The Photoexcited States of Organic Anions

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I. Introduction

The study of the chemistry of organic ions as reactive intermediates has been greatly facilitated by the advent of several solvent systems in which cations or anions possess reasonable stability. Recent interest in stable ions has its roots in the pioneering work of Olah[1] in developing the use of superacids in solvents of very low nucleophilicity for generating carbocations. This, in turn, has its anionic counterpart in the development and use, within many research groups, of strong bases and of polar, aprotic, highly basic solvents suitable for the study of carbanions. Subsequent work has established the structures of a wide variety of such charged species, and physical-organic studies of the reactions and the thermodynamic properties of these ions have become possible.

Many excellent reviews which discuss the ground-state properties and the reactions of both organic cations[2] and anions[3] are available. The characterization of the photoexcited states of these organic ions is much less completely developed, however. Although an early review on the photochemistry of carbonium ions has appeared,[4] no systematic overview of the chemistry of organic anionic excited states has been made. The purpose of this review, then, is to provide a perspective on the diverse body of experiments which contribute to an understanding of anion photochemistry. The work to be described will cover a broad spectrum of chemistry and should excite chemists whose research interests lie in synthetic or mechanistic organic chemistry, in theoretical chemistry, or in photophysics.

Carbanion ground-state properties and reactions have often been shown to be significantly influenced by interactions with solvent and/or counterions, and the importance of such effects in photoexcited states should surely be expected. Thus, the ideal study of the photoreactions of free carbanions is difficult to achieve, and, as a class, studies of organic anions are often conducted as ion pairs. The cations with which carbanions generally have the weakest interactions are the alkali metal ions. Sodium, potassium, and the heavier elements of group 1 form highly polarized bonds with organic anions and the reactivity of their organic salts should approximate those of the free anions. The extent to which they ionize in solution, however, is highly dependent on the solvent and the extent of delocalization in the anion.

From solubility and stability considerations, organolithium compounds and Grignard reagents are particularly convenient polar models for carbanion reactivity, although the extensive solvation and/or aggregation in this group of compounds must be recognized. The use of organoalkali metals as carbanion models can be justified by the similarity of position of an intense infrared band (at ca. 1535 cm^{-1}) for allyllithium, -sodium, and -potassium both as Nujol mulls[5] or as solutions in ether, THF, or other solvents.[6–7] The same band in allylmagnesium reagents appears at 1565–1580 cm^{-1}, much nearer to the normal $C{=}C$ stretching region, and is consistent with greater covalent bonding with magnesium than with the alkali metals.[8] Since, in addition, resonance-stabilized alkyllithiums often behave chemically and spectroscopically as if they were carbanions,[3,9] for the purpose of this review they will be considered as being in the same class.

Although Grignard reagents are less troubled by solution aggregation than are alkyllithiums,[10] alkylmagnesium halides are more extensively covalently bound and presumably in equilibrium with dialkylmagnesiums. Since extensive ionization to carbanions does not occur easily in Grignard reagents, only a few examples of magnesium salts will be considered.

Extensive work on the photolysis of other families of compounds in which organic ligands are bound to metals is available, but much of this transition-metal organometallic photochemistry is associated not with absorptive transitions in the organic portion of the molecule but rather at the metal. These many interesting reactions, often involving metal-to-ligand charge transfer, have been recently reviewed[11] and will not be considered further here.

Our attention will focus on those highly polarized organometallic compounds whose reactivity fits two characteristics: (1) the primary light absorption involves transitions within states associated with the organic portion of the molecule and (2) ground-state thermal reactions parallel those which might be expected of the corresponding free anion.

The interest of the review, then, will be focussed on organoalkali metal compounds with occasional comparisons to other organometallics. The major areas of coverage will describe, first, the spectral properties of such anions (and the structural conclusions which can be derived therefrom) and, second, the

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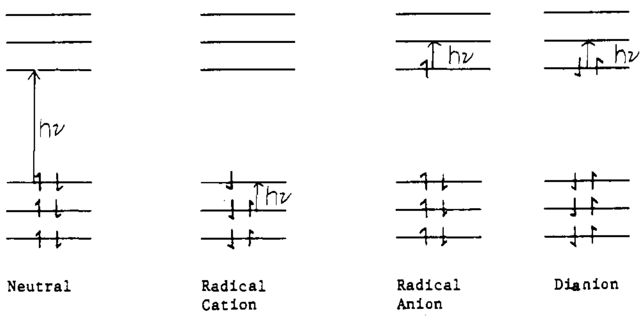


Figure 1. Electronic transitions in alternant hydrocarbons and their ions.

TABLE I. A Comparison of Absorption Spectra of Some Radical Cations, Anions, and Dianions

neutral precursor	λ_{max}, nm radical cation	radical anion	dianion	ref
perylene	543	555	559	13
anthracene	~385	~435		17
tetracene	~280, 355, 390, 690, 770	~270, 345, 385, 740, 800		17, 58

photochemical reactions of these compounds (ranging from simple electron transfer through geometrical isomerizations to the more complex photochemical pericyclic reactions and stepwise bond-forming reactions).

II. Spectroscopy of Alkali Metal Salts of Organic Anions

A. Absorption Spectra

Any discussion of the photoreactivity of organic ions should begin with the primary absorptive event. Since the formation of charged species from neutral precursors is almost always accompanied by a shift in the absorption maximum to significantly longer wavelengths, the photoreactions and spectroscopy of carbanions will often involve excitations which occur in the visible or long-wavelength ultraviolet spectral regions. The ability to employ lower energy photons as activating reagents should, in principle, allow ion photochemistry to proceed with fewer competing pathways and, in many cases, to give simpler product distributions than the complex mixtures sometimes encountered in photolyses with highly energetic photons from excitations in the near-UV region. Thus, one practical reason for examining the spectroscopy and photochemistry of such ions lies in the potential for using visible light to initiate chemical reactions.

1. Radical Anions

a. Transition Energies

The most easily understood rationale for the bathochromic spectral shifts in radical anions is derived from simple Hückel theory[12] and is best illustrated in the absorption spectra of hydrocarbon radical anions and dianions. The electronic spectra in these radical ions can be attributed to π,π^* excitations, with singly excited configurations resulting from the promotion of an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The symetrical pairing relationship[13] between the bonding and antibonding orbitals about the energy of a localized 2p orbital in alternant hydrocarbons requires that the HOMO-LUMO gap in radical anions and/or dianions be nearly equivalent to that in the radical cation of the same carbon skeleton (Figure 1) and indeed radical cations, anions, and dianions often have reasonably similar electronic spectra (Table I).

TABLE II. Typical Absorption Maxima for Several Types of Radical Anions

neutral precursor	λ_{max}, nm	solvent	associated cation	ref
benzene	675	DME	K	24
biphenyl	400, 625	THF	Na	25
naphthalene	370, 430, 460	THF	Li	26
naphthalene	260, 321, 361	dioxane	K	27
naphthalene (dianion)	230, 435	dioxane	K	27
1-methylnaphthalene	255, 325	dioxane	K	27
anthracene	360	dioxane	K	27
anthracene (dianion)	360, 444, 553, 613	dioxane	K	27
pyrene	263, 303, 323, 385, 495, 735	THF	Na	25
tetraphenylethylene	370, 490, 660	THF	Na	28
benzophenone	654	THF	Li	29
p-benzoquinone	408, 430	aq ethylene glycol	K	31
benzophenone anil	500	dioxane	Ba	32
azobenzene	315, 420, 605	THF	Li	33

Theory[14] predicts that significant configuration interaction between the two lowest energy transitions in the radical ions should generally result in a strong and a weak absorption band if the molecular framework is constrained to planarity. Accordingly, excellent agreement between calculated and observed spectra has been obtained not only for a variety of alternant aromatic anions but also for anions derived from polyacenes and olefins.[14-21] Dianions of aromatic hydrocarbons usually exhibit analogous slightly blue-shifted long-wavelength transitions with somewhat greater extinction coefficients. The complete occupancy of the neutral LUMO in the dianion confers spectral simplicity on such structures and should nearly double the dipole strength of the transition. Dianions may exist either as ground-state singlets[22] or as triplets,[23] the latter being most commonly found in molecules with higher order symmetry. The observed spectral properties of some typical, arbitrarily chosen members of this family are compiled as examples in Table II. As the table clearly shows, nearly all such radical anions absorb in the visible, exhibiting an absorption maximum whose position varies with solvent, cation, and charge type.

A more complete discussion of the spectroscopy of these ions has been given by de Boer,[17] by Rao et al.,[18] and by Kaiser and Kevan.[34] These sources tabulate most absorption spectral data available for anion radicals prepared before 1970. Appendix Table A.I, which lists the spectral properties of more recently generated anions, should thus be considered a supplement for the earlier tables. The following section will, as well, summarize the general conclusions of such spectroscopic studies of radical anions and will warn the uninitiated of potential complications in the interpretation of absorption spectra of these anions.

b. Cation and Solvent Effects in Aromatic Radical Anion-Alkali Metal Pairs

The usual technique for formation of aromatic anions is direct reduction, either chemically with alkali or alkaline earth metals or electrochemically. The position of this equilibria in ethereal solvents has been extensively studied by Shatenshtein and coworkers[35] and is dependent on temperature, cation, and, especially, steric effects in the solvent or hydrocarbon precursor.

$$ArH + M \rightleftharpoons [ArH]^- \cdot + M^+$$

Radical anions have also been generated by electron transfer from carbanions to the aromatic hydrocarbon[36-40] and by pulse radiolysis.[41] The formation of charge-transfer complexes and/or exiplexes by organic photochemical routes[42,43] has provided both alternatives access to many radical anions and an elegant demonstration of Mulliken's theory of excited-state interactions.[44]

With the usual reductive techniques, the resulting mono- or dianions are then intimately associated with a metal counterion. This ion-pairing (and/or the solution-phase association phenomena which accompany it) has been observed to cause profound spectral changes. Absorption spectroscopy has, for that reason, proved to be one of the most useful characterizations for the degree of ion-pairing in solution-phase anions.

