

# Electron-Transfer Mechanisms in Photochemical Transformations of Iminium Salts

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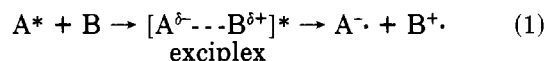
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Studies in the area of organic photochemistry have focused on two interrelated aspects of excited-state chemistry. Investigations of photophysical phenomena have probed the mechanisms for excited-state deactivation by emission, radiationless decay, and energy transfer. The chemical reactivity of organic excited states has been explored with the intent of uncovering new reaction processes, detailing their mechanisms and elucidating the factors that control reaction efficiencies and selectivities manifested in regiochemistry and stereochemistry. In a number of cases, the reactions uncovered possess the proper characteristics to be applicable as synthetic methods. These investigations have concentrated mainly on classical photochemical processes exemplified by ketone hydrogen atom abstractions, olefin cis-trans isomerizations or cycloadditions, conjugated ketone rearrangements, arene photoisomerizations, and polyene electrocyclicizations. In recent years interest has grown in a new area of photochemistry involving excited-state electron transfer. Exploratory and mechanistic studies in this area have uncovered novel pathways for excited-state quenching, photosensitization, and reaction initiated by single electron transfer (SET) from or to excited states of organic systems. Many of the photochemical transformations proceeding by SET mechanisms appear to be particularly suited to synthetic practice. The aim of this Account is to briefly outline the general features of SET in excited-state chemistry and to review the results of our recent photochemical studies of systems containing the iminium cation grouping.<sup>1</sup>

The concepts that serve as the foundation for an understanding of excited-state SET have their origins in early investigations of excited-state complex formation. The body of data accumulated on this subject suggests that a wide variety of excited-state processes occur via the intervention of complexes formed by encounter of excited-state molecules with ground-state species of the same (forming homodimers or excimers) or different (forming heterodimers or exciplexes) identity.<sup>2</sup> The stabilities of the complexes relative to precursor excited states were initially attributed to exciton resonance interactions involving delocalization of excitation over both components.<sup>3</sup> It is now clear that charge transfer serves as another important component of excited-state complex stabilization.<sup>4</sup> This postulate is substantiated by observations that demonstrate that the wavelength maxima for emission from,

and thus energy of, exciplexes are dependent upon both the ionization potentials of donors and electron affinities of acceptors in the pairs<sup>5</sup> and the solvent polarity.<sup>6</sup> In addition, excitation of ground-state charge-transfer complexes can be used to directly populate the exciplex state.<sup>7</sup> Perhaps the most pertinent information supporting the notion of charge transfer in exciplexes is found in the observed correlations existing between the rate constants for fluorescence quenching and predicted free energies for electron transfer in systems for which exchange energy-transfer mechanism are inoperative. Weller<sup>8</sup> has noted that relationships exist connecting observed fluorescence quenching rate constants with calculated free energies for SET ( $\Delta G_{et}$ ) in singlet excited donor-acceptor systems. Functions relating SET rate constants ( $k_{et}$ ) with  $\Delta G_{et}$  derived by Balzani, Scandola, and Schuster<sup>9</sup> on the basis of theoretical considerations have the same general characteristics as those empirically determined by Weller. Accordingly, fluorescence quenching via exciplex formation appears to be controlled by electron transfer, the facility of which is governed by the oxidation and reduction potentials of the donors and acceptors along with the energy of the populated excited state.

An important chemical consequence of charge transfer in excited-state complexes is found in the nature of decay pathways available to these systems in polar solvents. Deactivation of singlet exciplexes, for example, can occur by a number of familiar routes including emission, intersystem crossing, and radiationless decay. However, return to the ground-state manifold can take place by a unique pathway involving complete electron transfer with concomitant radical ion formation (eq 1). Characteristic of this feature is the observation



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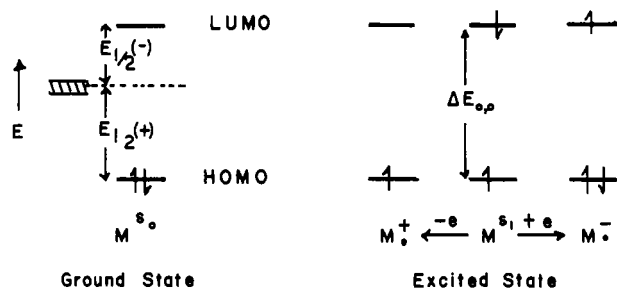
(6) Knibbe, H.; Rehm, D.; Weller, A. *Ber. Bunsenges. Phys. Chem.* 1968, 72, 257. Ware, W. R.; Richter, H. P. *J. Chem. Phys.* 1968, 48, 1595.

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(8) (a) Beens, H.; Weller, A. *Chem. Phys. Lett.* 1968, 2, 140. (b) Rehm, D.; Weller, A. *Isr. J. Chem.* 1970, 8, 259.

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Patrick S. Mariano was born in 1942 in Passaic, NJ. He received his B.S. in Chemistry at Fairleigh Dickinson University and his Ph.D. from the University of Wisconsin. Following 2 years of postdoctoral work at Yale University, he joined in 1970 the faculty at Texas A&M University, and in 1979 he moved to the University of Maryland, where he is presently Professor of Chemistry. His research interests are the development of new synthetic methodology and natural product synthesis. He was Camille and Henry Dreyfus Teacher-Scholar Awardee, 1975-1980.



**Figure 1.** Simple MO view of ground- and excited-state electron transfer showing how excitation ( $\Delta E_{0,0}$ ) serves as the thermodynamic driving force for ET to overcome barriers associated with the ground-state oxidation ( $E_{1/2}(+)$ ) and reduction ( $E_{1/2}(-)$ ) potentials.

that exciplex lifetimes and emission efficiencies are attenuated in proceeding from solvents of low to high polarity.<sup>10</sup> In addition, exciplex-derived radical ions have been detected by use of various spectroscopic techniques.<sup>11</sup> The charged radical species formed in this way are capable of participating in a number of different chemical processes owing to their high energy content and unique electronic characteristics (vide infra).

