THF was evaporated under reduced pressure. The residual *N*-carboxy anhydride (NCA) of L-valine was polymerized at 30 °C in dioxane containing 1/20 equimolar triethylamine as a catalyst. After the solution was left standing for 4 days, poly-L-valine was collected as a precipitate and washed with dioxane. The completely dried THF and dioxane were used in these procedures, because the NCA is very sensitive to moisture: yield, 33%; IR (KBr) $\nu_{C=O}$ 1630 cm^{-1}; $[\alpha]^{20}{}_D$ −150° (*c* 1, trifluoroacetic acid); M_r ca. 2000.[18]

Poly-L-valine-Coated Graphite Electrodes. A polycrystalline graphite plate (2 × 4 cm) polished with a fine emergy paper was dipped in trifluoroacetic acid solution of poly-L-valine (0.5–1.0 w/v %) for 15 min. The graphite plate was dried for 5 min under the atmospheric pressure and then for 30 min under reduced pressure.

Electrolysis. The electrolytic reduction of citraconic acid (**1**) and 4-methylcoumarin (**3**) was carried out by means of the controlled potential or constant current method at 0 °C in a divided cell. Details of electrolytic condition are given in Table I.

Product Analysis. After the electrolysis, ethanol in the catholyte was distilled away under reduced pressure and the residual solution was acidified with aqueous sulfuric acid. The hydro dimer, if formed, was filtered off, and the filtrate was extracted repeatedly with ether. The combined ethereal solution was evaporated to dryness, and the recrystallization of the residual solid from an ether–benzene mixture afforded the pure hydrogenated products **2** and **4** which could be confirmed by melting points and NMR spectra.

Optical rotation of compounds was measured in 1–5-cm cells of a highly sensitive polarimeter (Union Co. automatic digital plarimeter, Model PM-101). The $[\alpha]^{20}{}_D$ of **2** and **4** were measured in ethanol and benzene, respectively, and the optical yields were calculated with reference to values reported for the optically pure enantiometers: $[\alpha]^{20}{}_D$ 17.9° (*c* 4.4, ethanol)[21] for **2** and $[\alpha]^{20}{}_D$ 32° (*c* 1, benzene)[22] for **4**.

Acknowledgment. This study was performed as a preliminary investigation for a project supported financially by the Grant-in-Aids for Scientific Researches from the Japanese Ministry of Education.

Registry No. 1, 498-23-7; (*R*)-(+)-**2**, 3641-51-8; **3**, 607-71-6; (*R*)-(+)-**4**, 30825-55-9; poly-L-valine, 25667-19-0; graphite, 7782-42-5; L-valine homopolymer, 25609-85-2.

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Isomerization of Hexamethyl(Dewar benzene) to Hexamethylbenzene Catalyzed by Electron Acceptors. Thermal Generation of an Exciplex

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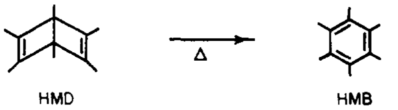
Abstract: The reaction of hexamethyl(Dewar benzene) (HMD) with ground-state electron acceptors and with singlet and triplet excited electron acceptors reveals parallel behavior. The thermal acceptors catalyze the conversion of HMD to hexamethylbenzene (HMB) without formation of ions free in solution. The excited-state acceptors in some cases give ions, and in others only neutral ground-state products. The behavior of these electron acceptors is interpreted to indicate that formation of an exciplex in both the thermal and photochemical reactions initiates the process responsible for isomerization. In some cases electron transfer in the exciplex and dissociation lead to ionic products.

The chemical and physical properties of strained hydrocarbons have long fascinated chemists striving to understand the details of structure and reactivity.[1] Dewar benzene (bicyclo[2.2.0]-hexa-2,5-diene) and its derivatives rank among the most noteworthy compounds in this group. The first Dewar benzene derivative was prepared by van Tamelen and Pappas[2a] and they subsequently prepared the parent hydrocarbon.[2b] Hexamethyl-(Dewar benzene) (HMD) was prepared conveniently, and in high yield, by Schäfer[3] using an aluminum chloride catalyzed cyclotrimerization of 2-butyne. The ready availability of HMD has made it the favorite substance for investigation of the Dewar ring system.

One of the remarkable properties possessed by HMD is its thermal stability. Thermolysis in inert solvent converts HMD primarily to hexamethylbenzene (HMB), eq 1.[4] At 150 °C this reaction has a half-life of over 3 h and a measured activation energy of 37 kcal/mol despite being exothermic by nearly 60 kcal/mol.[5] The high activation energy has been attributed in part to the symmetry forbiddeness of the thermal rearrangement,[6] and the nature of the reaction transition state for Dewar benzene has been extensively probed.[7] The high exothermicity of the rearrangement of the Dewar structure to its more familiar aromatic isomer provides the energy for chemiluminescence observed from some derivatives.[8] The strain of the Dewar isomer, estimated to be 45 kcal/mol,[5] raises the energy of the highest occupied molecular orbital and concomitantly lowers the ionization potential[9] and oxidation potential.[10] This feature may account for some of the metal-catalyzed rearrangements[11] and the unusual photochemistry of HMD.



HMD HMB (1)

Evans and co-workers[10] photosensitized the isomerization of HMD with naphthalene. They observed quantitative conversion

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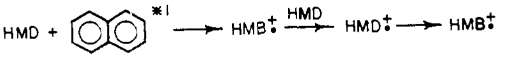
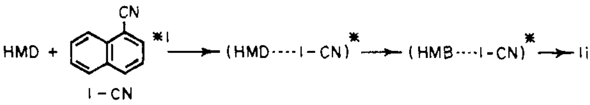
of HMD to HMB and, in polar solvents, concentration-dependent quantum yields ranging up to nearly 100. These observations, among others, led them to postulate a chain decomposition of HMD with hexamethylbenzene radical cation ($HMB^{+\cdot}$) as the chain-carrying agent (eq 2). Taylor[12] found that in nonpolar



(2)

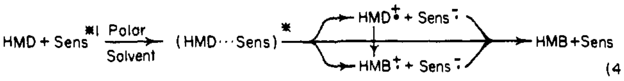
solvents the 1-cyanonaphthalene photosensitized conversion of HMD led adiabatically to an exciplex of HMB and cyanonaphthylene which was detected and characterized by its emissive properties (eq 3). In a recent series of papers, Jones and co-



(3)

workers[13] have extended the study of the adiabatic rearrangement of HMD to other sensitizers and have postulated wavelength-dependent ion formation from irradiation of HMD "charge-transfer" complexes in polar solvents.