In 1954, Winstein et al.[45] and Sadek and Fuoss[46] independently presented chemical evidence for the existence of distinct closed-shell ion pairs, respectively, in the solvolysis of arylsulfonates and in conductivity measurements of tetrabutylammonium bromide solutions.

$$\mathrm{RX} \rightleftharpoons \mathrm{R^+X^-} \rightleftharpoons \mathrm{R^+}\|\mathrm{X^-} \rightleftharpoons \mathrm{R^+} + \mathrm{X^-} \qquad (1)$$

In the following year, Morantz and Warhurst recognized analogous phenomena in radical ions in their studies of the reactions of organic halides with organosodium compounds.[47] The conceptual validity of this idea has been widely established in the intervening years in studies of many closed- and open-shell anions and has been effectively used to explain the observed structure–reactivity correlations, as well as the intricate stereochemical detail, often encountered in carbocation and carbanion reactivity. The thermal reactivity of paired organic anions has been the subject of excellent and extensive reviews[3e,48-52] and will not be discussed further. These studies have shown an important dependence of the absorption spectra not only on the identity of the associated cation but also on temperature.

The existence of a temperature effect can be attributed either to equilibria within ion-pair types analogous to those discussed above (eq 2) or to disproportionation equilibria (eq 3). Both types

$$\mathrm{R^{-}\cdot\, M^+} \rightleftharpoons \mathrm{R^{-}\cdot}\,\|\,\mathrm{M^+} \rightleftharpoons \mathrm{R^{-}\cdot} + \mathrm{M^+} \qquad (2)$$

$$2\mathrm{R^{-}\cdot} \rightleftharpoons \mathrm{R^{2-}} + \mathrm{R} \qquad (3)$$

of equilibria can be easily affected by solvation and cation effects, dianions being more strongly associated with counterions than monoanions. Carter et al.[29] were the first to consider quantitatively the shift of the absorption maxima with the size of the associated alkali metal. They observed that the absorption maximum of the several radical anions moved progressively to longer wavelengths as the interionic separation (i.e., cation size) increased. The effect of the cations suggested that contact ion-pairing was the dominant interaction. For example, the absorption maximum of naphthalene radical anion moves progressively from 775 to 806 nm as the counterion is changed from $\mathrm{Li^+}$ to $\mathrm{K^+}$,[53] and the absorption maxima for alkali metal salts of fluorenone ketyl range from 448 to 465 nm in the same series.[29] Adherence to Beer's law was observed and was taken as evidence for the existence of monomeric ion pairs.

In contrast to the red shift of $\lambda_{\max}$ with the radius of the alkali metal cation, solvent perturbations (red shifts with increased solvent polarity) were greatest for the smallest ions.[29] Analogous observations in bi-, tri-, and quaterphenyl and in polycyclic aromatic radical anions led Hoijtink and co-workers to conclude that stronger ionic attractions are felt in the ground than in the excited state. This tendency is greatest in contact ion pairs, which are favored in the above equilibria by increasing cation radius, decreasing solvent dielectric, and increasing temperature.[54] The seeming generality of such conclusions is evident, since McClelland has observed analogous shifts in alkali ketyls,[55] an inference which has been justified also by molecular orbital calculations.

TABLE III. Typical Shifts in Absorption Maxima in Free and Associated Ion Pairs[58]

anion	free ($\lambda_{\max}$, nm)	associated ($\lambda_{\max}$, nm)
terphenyl$^{-}\cdot$	481, 441	461, 424 ($\mathrm{Na^+}$)
biphenyl$^{-}\cdot$	636, 405	613, 400 ($\mathrm{Na^+}$)
tetracene$^{-}\cdot$	806, 402, 357, 284	793, 398, 356, 283, ($\mathrm{K^+}$)
		793, 398, 356, 283 ($\mathrm{Na^+}$)
tetracene^{2-}	671, 402	621, 356 ($\mathrm{2K^+}$)
		606, 352 ($\mathrm{2Na^+}$)
		585, 340 ($\mathrm{2Li^+}$)

In McClelland's model, an alkali ion is treated chiefly as positive charge at its nucleus, and the change in the interaction energy of these positive and negative ions at various geometries is calculated. Using perturbation theory in this way, one can construct a three-dimensional surface for ground and excited states. If the Franck–Condon principle applies for anionic excitations, such surfaces can directly give the transition energy for a given excited ion pair. The argument thus neglects any energy level mixing, concentrating instead on the two molecular orbitals involved in a given transition.

Ion-pairing should also be responsive to solvation and temperature since the absolute free enthalpy of solvation should increase with increasing dielectric of the medium as well as with decreasing interionic radius. Contact (or tight) ion pairs are formed in less polar solvents whereas solvent-separated pairs predominate in more polar solvents. For example, one can divert contact- to solvent-separated pairs by the addition of glymes to THP solutions of radical anions.[56] Since the solvent dielectric decreases with increasing temperature, these considerations alone would predict significant dependence of ion-pairing association on metal ion radius and solvent dielectric. Such observations have been made by the Hoijtink group, for example, in their studies of the effect ion-association on the electronic spectra of biphenyl, *p*-terphenyl, and *p,p'*-quaterphenyl in THF or in 2-methyltetrahydrofuran[54] (2-MeTHF).

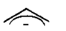
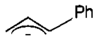
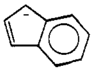
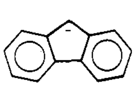
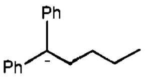
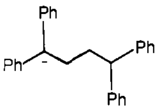
These solvation effects are thermodynamic in origin. For example, the enthalpy of association of $\mathrm{Na^+}$ with naphthalenide ions varies by about 5 kcal/mol in the solvent series: THF, 2-MeTHF, tetrahydropyran (THP).[57] Typical values for such entropy effects range from -10 to -2 kcal/mol. Similarly, the sodium salts of a variety of aromatic radical anions have been shown to exist as contact pairs in dimethoxyethane, with a much greater fraction existing as solvent-separated pairs in tetrahydrofuran.[56] Thermodynamic parameters for solvation in this solvent series have been determined; these suggest the importance of entropy effects since the dissociation of contact ion pairs is accompanied by large negative values of ΔS (-52 eu for biphenyl radical anion in THF), whereas more modest negative entropies are observed (<-20 eu) for solvent-separated pairs.

Solvation effects are sometimes dramatically different if one solvent molecule intervenes between charged centers and if more than one layer of solvent molecules separates the ion. In fact, absorption spectra of free ions often closely mimic those of ion pairs limited by electrostatic interaction through several solvent molecules.[58] In general, contact ion pairs exhibit absorption maxima at shorter wavelengths than do solvent-separated pairs. The magnitude of difference in wavelength maxima of these pairs is highly variable, ranging from modest (2–3 nm) to substantial (>60 nm) separations. Some typical maxima shifts for these equilibria are presented in Table III.

c. Disproportionation of Aromatic Radical Anions

Complicating these ion-pairing equilibria in radical anions are disproportionation equilibria.[60-66] In addition to the reactions shown in eq 3, disproportionation with ion pairs is often important

TABLE IV. Some Representative Carbanion Absorption Maxima

carbanion	cation	solvent	λ_{max}, nm	ref
	Li	THF	315	79
	Li	THF	395	79
	Li	THF	~530, 565	79
	—	(gas phase)	363	73
	Li	THF	503	80
$PhCH_2^-$	Na	THF	350	81
Ph_3C^-	Cs	c-$C_6H_{11}NH_2$	488	82
	Li	DME	344	83
	Li	THF	349, 373	84
	Li	DME	373	84
	Na	DME	358, 373	84
	K	DME	362	84
	Ba	THF	347	85
	Li	THF	496	86
	Li	THF	485	86

(eq 4 and 5), as has been shown independently by Roberts and

$$2R^{-}\cdot, Na^{+} \rightleftharpoons R + R^{2-}, 2Na^{+} \qquad (4)$$

$$R^{-}\cdot, Na^{+}, R^{-}\cdot \rightleftharpoons R + R^{2-}, Na^{+} \qquad (5)$$

Szwarc[60] and by Garst and Zabolotny[28] in the tetraphenylethylene dianion. Thus, the red spectra shifts observed by Hoijtink and Zandstra on warming naphthalene radical anion from −120 to 0 °C correspond to a displacement of this equilibrium from the radical anion toward the dianion.[19]

These disproportionation equilibria are dramatically influenced by solvation and cation effects, the equilibrium constant varying by as much as a factor of 10^6 upon changing from small alkali metal cations to bulky tetralkylammonium ions.[61,62] Typically, the importance of disproportionation decreases as the solvent is changed from dioxane to tetrahydrofuran to diglyme to dimethoxyethane.[28] With free ions formed in highly polar aprotic solvents like hexamethylphosphoramide, the driving force for disproportionation is lost since disproportionation 3 is expected to be less exothermic than either disproportionation 4 or 5. Radical anions then dominate such equilibria.

d. Substituted Aromatics and Other Radical Anions

Although only limited studies of substituent effects on absorption spectra of radical anions have been made, the conclusions of several such studies merit attention. Deuteration has been reported to produce little effect on these absorption spectra.[63] Methyl substitution causes red shifts in the anion radical or benzene and some of its derivatives.[64-66]

The radical anions of naphthalene and phenanthrene show absorption spectra which are responsive to substituents.[67] Available spectral data on other recently prepared heterocyclic analogs of the aromatic radical anions have been included in Appendix Table A.I.

