts that there should be an upper limit for these quantum yields when sufficient spin–orbit perturbation is present.[6,7] We wish to report the first evidence that this limit may be reached in the presence of a heavy-atom solvent.

One will observe from the data in Figure 1 that the quantum yield of dimerization increases very rapidly as the concentration of ethyl iodide is increased from 0 to 10 mol %.[3] Further increases in the concentration of heavy-atom solvent, however, result in a gradual decrease in the quantum yield of dimerization. This behavior may be attributed to two competing processes, namely intersystem crossing from the first excited singlet to the first excited triplet, and deactivation of this

(1) Photochemical Reactions. IX. For part VIII, see D. O. Cowan and W. W. Schmiegel, *J. Amer. Chem. Soc.*, **94**, 6779 (1972).
(2) D. O. Cowan and R. L. Drisko, *J. Amer. Chem. Soc.*, **92**, 6281 (1970).
(3) B. F. Plummer and R. A. Hall, *Chem. Commun.*, 44 (1970).
(4) J. Meinwald, G. E. Samuelson, and M. Ikeda, *J. Amer. Chem. Soc.*, **92**, 7604 (1970).
(5) B. F. Plummer and D. M. Chihal, *J. Amer. Chem. Soc.*, **93**, 2071 (1971).
(6) B. F. Plummer and W. I. Ferree, Jr., *J. Chem. Soc., Chem. Commun.*, 306 (1972); *J. Amer. Chem. Soc.*, **95**, 6709 (1973).
(7) D. O. Cowan and R. L. Drisko, *J. Amer. Chem. Soc.*, **92**, 6286 (1970).
(8) Irradiations were performed on a merry-go-round apparatus using a 450-W Hanovia medium-pressure mercury arc lamp in a water-cooled Hanovia Vycor immersion vessel. A combination of Corning CS-0-52 and CS-7-37 filters was used which produced a narrow band around 365 nm. Irradiation times varied from 8 to 20 hr depending on the quantum yields of the samples. Each sample was degassed with five freeze–thaw cycles before the irradiation. The extent of conversion (<10%) was determined by measuring the optical density of acenaphthylene at 340 nm. The incident light intensity was measured by actinometry with ferrioxalate. At the concentration of acenaphthylene (0.1 *M*) that was used, virtually all of the light was absorbed.
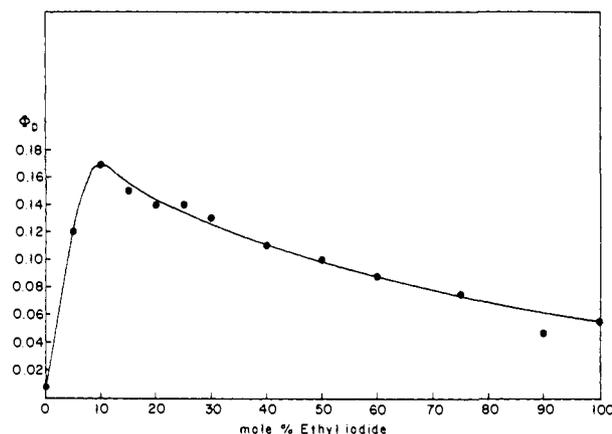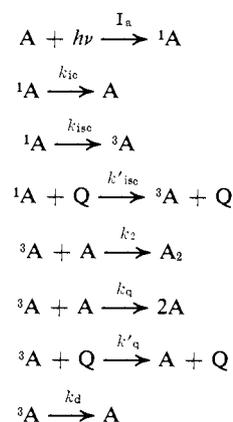
triplet to the ground state. Heavy-atom solvents appear to have a far greater influence on the initial intersystem crossing rate of acenaphthylene than on any of the nonradiative intercombinational transitions that follow intersystem crossing. However, if the rate of intersystem crossing is sufficiently large, the quantum yield for this process should approach unity. Under these conditions, effects on other intercombinational processes such as deactivation of the triplet state should become important. The data conform very well with this description.

Figure 2 represents the reciprocal of the quantum yield of dimerization as a function of the ethyl iodide concentration.[9] The observed linear relationship is predicted if one considers the following simplified mechanism

$$A + h\nu \xrightarrow{I_a} {}^1A$$

$$^1A \xrightarrow{k_{ic}} A$$

$$^1A \xrightarrow{k_{isc}} {}^3A$$

$$^1A + Q \xrightarrow{k'_{isc}} {}^3A + Q$$

$$^3A + A \xrightarrow{k_2} A_2$$

$$^3A + A \xrightarrow{k_q} 2A$$

$$^3A + Q \xrightarrow{k'_q} A + Q$$

$$^3A \xrightarrow{k_d} A$$

where A = acenaphthylene and Q = ethyl iodide. Using the steady-state approximation, one obtains the quantum yield of dimerization, Φ_D.

$$\Phi_D = \left\{ \frac{k_{isc} + k'_{isc}[Q]}{k_{ic} + k_{isc} + k'_{isc}[Q]} \right\} \times$$

$$\left\{ \frac{k_2[A]}{k_2[A] + k'_q[Q] + k_q[A] + k_d} \right\}$$

The first term in this expression is the quantum yield of intersystem crossing, Φ_{isc}, which should approach unity