These observations are all consistent with the anticipated formation of a sensitizer–HMD exciplex (or excited charge-transfer complex). In nonpolar solvent the exciplex reactions are partitioned between direct diabatic formation of ground-state products and adiabatic formation of the HMB exciplex. While in polar solvents, the exciplex may dissociate into radical ions, before or after isomerization of HMD to HMB, in competition with ground-state product formation (eq 4).



(4)

We have investigated the reaction of HMD with ground-state electron acceptors, and with singlet and triplet excited-state electron acceptors by nanosecond laser spectroscopy. These studies reveal that certain ground-state electron acceptors mimic the behavior of the excited acceptors and catalyze the conversion of HMD to HMB. The effectiveness of the catalysis parallels the electrochemical reduction potential of the acceptor. Analysis of the spectra of the transient products formed from laser flash sensitization of the HMD isomerization reveals that triplet sensitizers uniformly give high yields of the appropriate radical-ion products, and large quantum yields for reaction are observed. With singlet sensitizers HMB forms high yields of the expected ions, but HMD gives fewer, if any, ions, and this amount is strongly dependent on the specific nature of the sensitizer. These findings provide some clarification of reaction sequences that have been described as single electron transfers.

Finally, the rate of conversion of $HMD^{+\cdot}$, or the triplet exciplex of HMD with sensitizer, is faster than the 15 ns that our apparatus can resolve. Thus the large activation barrier associated with the thermal transformation is apparently reduced a great deal by interaction with the excited sensitizer.[14]

Results

Ground-State Electron-Acceptor Catalysis of HMD Isomerization. Thermal electron-transfer reactions between ground-state, closed-shell, neutral substances have been postulated to occur in several reaction schemes[15] including those of organic peroxides[16] and organometallic systems.[17] We investigated the interaction of HMD with ground-state electron acceptors with the hope of observing a thermal electron-transfer reaction.

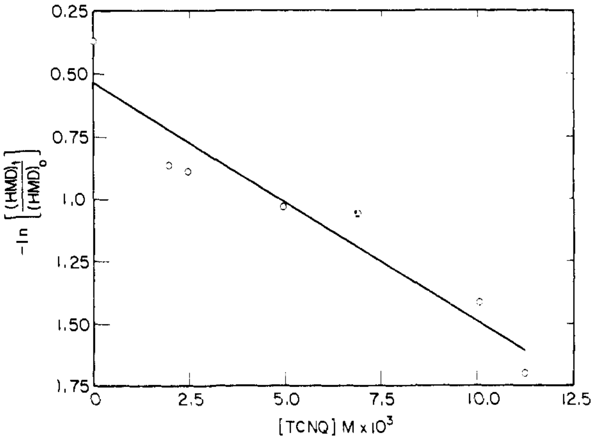
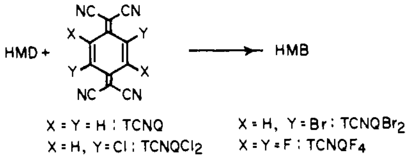


Figure 1. Effect of increasing TCNQ concentration on the observed rate constant of HMD isomerization to HMB in acetonitrile solution at 126 °C.

The electrochemical oxidation of HMD is irreversible and gives a wave with peak potential at about 1.6 V.[10,18a] The irreversibility is probably due to the rapid reaction of oxidized HMD. The transformation of HMD to HMB in acetonitrile can be catalyzed by some electron acceptors. The reduction potential of the acceptor appears to control the catalysis. *p*-Dicyanobenzene ($E_{red} = -1.64$ V)[18b] and *p*-dinitrobenzene ($E_{red} = -0.69$ V)[18b] have no effect on the thermal reaction of HMD. However, tetracyanoquinodimethane (TCNQ) in acetonitrile solution does accelerate the isomerization of HMD to HMB (eq 5).



(5)

Dilute solutions of TCNQ and HMD in acetonitrile do not exhibit any evidence of charge-transfer interactions. The absorption spectrum of the mixture is essentially identical with that of the sum of its components at the concentrations we use. This observation does not exclude the formation of weakly bound complexes, which we feel are present (vide infra). It is well known that HMB and TCNQ do give a characteristic charge-transfer absorption spectrum.[19] In fact, HMB–TCNQ complexes can be isolated from solution. This complicates the analysis of the kinetics of the TCNQ-catalyzed isomerization of HMD. As the product HMB is formed, it complexes with TCNQ, effectively lowering the concentration of the catalyst. To circumvent this difficulty we examined the kinetic behavior of the thermal process at high relative TCNQ concentrations and at low conversion where the amount of the catalyst remains essentially constant throughout the experiment.

Figure 1 shows the effect of adding increasing amounts of TCNQ to a 7.4×10^{-4} M solution of HMD in acetonitrile on the rate of isomerization to HMB. When reactions are carried to completion, essentially all of the starting HMD is converted to

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Table I. Thermal Electron Acceptors

acceptor	[HMD], M	EA, M	E_{red} vs. SCE	ΔG_{ET}	temp, °C	$t_{1/2}$, s[e]	k_{cat}, M^{-1} s^{-1}
p-dinitrobenzene	5×10^{-3}	0.05	-0.69[a]	52	130	5.9×10^{4}	none
p-dicyanobenzene	5×10^{-4}	0.01	-1.6[a,b]	74	145	2.5×10^{4}	none
TCNQ	7.4×10^{-4}	4.9×10^{-3}	$+0.125$[c]	33	126	5.6×10^{4}	1.16×10^{-3}
$TCNQCl_2$	5.0×10^{-4}	4.2×10^{-3}	$+0.41$[c]	27	95	3.9×10^{3}	5.8×10^{-2}
$TCNQCl_2$	9.9×10^{-4}	4.2×10^{-3}			95	4.4×10^{3}	
$TCNQCl_2$ + TMB (4.0×10^{-4} M)	9.9×10^{-4}	4.2×10^{-3}			95	4.2×10^{3}	
$TCNQBr_2$	5.0×10^{-4}	5.92×10^{-4}	$+0.41$[c]	27	95	5.9×10^{3}	6×10^{-2} [d]
$TCNQF_4$	9.9×10^{-4}	1.48×10^{-2}	$+0.53$[c]	24	23	2.3×10^{3}	2.3×10^{-2}
$TCNQF_4$ + TMB (6.7×10^{-4} M)	9.9×10^{-4}	1.45×10^{-2}			23	2.7×10^{3}	