The extensive spectroscopic work on many nonhydrocarbon anion radicals is beyond the scope of this review and the interested reader is referred to one of the previously cited sources[17,18,34] for more complete discussions. The same general conclusions made earlier for hydrocarbon anions regarding shifts in the absorption spectra with changes in associated cation or solvent are also applicable within these compounds, although the relative stabilities (e.g., the tendency for dimerization) differ substantially. Ketyls, in particular, are also known to form solution-phase ion aggregates easily (triple ions, ion quadrupoles, etc.).[68]

e. Radical-Anion Geometry from Absorption Spectra

An important capability of the absorption spectra is the identification of geometrical differences within various ion pairs. In particular, molecular symmetry is easily detectable. For example, the appearance of a band in the absorption spectrum of dilithiotetraphenylethylene in THF which was absent in HMPA (and disappeared on the addition of tetraglyme) suggested that asymmetry exists in the tightly associated ion pairs, i.e., that one lithium cation is fully solvated and the other effectively unsolvated and associated with the anion.[69,70] Absorption spectroscopy was also used to provide evidence for the geometry of the stilbene dianion as a twisted benzylidene, whose structure was also implied by its chemical reactivity.[71]

Thus, relative positions of absorption maxima in radical anions provide valuable information on the ion-pairing and geometry of these species as well as an independent tool for measuring disproportionation equilibria and relative reactivity.

2. *Carbanions (Closed-Shell Anions)*

a. Transition Energies

Analogous effects can also be observed in the absorption spectra of closed-shell anions. The most pronounced peaks in the optical spectra of carbanions can be attributed to π,π^* transitions. A dramatic shift is observed in the absorption maxima of organic anions to lower energies than required for excitation of their protonated precursors. For example, in heptatriene the π,π^* transition occurs at 272 nm,[72] whereas in the heptatrienyl anion, the analogous transition appears at 430 nm.[73] This effect can be attributed primarily to the increased nuclear shielding found in carbanions compared with their neutral precursors. The decreased field felt at each electron in the HOMO results in weaker attachment of such electrons and a more diffuse spatial arrangement of the electron density,[74,75] a distribution analogous to the delocalization effects (red shifts) observed in neutral polyenes upon increasing the conjugation length.

Several theoretical considerations of transition energies in carbanions have been undertaken. Hückel theory,[76] which predicts that the absorption maxima for polyene anions should lie near those of the neutral hydrocarbons with isoelectronic π systems, does not effectively account for the dramatic red shifts observed upon deprotonation. Much better agreement with experiment is obtained with a many-electron Pariser–Parr–Pople (PPP) calculation[73,77] if one reasonably allows lower absolute values for β (the resonance integral) and for γ (the electron repulsion integral). The free electron molecular orbital (FEMO) model of Kuhn,[78] in which the π electrons are confined to a well whose width corresponds to the length of the conjugated system, predicts red shifts in π,π^* transitions in anions but does not quantitatively model the observed maxima.[73]

Some representative absorption maxima for several types of resonance-stabilized carbanions are listed in Table IV in order to illustrate typical spectroscopic behavior. More extensive lists of carbanion absorption spectra are available,[3] and some more recently published carbanion spectra are tabulated in Appendix Table A.II. It should be noted that many of these optical transitions are quite broad and extend far into the visible absorption region.

b. Ion-Pairing and Association Phenomena

Studies concerned with the spectroscopic detection of ion pairs in carbanions are very numerous, and several excellent reviews are available which present details of the effect of ion-pairing on the spectroscopic properties and on the chemical reactivity of carbanions.[51,52,87] This review will therefore simply summarize the most pertinent generalizations from these studies, and the interested reader is encouraged to seek the cited works for more comprehensive coverage of the topic.

As with paired salts of radical ions, absorption peaks of carbanion–alkali metal pairs move to longer wavelength as the radius of the cation increases (see Table IV).[87] Presumably this effect can be attributed to Franck–Condon factors, i.e., to the tighter electrostatic interaction between anion and cation in the ground state than in the excited state. Hence, increasing the interionic separation by associating larger cations will destabilize the ground state more than the excited state and will produce the observed bathochromic shifts.

Solvent (and complexing additive) effects similar to those observed in radical anions might reasonably be expected in these ion pairs as well. Although the absorption spectra of free ions are sometimes nearly insensitive to solvent changes, pronounced effects have often been observed in ion pairs; increasing the polarity of the solvent or lowering the solution temperature often causes significant bathochromic shifts in the absorption maxima of these species. These effects originate either in dispersion of charge in ion pairs (external solvation) or in separation of the charged particles to solvent-separated or free ions. The latter possibility is also easily accomplished upon addition of additives capable of strong chelation with cations. Glymes,[88] crown ethers,[89] cryptates,[90] diamines,[91] and small quantities of compounds commonly used as dipolar aprotic solvents[87,92] (e.g., Me_2SO, HMPA, etc.) have been effectively used to separate ion pairs. Attributing a given solvent's ability to separate ion pairs (or to provide external solvation) to a single parameter has proved difficult,[48] and many steric and electronic factors play an important role in this complex problem.

The former effect, external solvation, greatly affects the state of aggregation and the reactivity of these salts: more significant spectral and reaction differences are observed with solvent changes within a family of contact ion pairs[93] than in a family of separated ions. The effectiveness of a given solvent in separating ion pairs is related to solvent basicity. For example, the importance of solvent-separated ion pairs in ethereal solvents decreases (with basicity[94]) in the order: oxetane > THF > THP > ethylene oxide. Steric effects in the solvent are undoubtedly comparably important, 2-MeTHF being, for example, about 15 times less effective at separating contact ion pairs than THF.[87]

The ease of forming solvent-separated ion pairs should also depend on the identity of the carbanion and reaction conditions. Increased charge delocalization in a more extensive conjugated system should lead to a larger fraction of solvent-separated pairs, and, for example, such separated pairs predominate in benzofluorenylsodium much more than in fluorenylsodium.[95] Cooling of contact-ion-pair solutions is often effective in transforming these species to solvent-separated pairs. This effect can be so dramatic that over a very narrow temperature range reversal of ion-pairing type can occur: for example, 9-hexylfluorenyllithium exists predominantly as a contact ion pair at −20 °C and virtually completely as a separated pair at −40 °C.[84] Similarly, several studies on the effect of pressure on the equilibrium between contact and separated ion pairs of fluorenyllithium in THF have shown that loose pairs predominate with increased pressure.[96,97] Temperature effects are mainly enthalpic, whereas pressure effects can be attributed to electrostriction effects, the volume contraction being caused by tighter binding of solvent to the cation in a solvent-separated pair.

Carbanions are less troubled by disproportionation and aggregation phenomena than are radical anions. They can participate in equilibria, however, in which contact and separated ion pairs exchange, particularly in the presence of cation complexing additives, e.g.,[89]

$$\mathrm{F, E, K^+ + F^-Na^+ \rightleftharpoons F^-, K^+ + F^-, E, Na^+} \qquad (6)$$

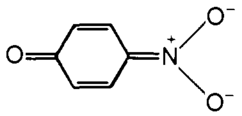
where F = fluorenyl and E = dibenzo-18-crown-6 ether, and several examples have been discovered in which more than one anion is associated with a cation (often divalent; e.g., eq 7). Association of ion pairs to dimers and higher aggregates is also known,[48,100] and the possibility of exciton transfer within such aggregates has been suggested.[98]

$$\mathrm{(F^-)_2Ba^{2+} \rightleftharpoons F^-Ba^{2+} + F^-} \qquad (7)$$

3. *Oxyanions*

Since the importance of hydrogen bonding has been shown to differ within carbanion ion-pair equilibria,[101] the detection of ion pairs, with the expected cation and solvent effects, should be anticipated in oxyanions. Dependence on pH of the ultraviolet spectra of compounds with easily exchangeable protons can often be observed; for example, the absorption maximum for 4-hydroxybenzophenone moves from ca. 275 nm in cyclohexane to ca. 300 nm in ethyl alcohol to ca. 360 nm in aqueous alkaline solution.[102] Thus, as before, anion formation is accompanied by a shift to longer wavelengths. In the example cited, the shift can be mainly attributed to a reordering of the normally lowest energy transition (n,π^*) and the close-lying charge-transfer state, a result consistent as well with the lack of normal n,π^* photoreactivity (hydrogen abstraction) observed in the photolysis of the anion.[103]