It is possible to develop a qualitative framework for predicting when SET pathways will compete with alternate modes of excited-state decay. A simplified molecular orbital view of redox systems (Figure 1) serves to demonstrate the axiom that electronic excited states are both better one-electron donors and better one-electron acceptors than the corresponding ground-state species. Thus, the excitation energy of the system ( $\Delta E_{0,0}$ ) serves as the thermodynamic driving force for electron transfer. A more precise formulation of the relationship between  $\Delta G_{et}$  and oxidation ( $E_{1/2}(+)$ ) and reduction ( $E_{1/2}(-)$ ) potentials and  $\Delta E_{0,0}$  is presented in eq 2.<sup>8b</sup> Furthermore, the empirically derived rela-

$$\Delta G_{et} = E_{1/2}(+) - E_{1/2}(-) - \Delta E_{0,0} - C \quad (2)$$

tionship between  $\Delta G_{et}$  and  $k_{et}$  suggests that the rate constants for electron transfer will approach the diffusion-controlled limit when electron transfer is exoergic ( $\Delta G_{et} < 0$ ). Therefore, preliminary information on the possible operation of SET mechanisms in a particular photochemical process can be gained by considering the experimentally determined electrochemical potentials, the excited-state energy of the donor-acceptor pair, and solvent polarity and by comparing the calculated value for  $k_{et}$  with rate constants for other excited-state deactivation modes.

Another important consideration in developing a framework for understanding excited-state processes initiated by electron transfer is the nature of the species that serve as reactive intermediates. The chemical selectivities of classical photochemical processes are often influenced by properties of the excited-state intermediates including electron-density distributions, orbital symmetries, and their unique nuclear coordinate vs. energy-distribution functions. Thus, reaction barriers

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that prohibit certain reaction types in the ground-state manifold are in some cases easily surmounted by excited-state systems.<sup>12</sup> Photosensitization by exchange energy transfer in which excitation energy is conveyed with conservation of multiplicity from sensitizer to acceptor serves as another mode for activating excited-state reaction pathways. The facility of this indirect method for forming potentially reactive excited states is governed by the relative excited-state energies of sensitizers and acceptors. The factors controlling excited-state reactions proceeding by SET mechanisms are distinctly different from those at work in classical photochemical processes. For example, in SET-sensitized processes the energetics of electron transfer determine the rates and efficiencies for sensitizer activation of acceptor molecules. Many examples exist in which SET photosensitization occurs even though classical energy transfer is extremely endoergic.<sup>13</sup> More importantly, the character of excited-state SET-initiated processes will reflect the fact that neutral or ion radicals serve as the key reactive intermediates. Thus, a framework for describing and predicting the chemical behavior of these processes can be developed by considering the reaction modes available to species of this type based upon inspection of electron impact or capture mass spectrometric fragmentations<sup>14</sup> and solution-phase electrochemical transformations.<sup>15</sup> It is perhaps not surprising to find that the fundamentals summarized above have been frequently used in recent years to rationalize and design a number of novel and interesting excited-state reactions.

### Photochemistry of Systems Containing the Iminium Cation Chromophore

Our recent studies in the area of electron-transfer photochemistry have concentrated on systems containing the iminium cation ( $R_2N^+=CR_2$ ) grouping. Quite frankly, our interests in these systems at the outset were stimulated by other considerations. First, although qualitative and quantitative aspects of nitrogen heteroaromatic salt<sup>16</sup> and neutral imine<sup>17</sup> photochemistry had been investigated, efforts probing mechanistic details and synthetic applications of simple iminium salt excited-state chemistry were scarce. Second, we felt that the studies of systems containing this grouping would be relevant to chemical phenomena associated with the visual processes, which involve excited-state transformations of protonated rhodopsin, the vision pigment containing a highly conjugated iminium cation chromophore.<sup>18</sup> Last, a simplified analysis of the characteristics of the iminium cation grouping suggested that the reactive modes of excited-state decay might resemble those of olefins and include such pathways as *E-Z*

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



(15) Mann, C. K.; Barnes, K. K. "Electrochemical Reactions in Nonaqueous Systems"; Marcel Dekker: New York, 1970.

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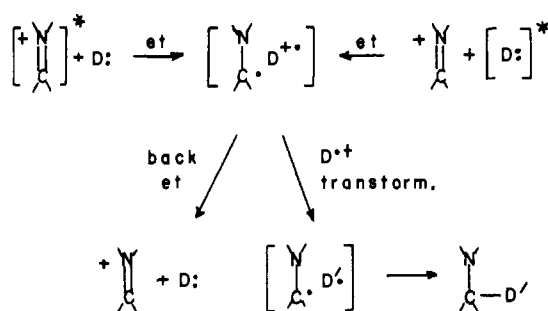
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Table I  
Ground- ( $E_{1/2}S_0(-)$ ) and Singlet-Excited- ( $E_{1/2}S_1(-)$ )  
State Reduction Potentials for Iminium Salt Systems

substances with iminium cation chromophore	$\Delta E_{0,0}S_1$ , eV	$E_{1/2}S_0(-)$ , V	$E_{1/2}S_1(-)$ , V
	4.3	-1.3	+3.0
	3.5	-0.9	+2.6
	3.5	-1.0	+2.5
	3.9	-1.0	+2.9

Scheme I



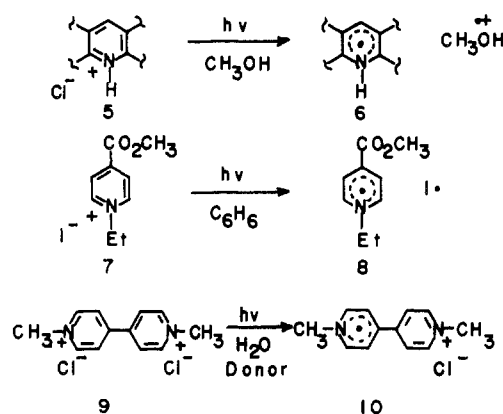
isomerization<sup>19</sup> and 2 + 2 cycloaddition.<sup>20</sup> However, a careful evaluation of the electronic features of iminium cations points out an excited-state property that dominates the photochemistry of these systems. Accordingly, the presence of the delocalized positive charge, which strongly influences the ground-state chemistry of iminium salts,<sup>21</sup> allows for ready participation in excited-state SET. Calculations taking into account excited-state energies and reduction potentials<sup>22</sup> of various iminium salts and related N-heteroaromatic cations (Table I) suggest that systems containing this grouping should serve as ideal acceptors in electron-transfer-initiated quenching and reaction processes (Scheme I) with a variety of electron donors including olefins and arenes ( $\pi$ -type donors) and alcohols and ethers (n-type donors) (Table II). Indeed, our observations have shown this to be true.