[a] Reference 18b. [b] Converted to SCE, given vs. Ag electrode in ref 18b. [c] Wheland, R. C.; Gillson, J. L. *J. Am. Chem. Soc.* 1976, *98*, 3916. [d] The limited solubility of $TCNQBr_2$ in CH_3CN limits the range of concentrations available for this acceptor. As a consequence there is more uncertainty associated with this value than for the others. [e] Standard deviations from triplicate determinations typically are 15% of the reported half-life.

Table II. Photochemical Electron Acceptors

acceptor	multiplicity of excited acceptor	[HMD], M	excited acceptor quenched, %	ϕ_{isom}	ΔG_{ET}, kcal/mol
1,4-dicyanonaphthalene	singlet	0.2858	~97	7.4	−19.5
1-cyanopyrene	singlet	0.0605	~96	7.8	−2.8
9-cyanophenanthrene	singlet	0.3196	>98	65	+1.4
tetrachlorophthalic anhydride	triplet	0.0763	*a*	213	−15.2
p-cyanoacetophenone	triplet	0.0566	>94	64	−3.7
anthraquinone	triplet	0.0696	*a*	44	−4.8

[a] The lifetime of these triplet acceptors is unknown, and therefore the amount intercepted is not calculable. We assumed 100% in estimating the ϕ_{isom}.

HMB, and all of the TCNQ present initially remains at the end of the reaction. Thus, the TCNQ is functioning as a true catalyst for the isomerization of HMD. The slope of the line in Figure 1 is proportional to the bimolecular rate constant for catalysis (k_{cat}), which for TCNQ in acetonitrile at 126 °C is 1.16×10^{-3} M^{-1} s^{-1}.

Similar results are obtained using the halogen-substituted TCNQ derivatives shown is eq 5.[20] Substitution of the hydrogens on TCNQ by an increasing number of increasingly electron-withdrawing halogen atoms makes the TCNQ a stronger oxidant. This is evident most clearly in the effect of these substituents on the reduction potentials (Table I). Our experiments reveal that the rate constant k_{cat} is directly related to the magnitude of the reduction potential of the TCNQ derivative. As the TCNQ becomes a stronger oxidant, its effectiveness as a catalyst increases. The most powerful oxidant we investigated, $TCNQF_4$, converts HMD completely to HMB at room temperature in a few minutes (Table I). Observation of a correlation of reduction potential and reaction rate is often interpreted to mean that rate-limiting electron transfer initiates the reaction.[17,21,22]

If $HMB^{+\cdot}$ is formed free in solution by the thermal reaction of HMD with TCNQ, then a chain reaction (eq 2) converting HMD to HMB should ensue. To test this possibility we investigated the effect of added 1,2,4-trimethoxybenzene (TMB) on the observed catalytic effect of $TCNQCl_2$ and $TCNQF_4$.

The oxidation potential of TMB is 1.12 V.[18b] Addition of $TCNQCl_2$ to an acetonitrile solution of TMB does not eliminate its oxidation wave.[23] The oxidation potential of HMB is 1.62 V.[10] Thus, $HMB^{+\cdot}$ should oxidize TMB rapidly and irreversibly to $TMB^{+\cdot}$, effectively eliminating the $HMB^{+\cdot}$ from further reaction when TMB is present. The trimethoxybenzene radical cation is not a potent enough oxidant to remove an electron rapidly from HMD. Therefore, if the chain reactions of eq 2 were initiated by the TCNQ, then addition of TMB should inhibit it (Scheme I).

Scheme I

$$\mathrm{HMD} \xrightarrow{\mathrm{TCNQ}} \mathrm{HMD}^{+\cdot} \longrightarrow \mathrm{HMB}^{+\cdot} \xrightarrow{\mathrm{TMB}} \mathrm{HMB} + \mathrm{TMB}^{+\cdot} \quad (6)$$

$$\mathrm{TMB}^{+\cdot} + \mathrm{HMD} \not\longrightarrow \mathrm{HMD}^{+\cdot} + \mathrm{TMB} \quad (7)$$

$$\mathrm{TMB}^{+\cdot} + \mathrm{TCNQ}^{-\cdot} \longrightarrow \mathrm{TMB} + \mathrm{TCNQ} \quad (8)$$

The results shown in Table I indicate that when TMB is present at a concentration equivalent to that of HMD there is essentially no inhibition of the TCNQ-catalyzed isomerization. This result weighs against the efficient formation of free radical ion intermediates in the catalyzed isomerization reaction. A further test of the mechanism can be made by using electronically excited states as the catalyst for isomerization.

Excited-State Electron-Acceptor Catalysis of HMD Isomerization. Electronic excitation causes an increase in both the oxidizing and reducing potential of a molecule. The energetic outcome of electron-transfer reactions involving an excited-state reagent is easily calculated from the well-known Weller equation[21b] (eq 9). In polar solvents the reaction of an excited electron

$$\Delta G_{ET} = 23.06[E(D/D^{+}) - E(A^{-}/A) - (e_0^{2}/\epsilon a)] - \Delta E_{0,0} \quad (9)$$

acceptor (or donor) with a ground-state donor (acceptor) that is exergonic according to eq 9 typically leads to radical ions. These ions can be detected by photoconductivity measurements or, more conclusively, by absorption spectroscopy.[21b,24] We analyzed the reactions of HMB and HMD with a series of excited-state electron acceptors by nanosecond laser spectroscopy. This investigation reveals some unusual details of these reactions (Table II).