An extensive study of the effect of solvent and of the associated cation on the long-wavelength absorption maxima of 26 phenolate and enolate anions led Zaugg and Schaefer to conclude that ion-pair equilibria are important in these ions. In dimethoxyethane (DME), nearly all the salts were associated, even at concentrations as low as 10^{-5} M. In such ion pairs, red shifts inversely proportional to the metal radius were observed (as had been discussed above for carbanions). Only in ions with enhanced chelating ability (e.g., the U-form β-dicarbonyl anions, where very tight ion pairs are formed) were the effects of ion association minor.[104] A major factor in the direction of the shifts of the absorption spectra of these ion pairs is the redistribution of charge upon excitation. For example, *p*-nitrophenoxide has a ground-state distribution as in **1**, whereas the excited state is better represented by **2**.[105] This stabilizing chelation effect in U-shaped anions is analogous to that predicted theoretically for the all-carbon pentadienyl analogues.[106]



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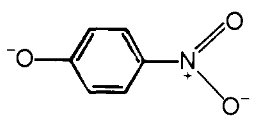

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In general, simple enolates and phenolates absorb strongly (ϵ 10^3–10^4) in the λ 300–400 nm region, probably often via π,π^* transitions.[104,107,108] Carboxylate anions typically display weak long-wavelength shoulders with poorly resolved vibrational structures characteristic of n,π^* transitions along with more intense π,π^* transitions in the same region.[108] Wavelength-dependent photolysis might therefore be expected in carboxylate anions and, for example, hydrogen abstraction by sodium β-methylcinnamate (**3**) occurs upon irradiation of the long-wavelength n,π^* bond, whereas the product from β-lactone formation is favored at shorter wavelengths.[109]

As with carbanions, ion-pair separation can be accomplished by the addition of cation complexing additives. The λ_{max} for the

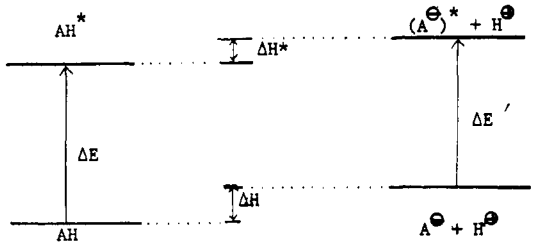
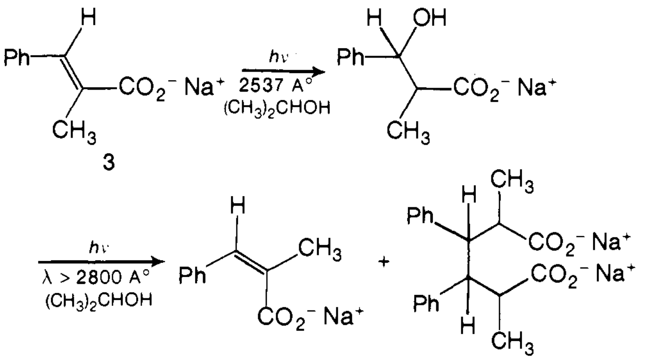


Figure 2. Förster cycle of ground- and excited-state acidities.[122]



sodium salt of 9-fluorenone oximate, for example, moves from 424 to 470 nm upon the addition of dibenzo-18-crown-6 ether.[110] The tendency of alkoxides to aggregate further makes spectral interpretation even more complex.[107] Aggregation in the excited state is also known in oxyanions, for emission from the excimer of pyrenesulfonate anion has been reported.[111]

Similar considerations apply in the interpretation of the absorption spectra of other heteroatomic anions and these will not be considered further here.

B. Emission Spectra

1. Emission from Oxyanion Excited States

The most thoroughly studied fluorescense or phosphorescence in anions is observed in the salts of organic compounds with easily exchangeable protons. Like the absorption spectra discussed above, these emission spectra often give detailed information about the extent of ionic association and, as well, allow measurement of excited-state lifetimes. Strong emission can sometimes be observed from anions: fluorescein and luciferin emit most efficiently in alkaline solution where they exist as dianions.[112] Among others, some familiar strongly fluorescent organic anions which have found very common utility in spectral characterization include eosin, erythrosin, 2-*N*-arylamino-6-naphthalenesulfonates (ANS), phenoxides, and their derivatives.[113] The sensitivity of ANS derivatives to solvent environment[113] has made it a very useful probe for photochemical environment, e.g., in studies in micelles.[114] Anion excited-state lifetimes are sensitive, too, to substitution and heavy-atom effects analogous to those observed in neutral precursors. Halogen substitution of fluorescein results in variations of Φ_f of over a factor of 40 because of enhanced intersystem crossing.[113]

As in the absorption spectra of oxyanions, the emission maxima often depend on pH of the medium. Because of the mirror-image relationship of fluorescence and absorption spectra, the direction of the shifts of emission upon protonation (red) is opposite that normally observed in absorption (blue). For example, the emission of the anion of cinchoninic acid is blue-violet (ca. 390 nm) whereas the most highly protonated form emits as blue-green (ca. 475 nm).[115]

Phosphorescence studies of organic compounds are usually conducted in rigid glasses to minimize collisional quenching and to maximize triplet lifetime. It has been shown, though, that room-temperature phosphorescence can be observed in many *ionic* materials if the salts are adsorbed on a filter paper or alumina matrix.[116] Such studies serve to emphasize the importance of a stabilizing environment on excited-state lifetimes and, hence, on the ability of an excited ion to do chemistry.

2. Quenching by Inorganic Anions

The quenching of fluorescence and/or phosphorescence of ions or neutral organic molecules by inorganic ions is often very efficient. Electron-transfer mechanisms (eq 8) have been suggested as being primarily responsible, for example, as in the

$$^1M^* + A^- \rightarrow M^- + A \qquad (8)$$

quenching of the triplet state of 9,10-anthraquinone-2,6-disulfonate[117] or of acetone fluorescence.[118] Although the quenching rate constants parallels the ease of oxidation of the anionic quencher, quenching sometimes proceeds by enhanced internal conversion or intersystem crossing, induced by MO coupling within the collision complex (**4**).[119] The geometric requirement

$$[^1M^* \cdots A^-]$$

4

for efficient quenching is presumably as important in anion quenching as it has been demonstrated to be in cation quenching.[120]

3. The Förster Cycle

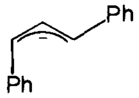
In theory, anionic excited states can be produced by the excitation of protonated precursors (if prototropic equilibria are rapid) since the acidity (or basicity) of excited states can dramatically differ from that of the ground state. Nearly 30 years ago, Förster showed that excited-state acidity can differ from ground-state acidity by factors as large as 10^{5-16}.[121] An estimate of excited-state p*K* is usually made by the Weller method[122] based on the Förster cycle (Figure 2). The difference between ground- and excited-state acid dissociation enthalpy is thus related to the difference in energy levels as measured by absorption or (to ensure 0,0 transitions) emission spectra. In a variety of studies of excited-state acidities of phenols and carboxylic acids, some generalizations have emerged: (1) phenols are stronger acids in the excited state than in the ground states whereas the reverse is true for carboxylic acids and (2) triplet excited states mimic ground-state acidity more closely than singlet states.[123] A successful chemical application of this Förster effect has been claimed in the acid-catalyzed photonitration of β-naphthol,[124] but this interpretation has been criticized.[125]

4. Emission from Carbanion Excited States

Studies which report emission from hydrocarbon anions are much more rare, and most examples of carbanion emission have been uncovered within the last decade. Emission is generally more easily observed in closed-shell anions than in open-shell ions (radical anions), although examples do exist of fairly strong emission from radical anions in the visible[126] and infrared regions.[127] Presumably this inefficiency in emission from radical-anion excited states is caused by fast nonradiative processes such as internal conversion within the doublet or quartet manifold or by competitive electron-transfer quenching of excited states by radical-anion ground states, a process which has extensive precedent.[16,128]

A striking observation in a variety of fluorescence studies is the dependence of fluorescence efficiency on ion-pairing types. For example, the cyclooctatetraene monoanion fluoresces strongly as a Cs^+, Rb^+, or K^+ salt (probably existing as $2M^+$ $COT^{-}\cdot$), but the analogous Na^+ and Li^+ salts completely fail to emit.[126] A closed-shell analogue can be found in the fluorescence of ethereal solutions of the lithium salts of 1,3-diphenyl-1-butene.[129a] Here the contact ion pair which exists at room temperature fails to emit but the solvent-separated pair formed at low temperatures fluoresces strongly. Geometry of the carbanion is also apparently important since the alkali metal salts of (*E,E*)-1,3-diphenylpropane (**5**) are intensely fluorescent in THF, while the corresponding *E,Z* isomer (**6**) is at best weakly fluorescent, despite the fact that both exist as loose ion pairs at low temperature.[129b] Several possible factors responsible for such behavior have been suggested:[126] (1) decreased rigidity or nonplanarity in some ion-pair forms, (2) the dependence of the relative positions of excited states of different multiplicity on ion-pairing and/or geometry, and (3) the energy ordering of charge-transfer states in ion-paired excited-state manifolds.