Before describing some of the characteristics of iminium salt electron-transfer photochemistry, it will be instructive to review selected studies with N-heteroaromatic salts in which spectroscopic methods have been employed to gain evidence for excited-state electron transfer. For example, LaBlache-Combier and his associates<sup>23</sup> have shown that irradiation of six-mem-

Table II  
Calculated Free Energies for ET From Selected  
Donors to Singlet Excited Iminium Salt Systems

ground-state donor	approximate donor oxidation potential ( $E_{1/2}(+)$ ), V	$\Delta G_{et}$ , eV, to iminium cation singlet excited states			
		1	2	3	4
$(CH_3)_3COH$	+2.5	-0.5	-0.1	-0.7	-1.7
THF	+1.9	-0.1	-0.7	-0.3	-1.3
$(CH_3)_2C=CH_2$	+2.3	-0.0	-0.6	-0.2	-1.2
$PhCH_3$	+1.3	-0.4	-1.0	-0.6	-1.6

bered monoaza aromatic compounds or their quaternary salt analogues **5** in  $CH_3OH-HCl$  solutions results in the



production of semiquinone radicals **6**, detected by electron spin resonance techniques. Methanol, owing to the presence of unshared electrons on oxygen, serves as the electron donor in these SET processes. Flash-photolysis studies conducted independently by Kosower<sup>24</sup> and Cozzens<sup>25</sup> with a number of substituted pyridinium iodides **7** have documented the occurrence of intramolecular electron transfer generating iodine atoms and the heterocyclic radicals **8**. Electron transfer in charge-transfer complexes is known to be responsible for the efficient fluorescence quenching of *N*-methylacridinium salts by various anions.<sup>26</sup> Similarly, fluorescence quenching by SET mechanisms is reported to occur for pyridinium and bipyridinium ions.<sup>27</sup> The bipyridinium cation radical **10**, detected in flash-photolysis studies by McKellar and Turner,<sup>28</sup> is produced by irradiation of the corresponding dication **9** in the presence of electron-donating alcohols and carboxylate ions.<sup>29</sup> These observations combine to suggest that compounds containing the  $R_2C=NR_2^+$  grouping will serve as acceptors in excited-state electron-transfer processes.

### Olefin-Iminium Salt Photoaddition Reactions

At the outset our calculations suggested that electron transfer from electron-rich olefins ( $E_{1/2}(+) < 2.6$  V) to

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(20) Cycloaddition to the C=N bond of imines has been observed in the following studies: Swenton, J. S.; Hyatt, J. A. *J. Am. Chem. Soc.* 1974, 96, 4879. Rodehorst, R. M.; Koch, T. H. *Ibid.* 1975, 97, 7298.

(21) Bohme, H.; Viehe, H. G. "Iminium Salts in Organic Chemistry"; Wiley, New York, 1976.

(22) Andrieux, C. P.; Saveant, J. M. *J. Electroanal. Chem.* 1970, 26, 223.

(23) Castellano, A.; Cateau, J. P.; LaBlache-Combier, A. *Tetrahedron* 1975, 31, 2255.

(24) Kosower, E. M.; Lindquist, L. *Tetrahedron Lett.* 1965, 4481.

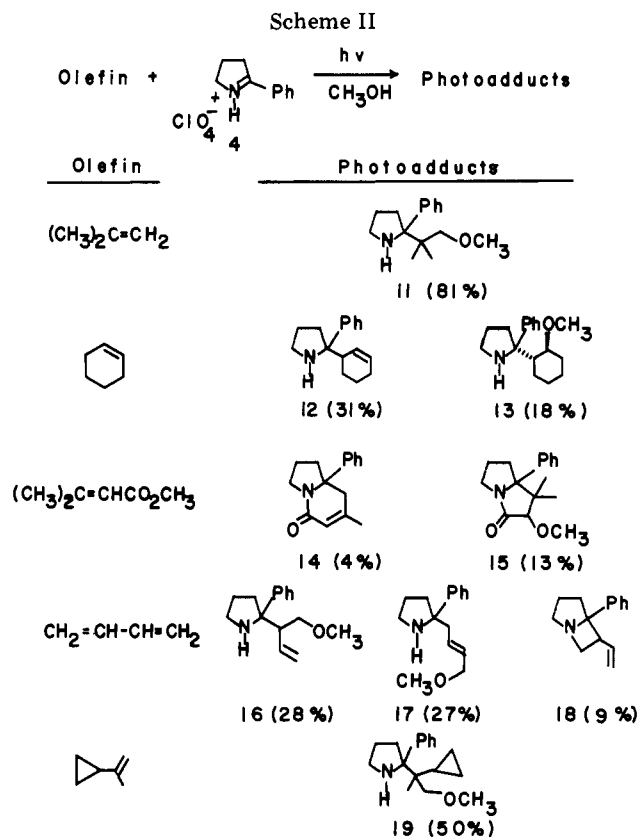
(25) Cozzens, R. F.; Gover, T. A. *J. Phys. Chem.* 1970, 74, 3003.

(26) Beaumart, T. G.; Davis, K. M. C. *J. Chem. Soc. B* 1970, 456.

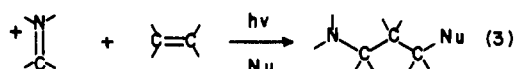
(27) McCall, M. T.; Whitten, D. G. *J. Am. Chem. Soc.* 1969, 91, 5681.

(28) McKellar, J. F.; Turner, P. H. *Photochem. Photobiol.* 1971, 13, 437.

(29) Barnett, J. R.; Hopkins, A. S.; Ledwith, A. *J. Chem. Soc., Perkin Trans. 2* 1973, 80. Ledwith, A.; Russell, P. J.; Sutcliffe, L. H. *J. Chem. Soc., Chem. Commun.* 1971, 964. Brown, N. M. D.; Crowley, D. J.; Murphy, W. J. *J. Chem. Soc., Chem. Commun.* 1973, 592.