The fluorescence of 1,4-dicyanonaphthalene (DCN) in acetonitrile is quenched at a rapid rate by both HMD and HMB; k_q

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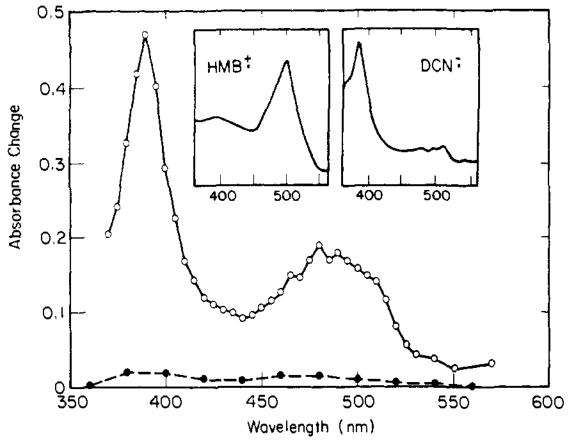

Figure 2. Transient absorption spectra obtained 100 ns after pulse irradiation of DCN in acetonitrile containing 0.053 M HMB (open circles) or 0.058 M HMD (solid circles). The insets show the spectra of $HMB^{+\cdot}$ obtained by pulse radiolysis at 77 K (ref 33) and $DCN^{-\cdot}$ formed by reduction with metallic potassium.

= 1.1×10^{10} and 2.0×10^{10} M^{-1} s^{-1}, respectively. This is not unexpected, since application of eq 9 indicates that electron transfer from either HMD or HMB to the first excited singlet state of DCN should be exorgonic by ca. 20 kcal/mol. In fact, electron transfer is confirmed for quenching of DCN^{*1} by HMB in acetonitrile solution by the observation of absorptions of the corresponding ions recorded 100 ns after irradiation with a ca. 13-ns-long light pulse at 337 nm from a nitrogen laser (Figure 2).[25] We were quite surprised, however, when we discovered that the reaction of HMD with DCN^{*1} does not lead to a discernible yield of ions under identical conditions (Figure 2). Thus, although electron transfer is energetically possible in this case, it is not observed. Moreover, since DCN^{*1} does isomerize HMD to HMB (see below), the major interaction between HMD and DCN^{*1} must not have any states or intermediates in common with the reaction of HMB and DCN^{*1} other than ground-state products.

The quantum efficiency for isomerization of HMD to HMB by DCN^{*1} is greater than unity and depends on the concentration of HMD (Table II). This observation indicates the operation of a chain mechanism similar to that described in eq 2. However, the initiation of the chain (i.e., formation of $HMB^{+\cdot}$) may be a consequence of reaction of HMB with DCN^{*1} since it is impossible to measure the quantum yield when no conversion has occurred. Also, the quantum yield for DCN-sensitized isomerization is more than an order of magnitude smaller than that obtained for some triplet acceptors which appear to generate ions from HMD in high yield (see below). Thus, not in this case, nor as has been noted in other examples previously reported,[10,13] should quantum yields of isomerization greater than unity be taken as evidence demanding efficient formation of ions from reaction of an acceptor with HMD.

The reaction of other singlet excited electron acceptors with HMB and HMD gives results that appear to depend on the specific nature and energetic properties of the acceptor. Thus the electron-transfer reaction of 9-cyanopyrene (CPY) singlet with HMB or HMD is calculated to be exothermic by ca. 3 kcal/mol, and both compounds quench CPY fluorescence. In this case, transient absorption spectroscopy reveals the formation of ions from both HMB and HMD. However, the yield of ions from HMD is ca. four times lower than that obtained from reaction with HMB.

Electron transfer from HMB or HMD to singlet excited 9-cyanophenanthrene (CPH) is endorgonic, according to eq 9, by ca. 1.4 kcal/mol. When HMB is used to quench CPH fluorescence in acetonitrile or benzonitrile solution, a new broad emission with a maximum at 405 nm and a lifetime of 48 ns in benzonitrile is observed. This emission is probably from a CPH–HMB exciplex. Investigation of this reaction by laser spectroscopy reveals that neither HMB nor HMD gives a detectable yield of ions. Instead, at low concentrations of HMD or HMB, triplet CPH with an absorption maximum at 490 nm is the major transient observed. At high concentrations of these quenchers, a new species with apparent maxima at 420 and 450 nm (Figure 3) and a lifetime in acetonitrile of ca. 700 ns when [HMD] = 0.47 M is obtained. This new species is not the emissive exciplex since it is formed from both HMB and HMD, and no exciplex emission is observed with HMD. Also, the lifetime of this new species is considerably longer than that of the emissive exciplex. However, by measuring the relative yield of this species as a function of the HMD concentration, it appears that it is a 1:1 complex. Moreover, this species appears to be capable of isomerizing HMD to HMB since its lifetime is dependent on the HMD concentration, and a quantum yield of over 60 is obtained for this reaction. Finally, formation of this transient species does not result in consumption of CPH, since it remains after the HMD is converted to HMB. The structure of the new transient species is not revealed by these experiments, but it may correspond to a relaxed, nonemissive exciplex that is energetically incapable of separating into ions. This species may react with HMD in a termolecular process similar to exciplex substitution[26] to cause its isomerization.

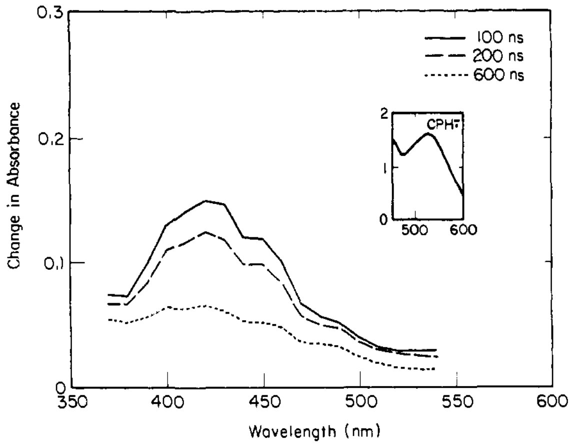

Figure 3. Transient spectra obtained from pulse irradiation of CPH in acetonitrile containing 0.47 M HMD. The absorption spectrum of $CPH^{-\cdot}$ is reported to have a maximum at 528 nm,[34] and is shown in the inset.