5



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The transition energies of fluorescence spectra also depend on ion-pairing and charge type. The fluorescence spectrum of cyclooctatetraene dianion in 2-MeTHF is broad and structureless with a maximum near 530 nm, whereas the emission from $2K^+COT^{-}\cdot$ exhibits vibrational detail with its most intense absorption maximum at about 420 nm.[126] The alkali metal salts of fluorenyl anion fluoresce at 528 nm as free ions and at 534–545 nm as contact ion pairs.[130] Analogous shifts can be observed in azafluorenyl anions and their derivatives and in the carbanions of xanthene and thioxanthene.[129] Shifts of the emission maximum are often dependent on the cation radius and solvent (ion-pairing). Effectively increasing the cationic radius causes a blue shift in the emission spectrum and, as noted before, a red shift in the absorption spectrum. Presumably, the previous arguments cited (greater perturbation of the ground than the excited state by an associated cation because of Franck–Condon destabilization) are responsible. A reasonable scenario for the association of a cation is depicted in Figure 3,[130] where ΔE_0 and ΔE_1 represent the 0,0 absorption transitions for the free ion and ion pair, respectively, and ΔE_0 and ΔE_2 represent the corresponding emissive transitions. The stabilization of the excited-state ion pair before emission (ΔE^* for contact ion pairs) follows from the observation that excited-state lifetimes, typically $>10^{-8}$ s, are significantly longer than typical cation or solvent relaxation times ($\sim 10^{-10}$ s).[12] This explanation is also consistent with the observations that emission blue shifts are observed upon addition of crown ethers as cation complexes[131] and that strong red shifts attributed to exciton coupling usually accompany further ion-pair aggregation.[98,130]

The type of anion–cation binding may also vary in the ground and excited states. It has recently been shown, for example, that whereas Na^+ and K^+ are probably coordinated with the lone pair on nitrogen in the indolyl anion as a ground-state σ complex, in the S_1 state both σ and π complexes occur.[131] This conclusion was based on the observation of temperature dependence of the indolyl fluorescence spectrum and the prediction that σ complexes should fluoresce at higher energy than the solvent-separated pair and that π complexes should fluoresce at even a lower energy. The efficiency of fluorescence from either σ or π complexes depends on the inaccessibility of other deactivation routes. The anion of 9,10-dihydroanthracene[132] and the dianion of cyclooctatetraene[126,133] display fluorescent spectra which are dependent on the excitation wavelength. In both cases, fluorescence quantum yields decrease at shorter wavelength since competing photochemistry occurs with more highly energetic excitation; respectively, photooxidation and photoinduced electron ejection become important. These are more thoroughly discussed in subsequent sections.

III. Photochemical Reactions of Alkali-Metal Salts of Organic Anions

It has been demonstrated that the photoreactions of a variety of cations differ significantly from the excited-state reactions observed in the structurally analogous neutral compounds.[74,134] Unique photochemistry might similarly be expected in anions and the following section reviews general reaction types which have been observed.

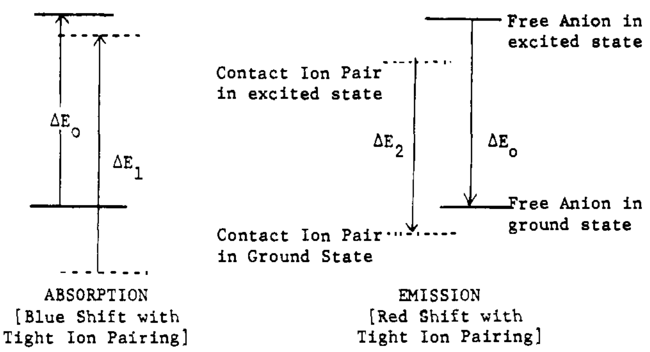


Figure 3. Cation effects on absorption and emission spectra of carbanion–alkyl metal pairs.[128]

A. Electron Ejection

1. Gas-Phase Experiments

The observation of longer wavelength transitions in the absorption spectra of organic anions suggests that photoinduced electron loss and/or exchange should be much easier in these anions than in their neutral precursors. In the absence of solvent stabilization, anion excited states often rapidly eject electrons upon photolysis, and gas-phase studies of this autodetachment process

$$A^- \xrightarrow{h\nu} A + e^- \tag{9}$$

are best conducted by spectroscopic techniques. Temporary anions, those which have ground states lying above that of the neutral molecule, as well as longer lived, often resonance-stabilized anions have been recently studied and brief reviews of the theoretical work,[135] and experimental results obtained by electron transmission spectroscopy[135b] and by electron photodetachment spectroscopy[136] are available. These techniques have proven useful for estimating both the energies and lifetimes of gas-phase anions. Only a brief treatment of the experimental techniques will be given here.

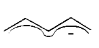
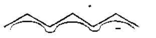
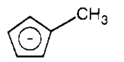
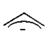
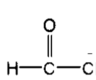
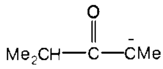
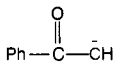
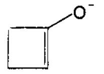
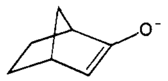
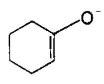
a. Electron Transmission Spectroscopy[135]

If an electron beam of measured energy is allowed to impinge into a gas-filled scattering chamber, scattering of the electron beam occurs. If the geometry of the chamber, the density of the gas, and the intensity of the initial electron beam are known, the unscattered current allows measurement of the cross section for electron scattering. Rapid variations in this cross section which are characteristic of anion formation allow for the characterization of even fairly ephemeral anions. Vibrational structure can be observed in sufficiently long-lived ions. Capture of incident electrons in other than the LUMO allows production of anion excited states. The vertical electron affinities obtained in studies of the negative ions of olefins, aryl hydrocarbons, aryl halides, amines, and heteroatomic aromatics usually range from about −1 to −5 eV. Only a few examples are known in which positive electron affinities are observed.

b. Electron Photodetachment Spectroscopy[136]

Gas-phase ionization potentials of organic anions have been measured for several complex anions by measuring changes in signal intensity during irradiation of the anions contained in the cavity of an ion cyclotron resonance (ICR) spectrometer.

TABLE V. Photoejection Thresholds for Some Organic Anions[a,b]

anion	λ_{max}, nm	ref
	[1362][a] (0.91)	73
	976	73
	674	138
	742	138
$PhCH_2^-$	[1404][a] (0.88)	139
PhO^-	526	140
PhS^-	501	140
F_3C^-	439	141
F_3Si^-	421	141
	519	142
	[2254][a] (0.55)	143
$N{\equiv}C{-}CH_2^-$	823	143
 $H-\overset{\overset{O}{\|}}{C}-\bar{C}H_2$	710	144
 $Me_2CH-\overset{\overset{O}{\|}}{C}-\bar{C}Me_2$	870	144
 $Ph-\overset{\overset{O}{\|}}{C}-\bar{C}H_2$	625	144
	698	145
	795	145
	822	145
CH_3O^-	780	146
Me_3CO^-	663	146
CH_2^-	[5803][a] (0.21)	147

[a] For λ_{max} longer than 1000 nm, threshold is also reported in eV (value in parentheses). [b] All measurements in gas phase.

Typically, the anions are formed by standard electron capture techniques and are trapped in the magnetic field of an ICR analyzer cell for about 100 ms. The ions are detected by monitoring the radio-frequency power absorbed from a tuned oscillator with and without monochromatic (pulsed and continuous) irradiation.[137] If the force constants of the ion and neutral obtained by electron loss are similar, the long-wavelength threshold of photoejection gives the adiabatic electron affinity of the neutral compound. This technique, analogous to laser photoelectron spectroscopy,[147] has been used to determine the ionization potentials of a wide variety of simple mono-, di-, and triatomic inorganic anions and has proved useful as well for the characterization of organic anions. The thresholds for photoionization observed for these organic anions are contained in Table V.

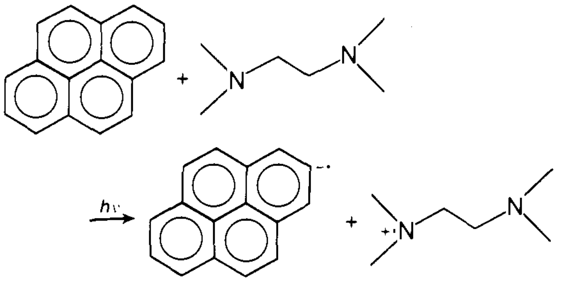
The photodetachment data expressed in the table represents limiting behavior since the transitions represented are usually complex functions of rotational, vibrational, and occasionally electronic transitions. Electronic transitions are particularly apparent in enolate anions[144] and polyene anions.[74] The detailed implications of these measurements on the spatial and symmetry properties of anion MO's and on substituent effects are beyond the scope of this review, but the obvious ease of photoinduced electron loss from anions is clear. The previously cited examples of absorption and emission spectroscopy in anions point out the importance of solvation in determining the fate of anionic excited states. Presumably either the excited ionic state is more stabilized in solution relative to the ground ionic state than is the neutral ground state or an ejected electron is destabilized in solution relative to an electron in free space.

2. Solution-Phase Experiments

a. Carbanions and Radical Anions

Photoejection from excited-state anions is also a well-documented process in condensed phases. For example, when glassy solutions of many aromatic hydrocarbon mono- and dianions are irradiated with ultraviolet light photoejection occurs,[19,148] with the ejected electron being trapped (and observed spectroscopically) in cavities in the rigid solvent. The photoionization potential parallels the electrochemical reduction potential.