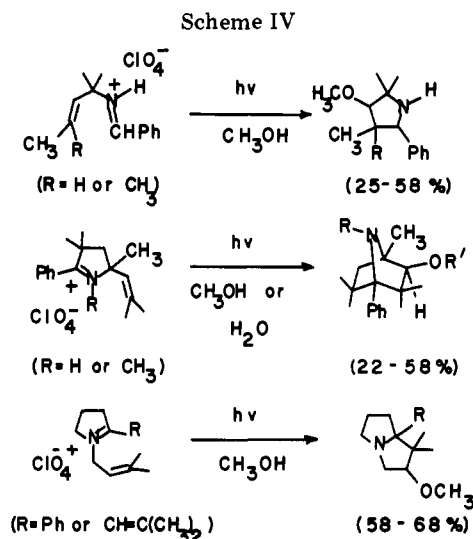
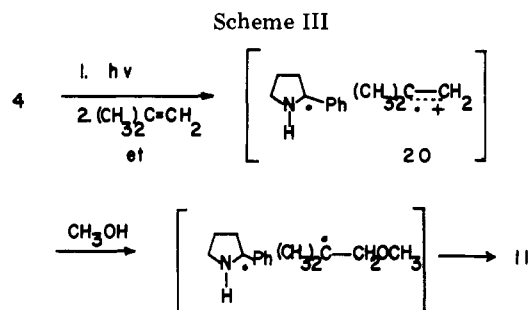


conjugated iminium salts should be energetically favorable. The observation that several electron-rich olefins serve as excellent quenchers of 2-phenyl-1-pyrrolinium perchlorate (4) fluorescence is consistent with this expectation.<sup>30</sup> Rate constants for quenching

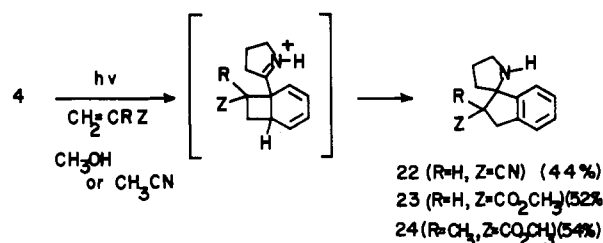


in these cases are near the diffusion-controlled limit even though classical quenching by the exchange energy transfer pathway is prohibited due to extreme endoergicity (ca. 10–20 kcal/mol). Indeed, electron transfer in the excited-state manifold appears to be responsible for the novel photoaddition and photocyclization reactions detected in the photochemistry of olefin-iminium systems (eq 3). For example, irradiation of 4 in methanol solutions containing isobutylene leads to efficient production of the (methoxyalkyl)pyrrolidine 11. Similar reactions occur between 4 and a number of other electron-rich olefins, including cyclohexene, butadiene, methyl  $\beta,\beta$ -dimethylacrylate, and isopropenylcyclopropane (Scheme II).<sup>30,31</sup>

Several features of these olefin-iminium salt photoadditions are worth noting in terms of their relationship to SET mechanisms and synthetic applications. First, the anti-Markovnikov regioselectivity observed for reaction of isobutylene with 4 is fully consistent with a mechanism involving initial production of the cation radical 20 by the SET process (Scheme III). Accordingly, methanol attack at the least substituted, charged position of 20 is expected to predominate and to produce the radical pair precursors to the adduct 11. Second, the efficiency of photoadditions, if SET



mechanisms are operable, should be dependent upon the olefin oxidation potential since this will have a pronounced effect upon the relative rates of electron transfer and other processes competing for deactivation of the iminium salt excited states. Observations made in study of photoreactions of 4 with the electron-poor olefins acrylonitrile, methyl acrylate, and methyl methacrylate are in accord with these expectations. Significantly,  $\beta$ -amino ether adducts such as those formed in reactions outlined in Scheme II are not generated in these cases. Instead, alternate reaction pathways involving olefin-arene  $\pi,2 + \pi,2$  cycloaddition and leading to the spirocyclic amines 22–24 are followed.<sup>30,32</sup> Last,



results from our investigations of various *N*-allyliminium salt systems show that SET-initiated photocyclizations occur to generate 3-pyrrolidinyl ethers or alcohols in monocyclic and bridged or fused bicyclic environments. Several early examples of transformations that demonstrate this feature are accumulated in Scheme IV.<sup>33,34</sup> In these cases, the cyclization regiochemistry is controlled by selective generation of 2-

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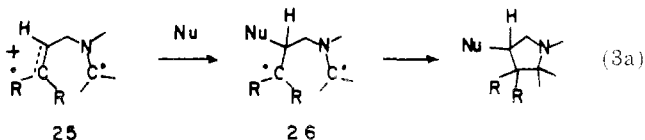
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(32) Mariano, P. S.; Leone, A. *Tetrahedron Lett.* 1980, 4581.

(33) Mariano, P. S.; Stavinoha, J. L.; Swanson, R. *J. Am. Chem. Soc.* 1977, 99, 6781.

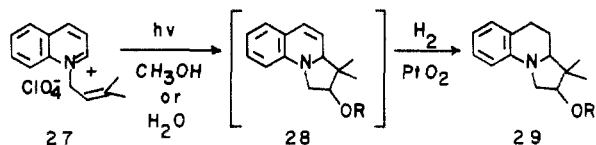
(34) Stavinoha, J. L.; Mariano, P. S.; Leone-Bay, A.; Swanson, R.; Bracken, C. *J. Am. Chem. Soc.* 1981, 103, 3148.

aza-1,5-diradicals **26** through nucleophilic addition to



the less substituted positions of the cation diradicals **25** arising by intramolecular electron transfer. Thus, intramolecular counterparts of the photoaddition reactions described in eq 3 are useful in construction of interesting heterocyclic ring systems.