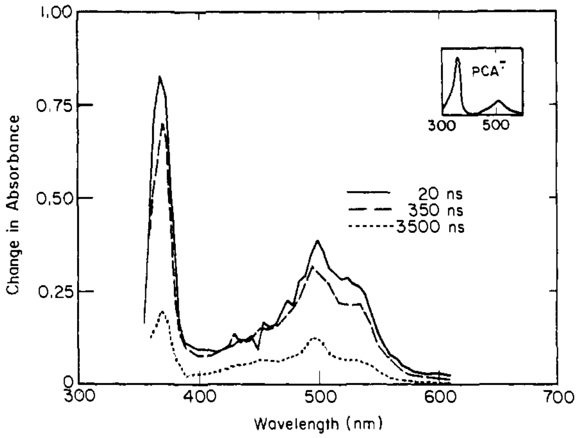

Figure 4. Absorption spectra obtained by photolysis of PCA in acetonitrile solution containing 0.051 M HMD. The inset is the absorption spectrum of $PCA^{-\cdot}$ reported by Adams, G. E.; Wilson, R. L. *J. Chem. Soc., Faraday Trans. 1* **1973**, 719.

The reaction of HMB and HMD with triplet-excited electron acceptors also reveals some details of these processes. Electron transfer from HMB or HMD to *p*-cyanoacetophenone triplet (PCA^{*3}) is calculated from eq 9 to be exorgonic by ca. 4 kcal/mol. Indeed, when PCA^{*3} in acetonitrile reacts with HMD, the transient absorption spectrum (Figure 4) shows $PCA^{-\cdot}$ at ca. 372

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[25] The laser apparatus has been described: Horn, K. A.; Schuster, G. B. *Tetrahedron* **1982**, *38*, 1095.

[26] Caldwell, R. A.; Creed, D.; DeMarco, D. C.; Melton, L. A.; Ohta, H.; Wine, P. H. *J. Am. Chem. Soc.* **1980**, *102*, 2369.

nm and HMB$^{+\cdot}$ at ca. 500 nm. Also, the quantum yield for isomerization of HMD to HMB is ca. 65, which demonstrates a chain process. However, when PCA^{*3} reacts with HMB no (or at least, very few) ions are formed. Instead, the transient absorption spectrum shows formation of PCA ketyl radical, and the dimeric products from this reaction reveal also that eventually hydrogen atom transfer followed by radical recombination has occurred.

The other triplet acceptors we investigated (Table II) give results that roughly parallel PCA. In all cases reaction with HMD gives HMB$^{+\cdot}$ and the appropriate radical anion. Also quantum yields much greater than unity, more than 200 for tetrachlorophthalic anhydride (TCPA), for isomerization of HMD are obtained.

Lifetime of HMD$^{+\cdot}$

The detection of HMB$^{+\cdot}$ from the reaction of HMD with an excited-state electron acceptor by laser spectroscopy provides the opportunity to measure the rate of isomerization of HMD$^{+\cdot}$ to HMB$^{+\cdot}$. Rearrangement of the neutral even-electron species requires considerable thermal activation which we anticipated would be reduced for the radical cation. Examination of the growth of the HMB$^{+\cdot}$ absorption following reaction of an electron acceptor with HMB in a variety of solvents over the temperature range from −20 to 25 °C shows that the reaction occurs within the ca. 15-ns risetime of the laser. This result indicates that the conversion of HMD$^{+\cdot}$, if it exists at all, to HMB$^{+\cdot}$ has an activation barrier, assuming a preexponential log A of 15.2 (the same value as for the reaction of HMD),[5] of less than 9 kcal/mol. Thus, the reduction in activation energy for isomerization of HMD by interaction with a powerful electron acceptor is at least 30 kcal/mol.[14]

Discussion

The results of the investigation of the reaction of HMD with ground-state and excited-state electron acceptors described above provides some illumination of the role of electron transfer which is accompanied by additional chemical change, in this case, isomerization of HMD to form HMB.

Figure 5 is a schematic state correlation diagram for the reactions of HMD with the ground- and excited-state electron acceptors (EA). The energy scale is constructed with HMB placed arbitrarily at 0 eV, and with the assumption that the stabilization of HMB and HMD by interaction with ground-state acceptors is small (weak, or contact, charge-transfer complexes). Also, since some of the redox reactions are irreversible, the peak potentials in acetonitrile solution are used in calculating the energies of the ions. For this reason the absolute magnitudes of the energies of the ions are probably not accurate, but their relative values should be correct.

The analogous behavior of the ground- and excited-state electron acceptor is apparent from inspection of Figure 5. Consider first the conversion of HMD to HMB catalyzed by TCNQ. In this case the activation energy is supplied thermally to what might be described as an encounter complex of HMD and TCNQ. As the energy of this complex rises along the thermal HMD to HMB potential energy curve, it intersects the descending (HMD$^{+\cdot}$ + TCNQ$^{-\cdot}$) to (HMB$^{+\cdot}$ + TCNQ$^{-\cdot}$) reaction curve, and the avoided crossing of these surfaces (the dotted region in Figure 5) generates the transition state of the catalyzed reaction.[27] It is clear from Figure 5 that there is sufficient energy for this system to proceed to HMB$^{+\cdot}$ and TCNQ$^{-\cdot}$. However, the experimental evidence indicates that this does not occur to a great extent. Instead, the products of the reaction are HMB and TCNQ. This is probably a consequence of the second avoided crossing of these surfaces, rather than immediate back electron transfer from ions, since generation of (HMB$^{+\cdot}$ + EA$^{-\cdot}$) photochemically leads to separation and detection of ions free in solution.