Photoionization from neutral hydrocarbons[149] and from more highly functionalized compounds[150] is, of course, also known and may proceed either directly or via triplet–triplet annihilation. The process is remarkably more efficient in anionic than in neutral compounds, a logical consequence of the spectroscopic studies discussed earlier. Such photoejection reactions from neutral molecules have been studied in their own right and as possible primary steps in such related reactions as the formation of exciplexes via excited-state electron exchange[151] (reaction 10) or to explain the activating effects of electron-donating substituents in aromatic photonucleophilic substitutions[152] (reaction 11). Both closed-shell and open-shell anions photoeject electrons. For example, the spectral properties of the ejected electron could be easily observed in photoejection from a variety of radical anions,[124,153] e.g., reaction 12. The 1,1,4,4-tetraphenylbutyl-1,4-dianion efficiently forms the free (or cation-paired) electron upon flash photolysis (reaction 13). No com-



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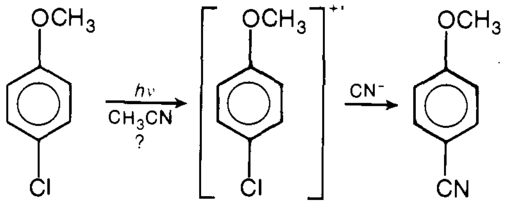

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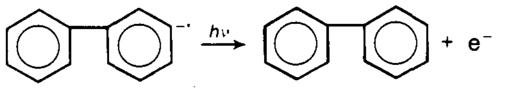

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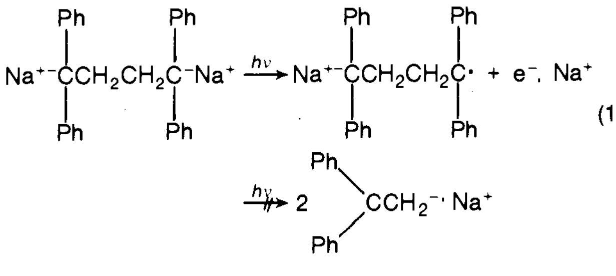


$$Na^{+-}\underset{Ph}{\overset{Ph}{C}}CH_2CH_2\underset{Ph}{\overset{Ph}{C}}{}^-Na^+ \xrightarrow{h\nu} Na^{+-}\underset{Ph}{\overset{Ph}{C}}CH_2CH_2\underset{Ph}{\overset{Ph}{C}}\cdot + e^-, Na^+ \quad (13)$$

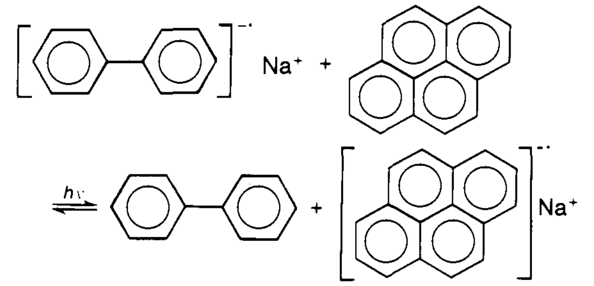
$$\xrightarrow{h\nu} 2\ (Ph)_2CCH_2^{-\cdot}\,Na^+$$

petitive photodissociation was observed. Alkyllithiums are known to behave similarly as photochemical electron sources.[154b]

Both mono-[153] and biphotonic[155] mechanisms have been suggested for photoinduced electron ejection in anions. Since the analogous process often occurs through Rydberg excited states in neutral molecules,[156] the importance of the low-energy transitions to diffuse MO's in the absorption spectra of anions is obvious. Anionic photoionization is thought to proceed via charge-transfer states in which solvent orientation, and hence charge dispersal, is particularly important.[157]

An orientational preference for the ease of photoejection can also be observed in the induction of dichroism caused by photoejection when rigid solutions of aromatic anions are irradiated with plane-polarized light.[19,158] Such studies allow the photoejection process to assist in the characterization of the direction of polarization of electronic transitions in an anisotropic substrate.

The most rigorous studies of the photoejection process in radical anions and dianions have been conducted by Szwarc and co-workers, and an overview of the details of the kinetics of the primary photoprocess and electron recapture is available.[159] Pronounced solvent and counterion effects on the efficiency of the photoejection have been observed, leading sometimes to the reduction by a factor of 10^{10} in the relative rate or equilibrium constants when a cation is constrained to accompany the electron. Some typical anionic secondary reactions which have been characterized by the Szwarc group include: electron capture by aromatic hydrocarbons or radical anions,[153] photoinduced electron transfers[159] (reaction 14), reversible disproportionations (eq 15), and electron transfer-mediated cis-trans isomerizations (eq 16).[159]



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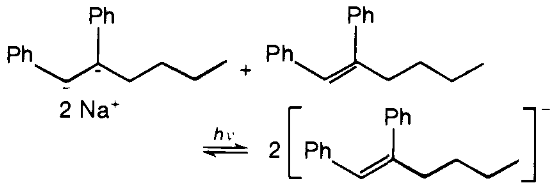

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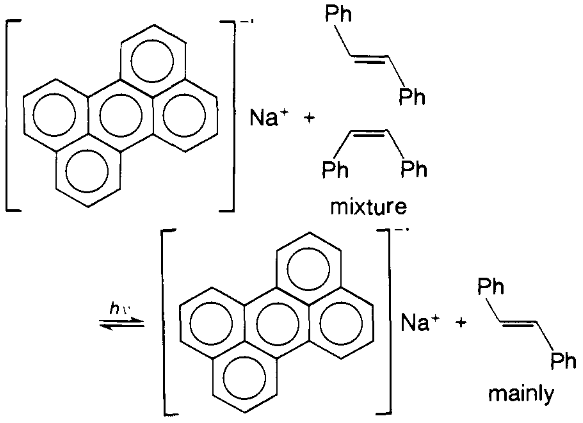
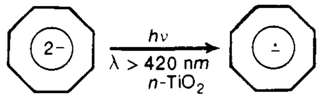


(16)

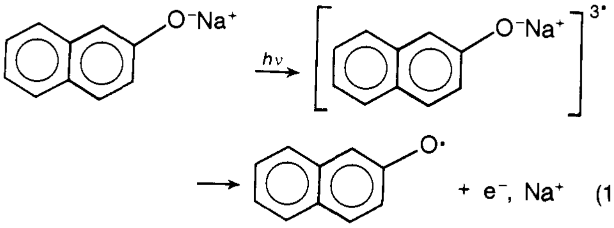
The pairing of an anionic excited-state donor with a reasonable electron acceptor (exciplex-like interactions) allows one to transfer electrons from the excited state even without removing the electron to a free, solvated state to be recaptured, in a second step, by the acceptor. Photocurrents can be observed, for example, when the cyclooctatetraene dianion is excited (with wavelengths longer than 420 nm) at the surface of an appropriate semiconductor[133,160] (acceptor) electrode (eq 17), despite the fact that normal photoejection occurs in solution only at wavelengths shorter than 335 nm.[123]



(17)

b. Oxyanions

Analogous photoejections can be sometimes observed in the alkali metal salts of phenols and carboxylic acids. For example, triplet phenoxides and naphthoxides[162] (reaction 18) emit spectroscopically detectable electrons upon photolysis and, in some cases, give reaction products derived from the oxidized radical. If the phenoxide photolysis is conducted in the presence of borohydride, the phenoxyl radical formed by electron ejection can be captured,[163] initiating a sequence in which reduction ultimately results, as in eq 19.



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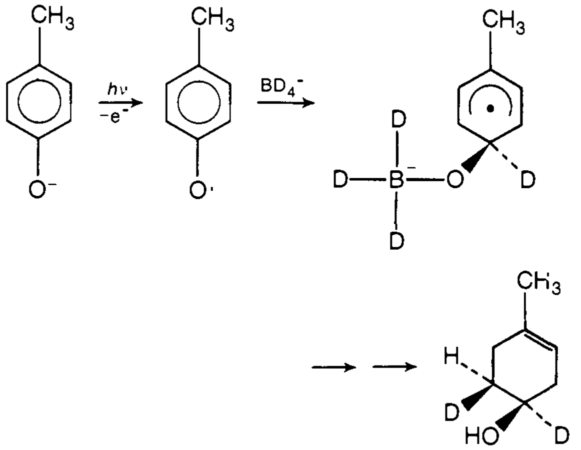


(19)

Photolysis of carboxylate anions may also proceed by initial photoejection. Miller and co-workers have shown, from kinetic consideration, that the photochemical pathway followed by sodium phenylacetate involves primarily the benzyl radical in water (presumably by photoinduced electron loss) whereas benzyl anion is the more important intermediate in alcohol (reaction 20).[164]

$$C_6H_5CH_2CO_2^-Na^+ \xrightarrow[H_2O\ \ -e^-,\ -CO_2]{h\nu} C_6H_5CH_2\cdot \longrightarrow PhCH_2CH_2Ph + PhCH_3 \quad (20)$$

$$\xrightarrow[ROH\ \ -CO_2]{h\nu} C_6H_5CH_2^- \longrightarrow PhCH_3$$

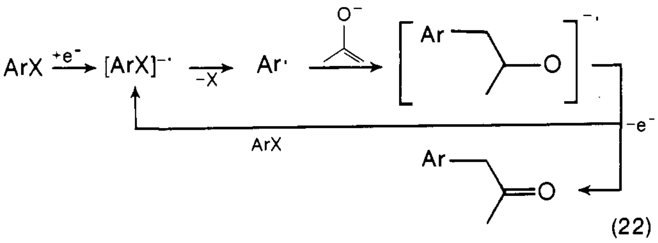
Decarbonylation, which was significant in the acid, was not observable in the salt. Subsequent study has shown that this fragmentation occurs through the anionic mechanism and has suggested that recapture of the ejected electron by the benzyl radical must be faster than hydrogen abstraction from solvent (reaction 21).[165] It is difficult to generalize on whether photoejection will occur efficiently; in fact, as many as 25 competing paths have been suggested in the photolysis of carboxylic acids.[164] There exist examples in which sodium salts are much

$$C_6H_5CH_2CO_2^- \xrightarrow[H_2O]{h\nu} PhCH_2\cdot + CO_2 + e_{aq}^-$$

$$PhCH_2\cdot + e_{aq}^- \xrightarrow{\text{fast}} PhCH_2^- \qquad (21)$$

less photoreactive than the carboxylic acid[166] and others where photoejection occurs only from the anion of a carboxylic acid.[167] Electron ejection from the carboxylate anion by a single photon process from the triplet state of phenylalanine occurs even when the molecule is excited in the aromatic portion so that ejection can occur only after intramolecular energy transfer.[168] Nonetheless, analogous photooxidations have been suggested in the photolysis of disodium oxalate at electrodes,[169] in the photolysis of the salts of sulfonic acids,[170] and in the photolysis of the uracil dianion.[171]