An evaluation of excited- and ground-state electrochemical potentials (see Tables I and II) indicates that salts of nitrogen heteroaromatic compounds should serve as efficient electron acceptors in excited-state processes. Spectroscopic investigation outlined earlier in this Account and related chemical studies<sup>35</sup> have invoked SET mechanisms to rationalize both photophysical phenomena and a variety of photoaddition, dimerization, and reduction reactions detected with pyridinium and related cationic systems. On the basis of these observations and those made in our earlier efforts, we anticipated that electron-rich olefins would serve as efficient donors in electron-transfer-induced addition and cyclization reactions with appropriately substituted aza aromatic salts. This hypothesis has been tested in exploratory studies with *N*-prenylquinolinium and -pyridinium perchlorates **27**, **30**, and **31**.<sup>36,37</sup> Irradiation of aqueous or methanolic solutions



of **27**, followed by reduction of the intermediate dihydroisoquinoline **28**, leads to formation of the benzindolizidines **29**. The pyridinium perchlorates **30** and **31** undergo analogous photocyclizations to yield the indolizidine ethers **32** and **33** when subjected to the irradiation-hydrogenation sequence. These reactions are closely analogous to those of the simple *N*-allyliminium salts described above. As in the case of the olefin-iminium salt systems, the efficiency of intramolecular electron transfer from olefinic to excited charged heterocyclic moieties in these salts should depend upon the degree of alkyl substitution on the alkene grouping owing to the relationship between charge stabilization and oxidation potential. This effect is seen in comparisons of fluorescence efficiencies ( $\phi_f$ ) of the quinolinium and isoquinolinium perchlorates listed in Table III. The decreases in  $\phi_f$  accompanying changes in the *N*-substituent in the sequence  $\text{CH}_3$ ,  $\text{CH}_2\text{CH}=\text{CH}_2$ , and

(35) For selected examples see: Van Bergen, T. J.; Kellog, R. M. *J. Am. Chem. Soc.* **1972**, *94*, 8451. Mader, F.; Zanker, V. *Chem. Ber.*, **1964**, *97*, 2418. Stermitz, F. R.; Wei, C. C.; O'Donnel, C. M. *J. Am. Chem. Soc.* **1970**, *92*, 2745. Stermitz, F. R.; Seiker, R. P.; Nicodem, D. E. *J. Org. Chem.* **1968**, *33*, 1136. Stermitz, F. R.; Roa, R.; Vyas, Ho J. *Chem. Soc., Chem. Commun.* **1967**, 326. Furihata, T.; Sagimori, A. *Ibid.* **1975**, 241. Happ, J. H.; McCall, M. T.; Whitten, D. G. *J. Am. Chem. Soc.* **1971**, *93*, 5496. Kawanisi, M.; Nozaki, H. *Tetrahedron* **1969**, *25*, 1125. Kano, K.; Matsuo, T. *Tetrahedron Lett.* **1975**, 1384. Kano, K.; Shibata, T.; Kajiyara, M.; Matsuo, T. *Ibid.* **1975**, 3693. Maturra, T.; Itahara, T.; Otsuki, T.; Sarto, I. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2698.

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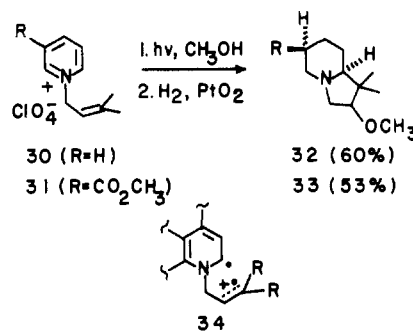
(37) Yoon, U. C.; Quillen, S. L.; Mariano, P. S.; Swanson, R.; Stavinoha, J. L.; Bay, E. *J. Am. Chem. Soc.* **1983**, *105*, 1204.

Table III  
Fluorescence Quantum Yields for *N*-Substituted  
Quinolinium and Isoquinolinium Perchlorates

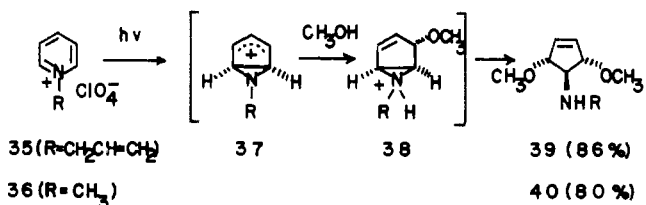
<i>N</i> -heteroaromatic perchlorate	R	fluorescence emission max. nm	$\phi_f^a$
	$\text{CH}_3$	402	0.85
	$\text{CH}_2\text{-CH}=\text{CH}_2$	418	0.26
	$\text{CH}_2\text{-CH}=\text{C}(\text{CH}_3)_2$	415	0.02
	$\text{CH}_3$	380	0.94
	$\text{CH}_2\text{-CH}=\text{CH}_2$	373	0.33
	$\text{CH}_2\text{-CH}=\text{C}(\text{CH}_3)_2$	380	0.01

<sup>a</sup> Conditions:  $\text{CH}_3\text{CN}$ , 25 °C, nondegassed.

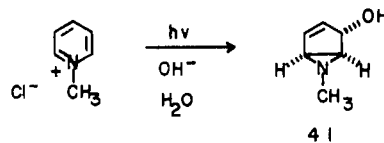
$\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)_2$  can be attributed to reversible intramolecular electron-transfer quenching of the heteroaromatic singlet excited states proceeding by way of the intermediate cation diradicals **34**. A chemical



consequence of side-chain alkyl substitution controlling electron-transfer rates is manifested in the photochemistry of *N*-allylpyridinium perchlorate (**35**). Irradiation

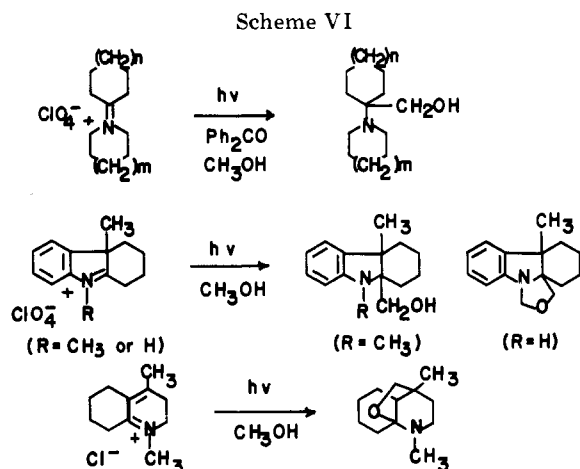
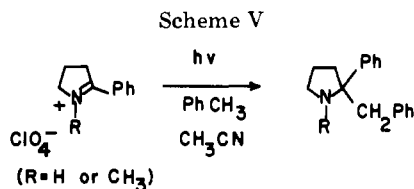


of **35** in methanol leads to formation of the amino-cyclopentane **39** in a remarkably high chemical yield (86%) and by a mechanism similar to that proposed by Wilzbach<sup>38</sup> to rationalize the photochemical transformation of *N*-methylpyridinium chloride under strongly basic conditions to the bicyclo amine alcohol **41**. Thus,