(9) The following parameters were derived by a least-squares treatment of data: slope (M^{-1}), 1.02 ± 0.03; intercept, 4.8 ± 0.2; correlation, 0.997. From the slope, the following rate ratio is obtained: $k'_q / k_2 = 0.10$.
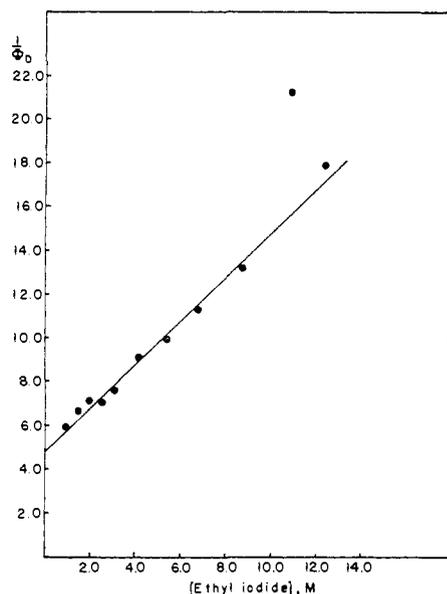
Figure 2. The dependence of $1/\Phi_D$ on the concentration of ethyl iodide.

as $k'_{isc}[Q]$ becomes very large. If $\Phi_{isc} \cong 1$, then one will obtain

$$\frac{1}{\Phi_D} = \frac{k_2[A] + k_q[A] + k_d}{k_2[A]} + \frac{k'_q[Q]}{k_2[A]}$$

which indicates that $1/\Phi_D$ should be a linear function of [Q], the heavy-atom solvent concentration.

The data in Table I indicate that as the concentration

Table I. Solvent Dependence of Product Distribution for Dimerization of Acenaphthylene

Mol % EtI[a]	% cis	% trans
0	56	44
5	19	81
10	18	82
15	22	78
20	21	79
25	23	77
30	29	71
40	28	72
50	24	76
60	27	73
75	30	70
90	29	71
100	32	68

[a] Cyclohexane was used as a cosolvent in all samples containing less than 100 mol % EtI.

of ethyl iodide increases, there is a moderate increase in the proportion of cis dimer that is formed.[10] This is in agreement with the findings of Hartmann, Hartmann,

(10) (a) Solutions of pure cis and pure trans dimers in cyclohexane were prepared and the molar absorptivities at 314 and 284 nm for each were determined: cis ϵ_{314} 1.78 × 10⁴, ϵ_{284} 1.02 × 10⁴; trans ϵ_{314} 3.93 × 10³ ϵ_{284} 1.18 × 10⁴. The composition of the product dimer mixtures was determined by measuring the optical densities of cyclohexane solutions of these dimers at 314 and 284 nm. From these optical densities and the corresponding molar absorptivities, the concentrations of the cis and trans dimers were calculated. (b) The dimer mixtures were prepared for analysis in the following manner. Each irradiated solution was transferred to a sublimer cavity, taken to dryness, and sublimed at 50° to remove unreacted acenaphthylene. The residue was then dissolved in enough cyclohexane to yield a ~5 × 10⁻⁵ M solution for uv analysis.

and Schenck who observed that the percentage of triplet-derived cis dimer increased as the polarity of the solvent system increased.[11] This is the result of increased stabilization of the transition state leading to the cis dimer relative to that leading to the trans.[7,11,12]

The results cited above indicate that there is a practical limit to the amount of heavy-atom solvent enhancement one can obtain for a given photochemical reaction. Attempts to exceed this limit may in fact lower the quantum yield of the desired product. Work is in progress to determine many of the above rate constants as well as to elucidate the mechanism of both external and internal heavy-atom perturbation.

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Structure and Basicity of Anions Generated α to the Carbene Carbon Atom of Transition Metal–Carbene Complexes

Sir:

The kinetic acidity of protons attached to the carbon atom α to the carbene carbon atom of transition metal–carbene complexes[1,2] implies the existence of an intermediate anion. Recently we reported the stoichiometric generation of such "carbene anions" (**2**) and their
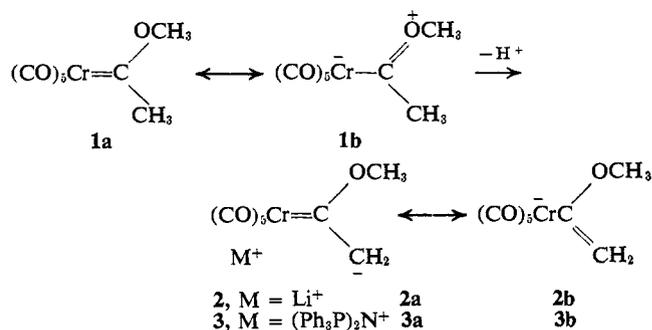
behavior as carbon nucleophiles in reactions with DCl, methyl fluorosulfonate, benzaldehyde, and acetyl chloride.[3,4] Here we report the isolation of a stable bis-(triphenylphosphine)iminium salt of **3**, the spectroscopic characterization of **3** as a vinyl chromium anion, and the remarkably high thermodynamic acidity of the transition metal–carbene complex **1**.

Quantitative generation of the lithium salt of the carbene anion (**2**) was achieved by addition of 1 equiv of *n*-butyllithium to a solution of (methylmethoxycarbene)-pentacarbonylchromium(0) (**1**) in tetrahydrofuran

(1) C. G. Kreiter, *Angew. Chem., Int. Ed. Engl.*, **7**, 390 (1968).
(2) The kinetic acidity of metal–carbene complexes has been used in structural elucidation studies of transition metal–carbene complexes: C. P. Casey, *Chem. Commun.*, 1220 (1970).
(3) C. P. Casey, R. A. Boggs, and R. L. Anderson, *J. Amer. Chem. Soc.*, **94**, 8947 (1972).
(4) C. P. Casey, R. A. Boggs, D. F. Marten, and J. C. Calabrese, *J. Chem. Soc., Chem. Commun.*, 243 (1973).