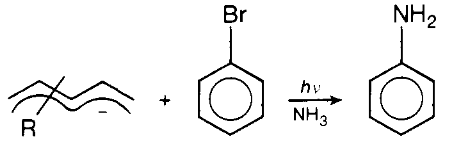
A reaction of significant importance based potentially on photoinduced electron ejection is the photoinitiation of $S_{RN}1$ aromatic substitution by enolate anions. The chemical aspects of this reaction have been widely investigated by Bunnett and co-workers[172] and others.[173] The close similarity of the results of reactions initiated by light and by the addition of potassium metal (as an electron source) suggests that in both cases an electron source initiates a chain process (reaction 22) which ultimately leads to aromatic substitution by the enolate. The photostimulation in such a scheme would be accomplished by photochemical electron transfer from the enolate anion to the substrate either in a charge-transfer complex or by photoejection from the anion and electron recapture by the aryl halide. When photoinitiated, such reactions commonly exhibit quantum yields in considerable excess of unity, e.g., 20–50 in the photostimulated reaction of the diethyl phosphite anion with iodobenzene.[174] Thus, the nonphotochemical propagation steps, as in (22), are established. The nature of the initial electron transfer is unclear: whether the enolate anion, some anionic aldol condensation product of the enolate,[107] or a charge-transfer complex of the anion and aryl halide absorb light remains generally unestablished. In reactions with iodobenzene, the reaction may also be initiated by iodobenzene-absorbed photons.[174]



(22)

Photostimulated reactions have also been observed with arenethiolate ions,[175] ketone enolates,[172] picolyl anions,[176] and the enolate of *tert*-butyl acetate.[174] A visible light-induced reaction of dimsyl anion gives the product expected of an $S_{RN}1$ reaction, but mechanistic studies suggest that this reaction proceeds by a pathway different from reactions identified as photostimulated $S_{RN}1$ reactions.[177]

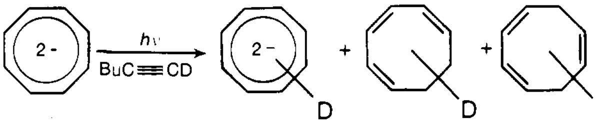
Although simple carbanions can be arylated by the $S_{RN}1$ mechanism if induced by alkali metals,[170] only a single successful photoarylation achieved by this method has been reported.[176] In fact, if substituted pentadienyl anions are irradiated with visible light in the presence of bromobenzene in liquid ammonia, aniline is a major product (reaction 23).[178] Nearly no alkylated product is isolated. The reaction, which does also proceed thermally, is accelerated by photolysis and probably involves benzyne formation. Apparently, either the charge-transfer interactions which are important in $S_{RN}1$ reactions are too weak in carbanionic nucleophiles for efficient initiation or other photochemical pathways are available to the carbanion excited states.



\+ others (23)

B. Altered Excited-State Reactivity

The promotion of an electron to a higher lying level in the excited state of a carbanion could, in principle, lead to either enhanced nucleophilicity/basicity (occupancy of a high-lying molecular orbital) or enhanced electrophilicity/acidity (creation of a vacancy in a lower lying molecular orbital) compared with ground-state properties. The spectroscopic evidence for ΔpK in excited states in fluorescent oxyanions has already been discussed, and enhanced excited-state protonation has been studied by ion cyclotron resonance spectroscopy.[179] The properties of weakly acidic proton donors also change upon irradiation. When the cyclooctatetraenyl dianion is irradiated in THF containing 1-hexyne-*1-d*, deuterium incorporation was observed in both products (1,3,5- and 1,3,6-cyclooctatrienes) and in the reactant (eq 24).[180] Thus, proton exchange occurred in the dianion excited state with the acidic alkyne proton and with the acidic proton of cyclooctatrienes produced by initial protonation. Neither proton source is sufficiently acidic to exchange with the ground-state dianion. Similarly, cyclononatetraenide gives, upon irradiation, a series of photoproducts obtained by protonation of the excited state by acids too weak to protonate it in the dark (reaction 25).[181]



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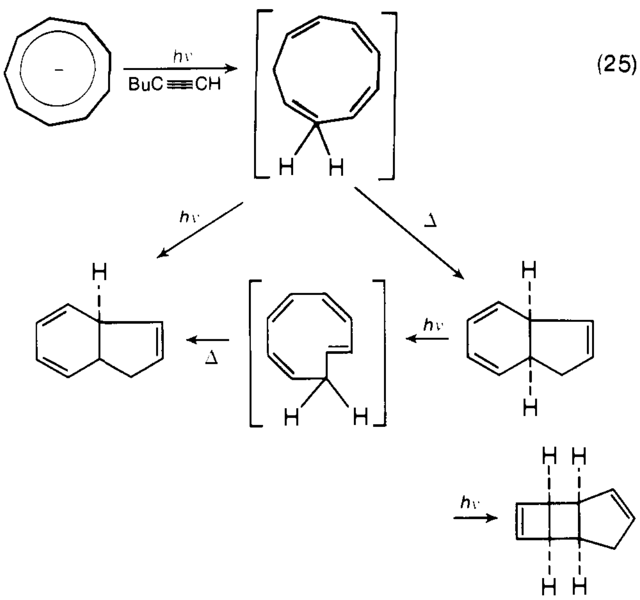
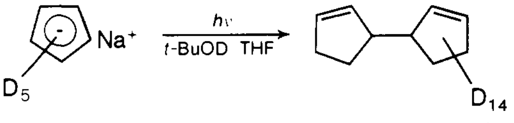


(25)

The incorporation of acidic protons in products need not always imply enhanced basicity in the excited state. In the photolysis of cyclopentadienide,[182] the product incorporates only deuterium in the reduced product when *t*-BuOD is present (reaction 26). Finding only the observed dicyclopentenyls suggests that a reasonable final step for product formation is coupling of cyclopentenyl radicals. These in turn may be formed by re-

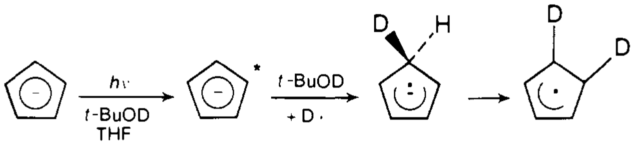


(26)

(meso and *d,l*)

spective hydrogen abstraction and protonation. Presumably abstraction must precede protonation since neither ground- nor excited-state cyclopentadiene could be shown to be implicated in the reaction.

The sole incorporation of deuterium from *t*-BuOD, in which deuterium is at a thermodynamically unlikely abstraction site, was explained as being most sterically accessible, i.e., in an optimal position, for abstraction (reaction 27).[182] Other possible routes to the reduced dimer were not excluded.



→ dimers (27)

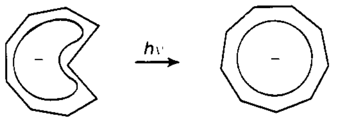
It should be possible to predict the direction of change in basicity upon forming the excited state if the π energy of the ground and excited states of a base and its conjugate acid are known.[183] Using these criteria, for example, cyclooctatetraenyl dianion should display enhanced basicity in the excited state and the benzyl anion should display reduced basicity in the excited states.[95,184] As discussed above, the first prediction has been verified and the second, which is much more difficult to test experimentally, remains untested.

C. Isomerizations

In addition to the changes in electron density (distribution) caused by photoexcitation, the bond orders are also dramatically altered. Thus, as with neutral molecules, photoisomerization should be expected in anions.

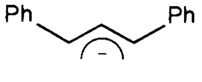
1. Geometric (*Cis–Trans*) Isomerizations

Although the barriers to rotation about the delocalized π systems of resonance-stabilized anions (10–30 kcal/mol)[3i,185] are significantly lower than those found in the neutral precursors with alternating bond orders, the barriers are sufficiently high so that geometrical isomerization occurs extremely slowly at low temperatures. Since, in addition, the cis–trans isomerization of olefins is one of the most efficient of known photochemical reactions,[186] the observations of cis–trans isomerization at low temperature might be anticipated as a similarly efficient anionic photoprocess. Accordingly, Boche and Bieberbach were the first to observe such a reaction, in which the potassium salt of the *cis,cis,cis,trans*-[9]annulene anion in THF at 15 °C (reaction 28)[187] is converted to its all-cis isomer.[187] Although this reaction does occur thermally as well, the activation parameters under these reaction conditions clearly establish that no significant thermal isomerization could have occurred under the irradiation conditions.