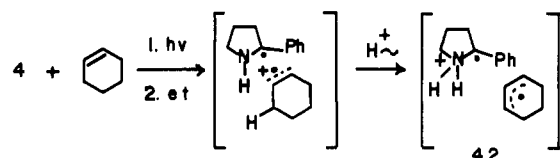
when intramolecular electron transfer is inefficient, alternate excited-state reaction modes can be competitive. In this case electrocyclicization in the pyridinium cation ring of **35** occurs to produce **37**, which then leads to the observed cyclopentene by sequential methanolysis steps. As expected, the *N*-methyl perchlorate salt **36** is also transformed to the cyclopentenylamine **40** (80%) when irradiated in methanol.

(38) Kaplan, L.; Pavlick, J. W.; Wilzbach, K. E. *J. Am. Chem. Soc.* **1972**, *94*, 3283.

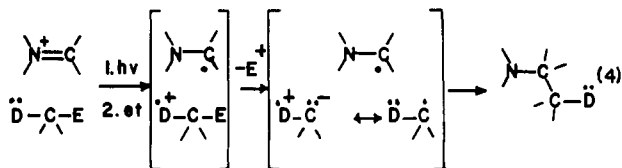


### Sequential Electron-Proton Transfer and Related Reactions

Observations made in the study of the cyclohexene-pyrrolinium perchlorate **4** photoaddition reactions indicate that another reaction pathway might be available



to cation radicals generated by excited state SET. Specifically, formation of the cyclohexenylpyrrolidines **12** most probably occurs via the radical pair **42** generated by a sequential electron-proton transfer sequence. Analogous mechanisms must be operating in the inter- and intramolecular photobenzylations exemplified by the reactions included in Scheme V.<sup>39</sup> More generally, reactions of this type fit into a broader group of electron-transfer-initiated processes, activated by loss of electrofugal groups from sites  $\beta$  to the cation radical centers (eq 4). Indeed, a variety of photoreactions of



this type have been uncovered in studies of amine-olefin additions,<sup>40</sup>  $\beta$ -aryl ether cleavages,<sup>41</sup> and  $\alpha$ -amino

(39) Quillen, S. L.; Lan, A.; Heuckeroth, R.; Klingler, L.; Mariano, P. S., unpublished results.

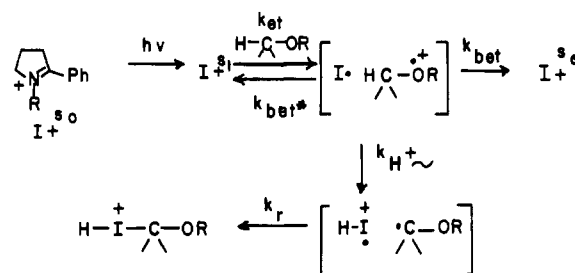
(40) Cohen, S. G.; Parola, A. H.; Parsons, G. H., *Chem. Rev.* **1973**, *73*, 141. Inbar, S.; Linschitz, H.; Cohen, S. *J. Am. Chem. Soc.* **1981**, *103*, 1048.

(41) Arnold, D. R.; Maroulis, A. *J. Am. Chem. Soc.* **1976**, *98*, 5931.

Table IV  
Fluorescence Quenching Data for Alcohol- and Ether-Pyrrolinium Salt Systems

pyrrolinium perchlorate	quencher	$E_{1/2}(+)$ , V	$k_q \times 10^{-8}$ , M <sup>-1</sup> s <sup>-1</sup>	$k_q^{OH}/k_q^{OD}$	$k_q^{CH}/k_q^{CD}$
4	CH <sub>3</sub> OH	3.8	0.65	1.36	1.50
	CH <sub>3</sub> CH <sub>2</sub> OH	3.5	2.0	1.41	
	(CH <sub>3</sub> ) <sub>2</sub> CHOH	3.2	7.3	1.25	1.12
	(CH <sub>3</sub> )COH	2.5	0.19	1.54	
	<i>p</i> -dioxane	2.0	37.0		
	(CH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> O	2.5	12.0		
43	THF	1.9	41.0		1.20
	45		51.0		
	CH <sub>3</sub> OH	3.8	0.54		1.19
	45		31.0		1.04

Scheme VII



Scheme VIII

Iminium Salt	R <sub>1</sub>	R <sub>2</sub>	Donor	Photoadduct
4	H	Ph	THF	42%
43	CH <sub>3</sub>	Ph	THF	66%
4	H	Ph	CH <sub>3</sub> OH	15%
43	CH <sub>3</sub>	Ph	CH <sub>3</sub> OH	43%
44	H	CH=C(CH <sub>3</sub> ) <sub>2</sub>	CH <sub>3</sub> OH	43%

acid<sup>42</sup> and 2-arylacetic acid<sup>43</sup> decarboxylations.

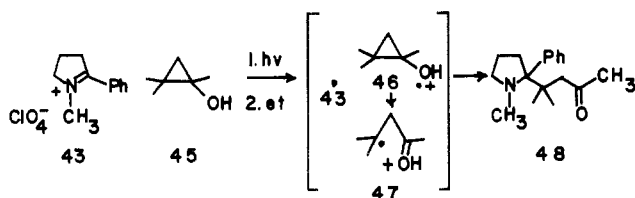
Alcohol and ether photoadditions to iminium salts comprise another family of reactions activated by sequential electron-proton transfer. Our efforts in this area were preceded by several studies that had uncovered a number of interesting examples of methanol photoadditions to simple iminium salts, included in Scheme 6.<sup>44</sup> More detailed photophysical and photochemical studies with the pyrrolinium perchlorates **4** and **43** have provided a mechanistic framework to more fully understand these processes.<sup>45</sup> The OD and CD

(42) Davidson, R. S.; Steiner, P. R. *J. Chem. Soc., Perkin Trans. 2* **1972**, 1357. Davidson, R. S.; Orton, S. P. *J. Chem. Soc., Chem. Commun.* **1974**, 209.