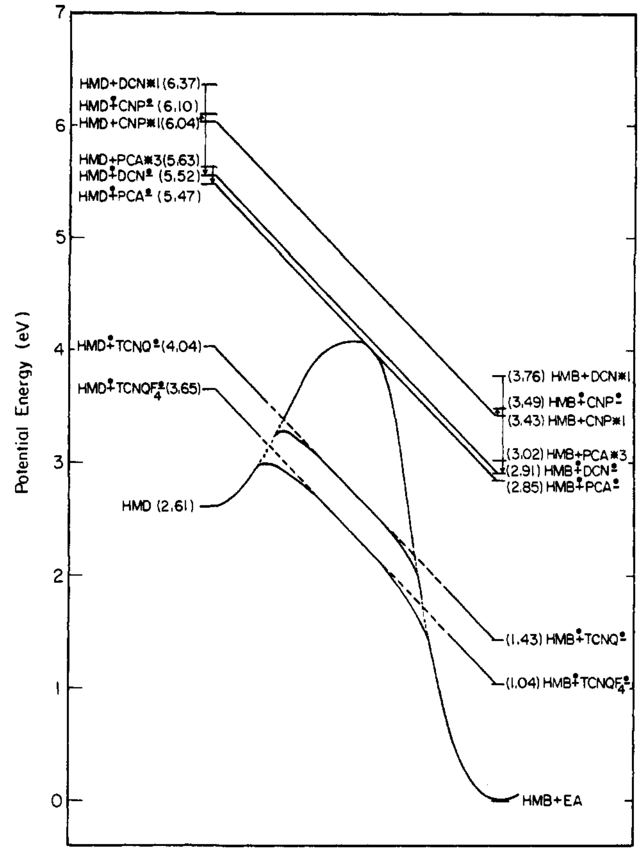

Figure 5. Reaction coordinate diagram for the conversion of HMD to HMB catalyzed by ground- and excited-state electron acceptors.

The correlation of the reduction potential of the electron acceptor with the measured catalytic rate constant is readily accommodated by this model. The point of first intersection of the potential energy surfaces depends on the reduction potential of the acceptor; the more easily reduced acceptors therefore have correspondingly lower activation energies.

The reaction path for the excited-state-catalyzed isomerization of HMD to HMB is revealed by analysis of Figure 5 to be simply related to the thermal reaction. However, instead of the reaction starting from the encounter complex of HMD and EA, it begins on the descending (HMD$^{+\cdot}$ + EA$^{-\cdot}$) surface which proceeds to cross the ground-state HMD to HMB potential curve at an energy near, or somewhat above, the thermal transition state. The consequences of this crossing depend on the specific nature of the excited electron acceptor. For the triplet acceptors we studied, the spin forbiddeness of the interaction with the singlet ground-state surface discourages formation of neutral products, and a relatively high yield of radical ions is obtained. For the singlet excited acceptors the partitioning between formation of ionic and neutral products appears to be controlled by the specific structure of the acceptor. For DCN^{*1} the avoided crossing leads, in essence, only to neutral products, although, just as in the thermal reaction, formation of ionic products is energetically allowed. In contrast, when the acceptor is CPY^{*1} ionic products are observed, but their yield is only ca. 25% of that obtained when HMB quenches this excited singlet. Finally, when CNP^{*1} is the acceptor, and formation of ions directly from the locally excited states is calculated to be unfavorable energetically, we observe what appears to be an exciplex-to-exciplex isomerization similar to that which occurs in nonpolar solvents where separation to ions also is energetically unfavorable.[12,13]

There have recently been a number of examples of thermal reactions that appear to proceed through odd-electron states formed by single electron-transfer processes.[16,17,28] A recent theoretical analysis of the S$_\mathrm{N}$2 reaction by Shaik and Pross[29]

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[27] Salem, L. *J. Am. Chem. Soc.* **1974**, *96*, 3486. Michl, J. *Photochem. Photobiol.* **1977**, *25*, 141.

[28] Gassman, P. G.; Olson, K. D.; Walter, L.; Yamaguchi, R. *J. Am. Chem. Soc.* **1981**, *103*, 4977.

describes this classical transformation as a single electron transfer taking place synchronously with bond reorganization. In this sense it may be reasonable to describe the thermal reaction of HMD with TCNQ also as a single electron transfer. Thus the transition state for this reaction, in essence, forms a dividing line between an "even-electron" and an "odd-electron" description of the reaction surface. In further support of this description we note that the usual requirement that the rate of an electron-transfer reaction follow the redox energetics of the components appears to be satisfied in this case. Also, in at least some of the photochemical examples, odd-electron products are observed from the reaction.

An alternative adiabatic description of the reaction surfaces in Figure 5 avoids the use of the phrase "single electron transfer". In this view there is a continuous transformation from an undetected (weak) HMD–TCNQ charge-transfer complex to the detectable HMB-TCNQ charge-transfer complex. However, application of this adiabatic path to the excited-state initiated process seems to require transformation of the (HMD· · ·EA) exciplex smoothly into the (HMB· · ·EA) exciplex, a transformation that clearly does not occur efficiently for the DCN^{*1}-initiated reaction.

A compromise view, consistent with all of the data, is to describe the descending portion of the ground-state acceptor initiated reaction potential energy curve between the avoided crossings as an exciplex. The structure and properties of this exciplex would be exactly analogous to those formed from the reaction of an excited singlet acceptor with HMD. When the descending exciplex surface meets the ground-state HMD to HMB surface, the resulting avoided crossing forms an intermediate, or, at least a "flatter" spot, that can partition between continued motion toward ions, as occurs for some excited-state accetors, or internal conversion to the ground-state surface and consequent generation of neutral products, which occurs for both thermally and photochemically initiated reactions.

The exciplex structure may not represent a stationary point for either the ground- or excited-state initiated reaction until the isomerization to HMB is complete. This suggestion is based on the observation of no apparent risetime for HMB$^{+\cdot}$ in the laser experiments. However, previous estimates by Jones and coworkers[13] place the maximum lifetime of this exciplex in nonpolar solvents at less than 1 ns, well below our resolution limit.

Finally, the catalysis of HMD isomerization by ground-state electron acceptors and the interpretation of this phenomenom in terms of exciplex formation offer an alternative explanation for the chemiluminescent properties of Dewar benzene and some of its derivatives.[8] One of the key observations in the investigation of this phenomenon is that thermolysis of the Dewar benzene in the presence of 9,10-dibromoanthracene (DBA) yields considerably more light than in the presence of 9,10-diphenylanthracene (DPA). This result has been interpreted to indicate formation of triplet benzene in the isomerization reaction. However, DBA is much more easily reduced than DPA and, therefore, according to the postulates described above, is expected to be a more effective catalyst, and consequently give a higher yield of exciplex. Once formed this exciplex can partition between several reaction paths, one of which leads to locally excited DBA which is detected by its emission.