(43) Davidson, R. S.; Steiner, P. R. *J. Chem. Soc. C* **1975**, 1682. Brimage, D. R. G.; Davidson, R. S.; Steiner, P. R. *J. Chem. Soc., Perkin Trans. 2* **1973**, 526. Brimage, D. R. G.; Davidson, R. S. *Ibid.* **1973**, 496.

(44) (a) Goth, H.; Cerrutti, P.; Schmid, H., *Helv. Chim. Acta* **1967**, *50*, 1759. Cerrutti, P.; Schmid, H. *Ibid.* **1964**, *47*, 203; **1962**, *45*, 1992. (b) Bault, R.; Meyers, A. I. *J. Chem. Soc., Chem. Commun.* **1971**, 778. (c) Whitten, D. G. "The Photochemistry of Heterocyclic Compounds"; O'Buchardt, Ed.; Wiley: New York, **1976**; p 524.

deuterium isotope effects on the rate constants for 4 and 43 fluorescence quenching by alcohols and ethers along with the correlations of  $k_q$  with estimated oxidation potentials of the quenchers (Table IV) are indicative of pathways for iminium salt singlet-state deactivation involving electron transfer. The mechanism for fluorescence quenching shown in Scheme VII accounts for these data. Furthermore, inclusion of proton transfer as one of the steps in the fluorescence quenching pathway is justified by the expectation that electron transfer in these systems would be endoergic (i.e.,  $k_{bet^*} > k_{et}$ ) or only slightly exoergic and by the observation that *tert*-butyl alcohol, which lacks  $\alpha$ -hydrogens, serves as a poor quencher. The photoaddition reactions involving the perchlorate salts 4, 43, and 44 summarized in Scheme VIII are consistent with these mechanistic postulates. Furthermore, studies with the tertiary alcohol 1,2,2-trimethylcyclopropan-1-ol (45) provides additional useful information about the nature of the fluorescence quenching and reaction processes. The comparative rate constants for pyrrolinium salt fluorescence quenching by 45 and *tert*-butyl alcohol (Table IV) suggest that the cyclopropane ring is involved in some way in the excited-state deactivation pathways. We proposed<sup>45</sup> that the facility of C-C bond cleavage in the radical cation 46 would introduce a new



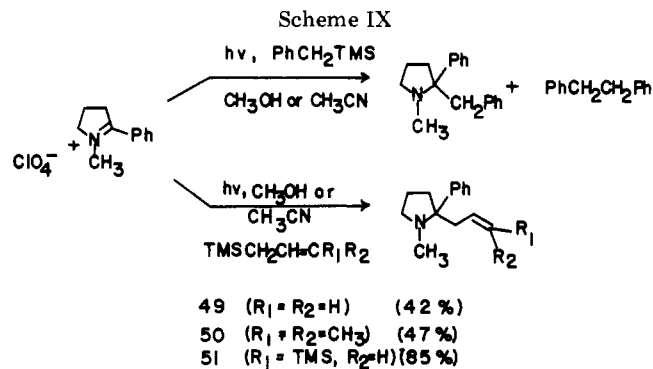
reaction mode (46  $\rightarrow$  47) that would compete with back electron transfer, producing the pyrrolidinylium salt singlet excited state. An alternative view, based upon observations made in studies of the electron-transfer photochemistry of strained-ring compounds,<sup>46</sup> is that conjugation of the hydroxyl and cyclopropane groups in 45 leads to a lower oxidation potential and, thus, enhanced electron-donating properties. Consistent with either rationale is the observation that 45 undergoes photoaddition to 43 to produce the pyrrolidinylium ketone 48. Thus, ring cleavage of the intermediate cation radical 46 is yet another example of a general mode for activating electron-transfer reactions.

### Allylsilane Photoadditions to Iminium Salts

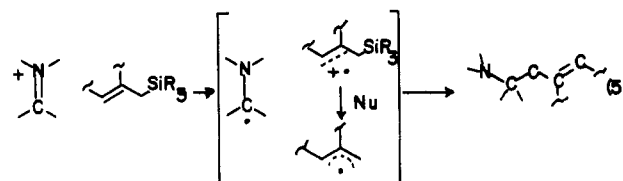
The results of our studies with olefin-, arene-, alcohol-, and ether-iminium salt systems suggested that cation radicals, generated by electron transfer from  $n$ - or  $\pi$ -type electron donors, undergo elimination of protons  $\beta$  to the charged site to form radical precursors of addition and cyclization products. These transformations serve to exemplify the general electron-electrofugal group transfer route outlined in eq 4. The reasoning embodied in this scheme has been used in designing additional systems to test mechanistic postulates and to probe the synthetic potential of this class

(45) Stavinoha, J. L.; Bay, E.; Leone, A.; Mariano, P. S. *Tetrahedron Lett.* 1980, 3455. Mariano, P. S.; Stavinoha, J. L.; Bay, E. *Tetrahedron* 1981, 37, 3385.

(46) Roth, H. D.; Manion-Schilling, M.; Jones, G. *J. Am. Chem. Soc.* 1981, 103, 1246. Albini, A.; Arnold, D. R. *Can. J. Chem.* 1978, 56, 2985. Gassman, P. G.; Olson, K. D.; Walter, L.; Yamaguchi, R. *J. Am. Chem. Soc.* 1981, 103, 4977.

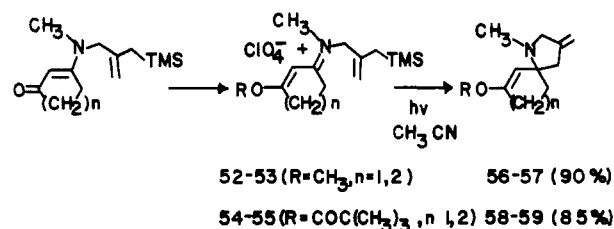


of excited-state reactions. For example, it was expected that cation radicals generated from allyl- or benzylsilanes would undergo rapid desilylation in the presence of even weak nucleophiles owing to favorable  $\sigma$  (C-Si bond)- $\pi$  interactions and the weak and polarized C-Si bond.<sup>47</sup> This SET-desilylation sequence would constitute an efficient method for generation of allylic or benzylic radicals capable of serving as precursors to addition products, as summarized in eq 5. Indeed, the



efficient photoaddition reactions observed to occur between the pyrrolinium perchlorate 43 and benzyltrimethylsilane<sup>39</sup> and the allylsilanes 49-51<sup>48</sup> (Scheme IX) demonstrate the validity of this suggestion. Evidence to support the conclusion that mechanisms for these reactions involve nucleophile-induced desilylation prior to carbon-carbon bond formation is found in the regiochemical selectivities for additions of the allylsilanes 50 and 51. In both of these the direction of addition appears to be controlled by steric factors that guide C-C bond formation in the ultimate radical pair to the less substituted, allylic radical carbons. Alternative pathways in which attack of the allylsilane occurs on the high energy singlet excited iminium cation or where cation radical pair coupling precedes desilylation would produce the unobserved, regioisomeric adducts.

The synthetic potential of allylsilane-iminium salt photochemistry has recently been tested in studies directed at the development of novel spirocyclization methodologies.<sup>49</sup> Accordingly, the iminium salts 52-55,



prepared by O-alkylation or O-acylation of the corresponding  $\beta$ -enamino ketones, were found to undergo

(47) Taylor, T. G.; Berwin, H. J.; Jerkunica, J.; Hall, M. L. *Pure Appl. Chem.* 1972, 30, 599. Brown, R. S.; Eaton, D. F.; Hosomi, A.; Taylor, T. G.; Wright, J. M. *J. Organomet. Chem.*, 1974, 66, 249. Pitt, C. G. *Ibid.* 1973, 61, 49.

(48) Ohga, K.; Mariano, P. S. *J. Am. Chem. Soc.* 1982, 104, 617.

(49) Tiner-Harding, T.; Ullrich, J. W.; Chiu, F. T.; Chen, S. F.; Mariano, P. S. *J. Org. Chem.* 1982, 47, 3360.

efficient cyclization upon irradiation in acetonitrile to produce the spirocyclic enol ethers or esters 56-59. The ease of formation of the salts coupled with the exceptional chemical efficiencies and structural outcomes of these cyclizations indicates that this methodology will have synthetic utility. The results also demonstrate the importance of trialkylsilyl substituents in electron-transfer photochemical studies both as mechanistic probes and as groups to control reaction efficiency and regiochemistry.

### Conclusions

In this Account the features of excited-state reactions proceeding by SET pathways have been outlined in a general way and then specifically by using examples taken from recent studies with iminium and related N-heteroaromatic salts. We have seen how simple methods can be employed in determining when electron transfer is possible in the excited-state manifold and

in predicting the types of reaction pathways that are available by considering the chemical nature of initially generated, charged radicals or diradicals. Moreover, in the cases of iminium salts, electron-transfer-induced photochemical processes appear to represent reasonably versatile carbon-carbon bond-forming methods that can be applied to the synthesis of heterocyclic ring systems. Continuing studies in this general area will no doubt uncover other new excited-state reactions, new mechanisms for old reactions, and new ways of constructing important molecular structures.

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## Is There a Bridge between *ab Initio* and Semiempirical Theories of Valence?

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Molecular electronic structure provides an understanding of physical properties of molecules, their reactivities, and the reaction pathways of complicated chemical reactions. Electronic structure theories have developed along the two strongly contrasting *ab initio* and semiempirical avenues. The former attempt to solve the molecular electronic Schrödinger equation to chemical accuracy. The semiempiricist despairs at the complexity of such calculations and employs experimental data to avoid evaluating the molecular integrals. Practioners of the *ab initio* and semiempirical theories often appear to react to each other as if they were members of warring tribes. This deep division between the *ab initio* and semiempirical approaches is perhaps best understood by a brief review of the history of the development of these methods.

Bonding theories were developed before the advent of large-scale digital computers. Electronic structure theories were first designed to obtain qualitative understanding of general classes of phenomena, and this led to the introduction of simple models.<sup>1-5</sup> A prototype of these early model theories is the Hückel theory for conjugated  $\pi$ -electron hydrocarbons with one  $p_\pi$

orbital per carbon atom. The total electronic energy  $E$  is written as a sum of occupied orbital energies  $\epsilon_i$ . The  $\epsilon_i$  are the eigenvalues of the Hückel-Schrödinger equation,  $H_\pi\phi_i = \epsilon_i\phi_i$ , where  $H_\pi$  is the undefined one-electron Hamiltonian operator. The molecular orbitals  $\phi_i$  are approximated by using a linear combination of the  $p_\pi$  orbitals.  $H_\pi$  is not explicitly represented as an operator. Rather, its nonzero matrix elements between the  $p_\pi$  orbitals are the diagonal one-center Coulomb integral  $\alpha = \langle\phi_i|H_\pi|\phi_i\rangle$  and the nearest-neighbor off-diagonal resonance integral  $\beta = \langle\phi_i|H_\pi|\phi_{i\pm 1}\rangle$ . The unavailability of accurate *ab initio* calculations of  $\alpha$  and  $\beta$  required that these two parameters be fit to experimental data for a typical molecular system. The theory then provides predictions on a wide class of similar chemical compounds.

Hückel theory is widely successful in explaining the extra stability, some spectral data, and dipole moments of a variety of conjugated hydrocarbons.<sup>1-5</sup> The simple model, however, has several problems. First, different values of  $\beta$  are required to calculate different properties such as heats of formation, spectral energies, and ionization potentials. Second, Hückel theory does not explain the spectra of aromatic hydrocarbons such

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(2) Murrell, J. N. "The Theory of the Electronic Spectra of Organic Molecules"; Wiley: New York, 1963.

(3) Dewar, M. J. S. "The Molecular Orbital Theory of Organic Chemistry"; McGraw-Hill: New York, 1969.

(4) Murrell, J. N.; Harget, A. J. "Semi-empirical Self-Consistent-Field Molecular-Orbital Theory of Molecules"; Wiley: New York, 1972.

(5) Jug, K. *Theor. Chim. Acta* 1969, 14, 91. Mingos, D. M. P. *Adv. Organomet. Chem.* 1977, 15, 1.