Conclusion

The study of the isomerization of HMD to HMB catalyzed by ground-state electron acceptors reveals a mechanism which is adequately described as the thermal generation of an exciplex. This can be compared with studies of thermal and photochemical reactions of tetracyanoethylene with organometals, for example, by Kochi and co-workers[17] and our studies of peroxide chemiluminescence,[16] where similar evidence is used to describe electron transfer to form a radical-ion pair. The difference in these views is subtle in that the exciplex can sometimes be a precursor to the radical ions. However, the findings described above indicate that radical-ion formation need not occur in these reactions, but sometimes is a consequence of exciplex dissociation. In this regard, it may be less confusing to refer to these processes as thermal exciplex transformations (TET) rather than as single electron-transfer (SET) reactions, recognizing, however, that in some cases electron transfer is the eventual result.

Experimental Section

General. HMD was purchased from Aldrich Chemical Co. and was distilled under vacuum from $LiAlH_4$. TCNQ was also supplied by Aldrich, and it was purified by chromatography on silica gel with CH_2Cl_2. The halogenated TCNQ derivatives were a gift of the DuPont Corp. and were shown to be analytically pure. All solvents used in the thermal kinetics and laser spectroscopy were distilled from appropriate drying agents; only the center cut was retained. 1,4-Dicyanonaphthalene[30] was prepared from CuCN and 1,4-dibromonaphthalene according to a method outlined in "Organic Synthesis" for 1-cyanonaphthalene.[31] 1-Cyanopyrene was prepared by the method of Lock.[32] It and the other photosensitizers employed were purified by recrystallization or sublimation. All glassware used in the thermal reactions of HMD was soaked in aqueous base, washed with copious amounts of distilled water, and dried thoroughly in an oven.

Instrumentation. The laser apparatus has been described previously.[25] Cyclic voltammetric measurement of redox potentials was done in acetonitrile solution, with 0.1 M tetrabutylammonium perchlorate as supporting electrolyte and an Ag/0.01 M $AgNO_3$ in acetonitrile as reference electrode. For those cases where reversible waves are obtained, the midpoint between the reduction and oxidation peaks is reported. Gas chromatography of mixtures of HMD and HMB for kinetic and quantum yield analysis was performed on an all-glass Varian 2700 with a 6 ft × $^1/_8$ in. glass column packed with 5% SE-30 on GasChrom Q using undecane as an internal standard. It is important to keep the injector temperature low (ca. 65 °C) to avoid isomerization of HMD when solutions containing TCNQ and its derivatives are analyzed.

Spectra of Radical Ions. The spectrum of HMB$^{+\cdot}$ was recorded by Professor E. Haselbach, l'Ecole Polytechnique Federale, Lousanne, by pulse radiolysis of HMB at 77 K and is shown as an inset on Figure 2.[33] All of the other radical ion spectra have been reported previously[34] except for that of DCN$^{-\cdot}$. We generated this ion by reduction of the neutral compound with potassium in a THF solution. The spectrum we obtained is shown as an inset on Figure 2. The spectra of the transient ion products obtained by laser spectroscopy agreed with those reported previously or obtained as described above.

Catalyzed Thermal Rearrangement of HMD. Solutions of HMD and the electron acceptor in acetonitrile containing internal standard were degassed (freeze–pump–thaw) and sealed in 7-mm o.d. Pyrex ampules. The concentration of electron acceptor typically covered the range from 10^{-2} to 10^{-3} M and the starting HMD concentration was typically 5 × 10^{-4} M. The ampules were placed in a thermostated oil bath maintained at a temperature sufficient to cause isomerization at a convenient rate for the acceptor used. The ampules were removed from the bath and analyzed by gas chromatography as described above. Least-squares analysis of the results, presented as a semilogarithmic plot in Figure 1 for TCNQ, gives k_{cat}. The reaction catalyzed by $TCNQF_4$ was so rapid that we could not degas these solutions by freeze–pump–thaw techniques.

The essentially quantitative nature of the catalytic isomerization was confirmed by ^1H NMR spectroscopy. A solution of HMD 0.4 M in CD_3CN containing 0.013 M $TCNQF_4$ was analyzed after 3 h at room temperature. Integration indicated about 70% conversion had occurred, giving HMB as the only product. Similarly, analysis of the UV spectra of reaction mixtures revealed that none of the TCNQ derivatives were measurably consumed by reaction with HMD.

Finally, we showed that addition of a small amount of Na_2CO_3 (mostly undissolved) to the reaction ampules did not inhibit the catalytic effect of the electron acceptor.

Quantum Yields. Quantum yields were determined using the ferrioxalate actinometer system as described by Calvert and Pitts.[35] The nitrogen laser beam, used as the photon source, was split into two using either a 50:50 or 90:10 beam splitter. The exact beam splitting was determined by placing ferrioxalate solution in both beams which in turn confirmed approximate linearity of the actinometer. For determination of the quantum yield of HMD isomerization, one beam was sent into the

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[29] Shaik, S. S.; Pross, A. *J. Am. Chem. Soc.* **1982**, *104*, 2708.

[30] Bradbrook, E. F.; Linstead, R. P. *J. Chem. Soc.* **1936**, 1739.

[31] *Org. Synth.* **1955**, *3*, 631.

[32] Lock, G. *Ber.* **1937**, *70*, 928.

[33] Private communication from Professor Haselbach.

[34] (a) CPY$^{-\cdot}$ and CPH$^{-\cdot}$: Panayotov, I. M.; Tsvetanov, Ch.B. *Monatsh. Chem.* **1970**, *101*, 1672. (b) TCPA$^{-\cdot}$: Shida, T.; Iwata, S.; Masashi, I. *J. Phys. Chem.* **1974**, *78*, 741. (c) Anthraquinone radical anion: Hayon, E.; Ibata, T.; Lichtin, N. N.; Simic, M. *J. Phys. Chem.* **1972**, *76*, 2072.

[35] Calvert, J. C.; Pitts, J. N., Jr. "Photochemistry"; Wiley: New York, 1966.

ferrioxalate solution and one into the sample cell containing HMD and electron acceptor. Both solutions were stirred continuously during irradiation. Laser pulses went into the sample at a frequency of about 1 Hz. The absorbance of both solutions was adjusted so that more than 99% of the laser light was being absorbed. After irradiation the absorption of the ferrioxalate solution was determined, and the amount of HMD converted to HMB was determined by gas chromatograph as described above. All solutions were taken to low conversion to minimize participation from HMB in the chain reaction sequence.

Photosensitization of HMB with PCA. A solution of PCA (0.03 M) and HMB (0.03 M) in acetonitrile was prepared and deoxygenated by purging with N_2. Irradiation at 337 nm with the nitrogen laser, or with 350-nm lamps in a Rayonet photoreactor, gave two major products. The first precipitated from the solution as the reaction progressed and was identified as decamethylbibenzyl:[36] mp 242–244 °C; ^{1}H NMR ($CDCl_3$) δ 2.27 (s, 18 H), 240 (s, 12 H), 2.88 (s, 4 H); mass spectrum (75 eV), *m/e* 322 (M^+), 161. The second product was shown to be the cross coupling product of the PCA ketyl radical and HMB radical by mass spectrometry.

Acknowledgment. This work was supported by a grant from the National Science Foundation. We thank Mr. James Wehmer for his help with the laser experiments and Mr. John Hurst for the use of his data reduction software.

Registry No. HMD, 7641-77-2; HMD^+, 85293-78-3; HMB^+, 34473-51-3; TCNQ, 1518-16-7; $TCNQCl_2$, 21004-03-5; $TCNQCl_2{}^+$, 85353-34-0; TMB, 135-77-3; $TCNQBr_2$, 56403-70-4; $TCNQF_4$, 29261-33-4; $TCNQF_4{}^+$, 85353-35-1; DCN^-, 68331-38-4; CPH^-, 68271-79-4; PCA^-, 59273-30-2; *p*-dinitrobenzene, 100-25-4; *p*-dicyanobenzene, 623-26-7; 1,4-dicyanonaphthalene, 3029-30-9; 1-cyanopyrene, 4107-64-6; 9-cyanophenanthrene, 2510-55-6; tetrachlorophthalic anhydride, 117-08-8; *p*-cyanoacetophenone, 1443-80-7; anthraquinone, 84-65-1.

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[36] Gorzny, K.; Maahs, G. Ger. Offen., 7 March 1974; *Chem. Abstr.* **1974**, *80*, 145715 y.

[2.1.1]Propellane. Reaction of 1,4-Diiodobicyclo[2.1.1]hexane with *tert*-Butyllithium and with Potassium Atoms

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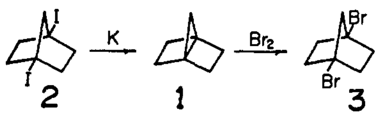
Contribution from the Departments of Chemistry, Yale University, New Haven, Connecticut 06511, and the University of Utah, Salt Lake City, Utah 84112.

Received November 22, 1982

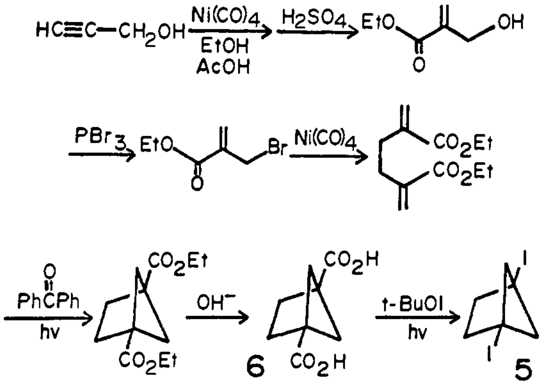
Abstract: The synthesis of 1,4-diiodobicyclo[2.1.1]hexane (**5**) is described. The reaction of **5** with *tert*-butyllithium in hexane gave the same type of products as previously observed in the reaction of 1,4-diiodonorbornane (**2**) with *tert*-butyllithium. Evidence has been presented indicating the latter reaction to proceed via the [2.2.1]propellane as an intermediate, and it appears likely that the [2.1.1]propellane was involved in the former reaction. The reaction of **5** with potassium atoms in the gas phase led to the formation of an unstable compound which has been isolated in a nitrogen matrix and tentatively identified as the [2.1.1]propellane on the basis of its infrared spectrum.

[2.2.1]Propellane (**1**) has received considerable study. Wilcox and Leung[2] examined the reaction of 1,4-dichloronorbornane with lithium and obtained only the dilithio compound, suggesting that the propellane may have been formed and then added lithium across the central C–C bond. We have studied the electrochemical dehalogenation of 1,4-dihalonorbornanes[3] and found norbornane, bisnorbornyl, and higher oligomers to be formed. They could most simply be derived by dehalogenation forming the propellane, followed by its reduction. Subsequently, Peters and Carrol[4] showed that 1-bromonorbornane was not an intermediate in the reduction of the 1,4-dibromide, and that the reaction was a net three-electron reduction. This provides strong evidence for the formation of **1** as the product of a two-electron reduction of the dihalide which then undergoes further reduction at the mercury electrode.

We also have examined the reduction of 1,4-diiodonorbornane (**2**) with *n*-butyl- and *tert*-butyllithium.[5] The major product was the corresponding 1-butyl-4-iodonorbornane. The reduction of 1-bromo-4-iodonorbornane with butyllithium led to the same product. This provided evidence for an intermediate in which both halogens had been lost, presumably the [2.2.1]propellane. Finally, we have studied the reaction of the 1,4-dihalonorbornanes with metal atoms in the gas phase, and have been able to trap the propellane (**1**) in a matrix at low temperature.[6] The infrared spectrum and the reaction with bromine to form 1,4-dibromonorbornane provided evidence for the assigned structure.



Scheme I



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[1] (a) Yale University. (b) Taken in part from the Ph.D. theses of W.E.P., 1980, and F.H.W., 1982. (c) University of Utah.

[2] Wilcox, C. F., Jr.; Leung, C. *J. Org. Chem.* **1968**, *33*, 877.

[3] Wiberg, K. B.; Bailey, W. F.; Jason, M. E. *J. Org. Chem.* **1976**, *41*, 2711.

[4] Peters, D. G.; Carrol, W. F., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 4127.

[5] Wiberg, K. B.; Pratt, W. E.; Bailey, W. F. *J. Am. Chem. Soc.* **1977**, *99*, 2297.

[6] Wiberg, K. B.; Walker, F. H.; Michl, J. *J. Am. Chem. Soc.* **1982**, *104*, 2056.

0002-7863/83/1505-3638$01.50/0