(28)

More recently, Parkes and Young have shown that, upon irradiation, changes in the visible spectrum of a dilute THF solution of 1,3-diphenylpropenyllithium could be explained as a photoinduced geometrical isomerization of the more stable trans,trans isomer **5** to the cis,trans isomer **6** (reaction 29).[129b]



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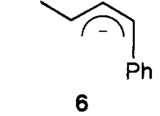

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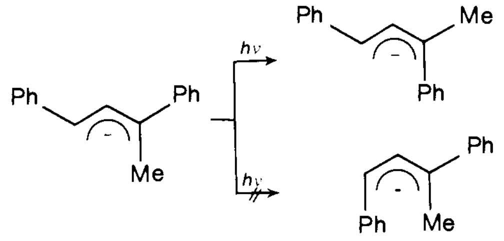


(29)

(30)

7

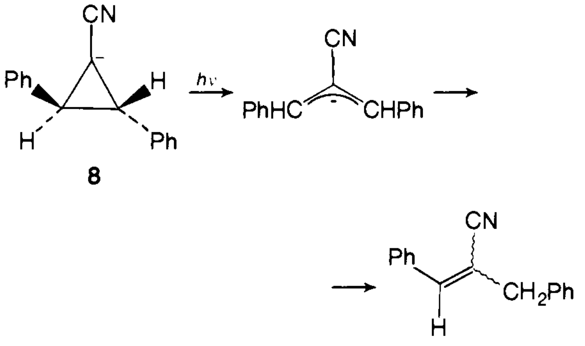
The methylated analogue experienced similar spectral changes, although the extent of conversion was lower. The observed rotation about only one bond of the π system is consistent with the extremely unfavorable steric interactions which would result if **7** were to be formed (reaction 30). No quantitative measurement of the efficiency was made, and the inability to observe the isomerization at NMR concentrations precludes a completely firm assignment of the product structure.

2. *Pericyclic Reactions*

The stereochemical course of electrocyclic reactions of anions, as well as neutral molecules, should be controlled by orbital symmetry, and many examples exist in which thermal concerted ring openings and ring closures of anions proceed by the paths predicted by the application of orbital topology rules.[188] In principle, electrocyclic reactions which occur through excited states should provide an easier approach to establishing concert than is available through thermal reaction paths, since photolysis can be conducted at sufficiently low temperatures that rotation about conjugated allyl systems can effectively be stopped. This, in turn, allows easier determination of the stereochemical mode of the electrocyclic reaction, a necessary criterion for demonstrating orbital topology control. This argument requires, of course, that the photochemical cis–trans isomerizations of the reactant and product be slower than the electrocyclic reaction being examined.

a. Ring Openings

Only a few examples of photochemical ring openings have been reported. A cyclopropyl-allyl anion conversion has been shown to proceed photochemically in Newcomb and Ford's studies of the cyclopropyl keteniminates **8** and the lithium enolate



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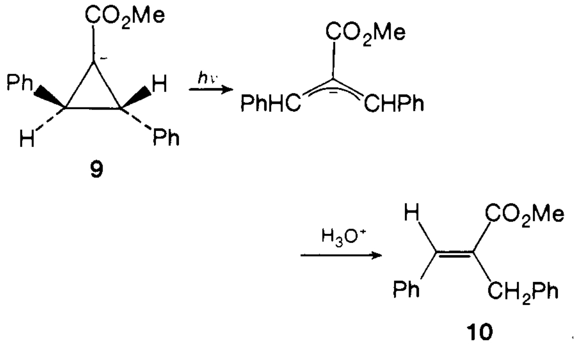
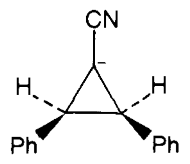


(32)

of methyl *cis,trans*-2,3-diphenylcyclopropane-1-carboxylate (**9**).[189] More complex reaction mixtures were obtained upon photolysis of the analogous *cis*-diaryl anions **11–13**. Theoretical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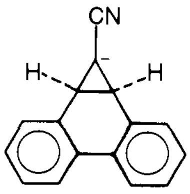
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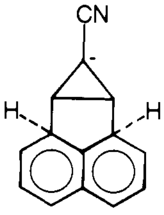
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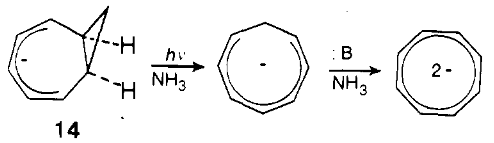
considerations predict thermal conrotatory opening for cyclopropyl anions[188,190] so that the photochemical reaction might be expected to be disrotatory. MINDO/2 calculations have, however, shown that the disrotatory mode which involves a Möbius, antiaromatic transition state proceeds by a different reaction pathway in the forward and reverse directions.[191] Such behavior is suggestive of implied orbital crossings so that concert in such photochemical reactions may be dependent on excited-state multiplicity.

The relative rates for thermal ring opening of **8** and **11** suggest control by orbital symmetry which directs the reaction along a conrotatory path where destablizing phenyl–proton interactions in the transition state from **11** are avoided in **8**. The analogous stereochemical consequences of the photoreactions 31 and 32 were not determined directly, but the isolation of **10** in reaction 32 and its absence from the thermal conversion suggest that the thermal and photochemical reactions proceed, as expected from orbital topology considerations, along separate surfaces.

The analogous conversion in heptatrienyl anions has also been reported. The bicyclo[5.1.0]octadienyl anion, **14**, when irradiated

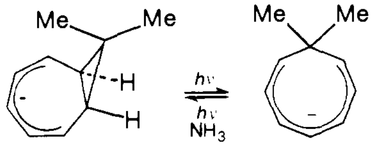


14 (33)

in liquid ammonia (reaction 33) containing excess base, formed the cyclooctatetraenyl dianion, possibly through the intermediacy of the cyclooctatrienyl anion which is rapidly deprotonated to the observed product under the reaction conditions.[192] Support for this mechanism is found in Staley and Pearl's irradiation of a derivative of **14** in which subsequent deprotonation of the ring-opened product is blocked. Thus, upon irradiation, a photoequilibrium between the dimethyl analogues of the above species is established (reaction 34).[193]

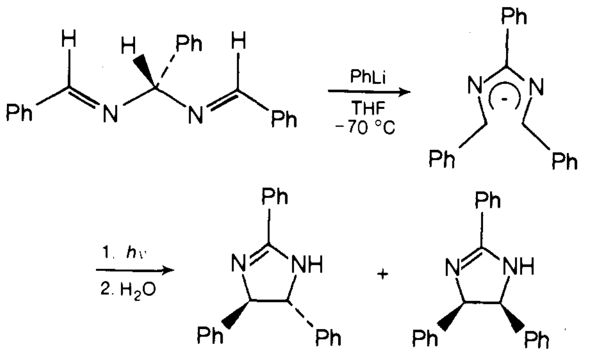
b. Ring Closures

In principle, all electrocyclic reactions should proceed in either direction if a sufficient thermodynamic driving force for product formation exists. Ring openings presumably proceed with relief of strain, but the reversibility of reaction 34 demonstrates that



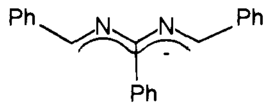
(34)

it should also be possible to form rings photochemically. If the transfer of charge from a less to a more electronegative atom occurs upon cyclization, such electrostatic stabilization of the ring closed form may provide a sufficient driving force for closure. In the photolysis of the anion of hydrobenzamide by visible light the fraction of the trans-cyclized product **15** obtained increased from 1 to 7 to 16% as the photolysis reaction temperature was lowered from −20 to −40 to −70 °C, respectively.[194]



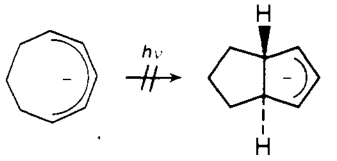
15 (35)

This process, shown in reaction 35, would be the expected result if the cyclization occurred exclusively through a U-shaped anionic intermediate and if the preferred disrotatory mode for thermal cyclization (from orbital symmetry considerations) competes more successfully with the photochemical conrotatory mode as the reaction temperature increased. Subsequent study, however, has shown the chemistry of the anion precursor can be better explained if the anion exists as a nearly planar W geometry **16**.[195] Cyclization could then occur either directly from


16

this geometry or by prior conversion to the S or U shapes before cyclization. Furthermore, the possible involvement of an extra lone pair from nitrogen might further complicate the reaction. The necessity of sorting the contributions of these complex factors makes the product geometry in the photochemical cyclization of the highly colored intermediate very difficult to interpret.

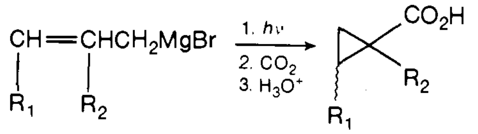
Attempts in our laboratory to induce cyclization of a pentadienyl system, the cyclooctadienyl anion (eq 36), have so far



(36)

been unsuccessful.[196] Presumably, the product incorporates so much strain that, even if the proposed cyclization did occur, thermal ring opening to a *trans*-pentadienyl π system followed by rapid isomerization could provide an efficient route for reversion to the reactant.

Although allyllithium ⇌ cyclopropyllithium photoconversion proceeds toward allyl[189] for substituted systems,[189] the parent Grignard reagents proceed toward the cyclized form.[197] Thus, a family of allyl Grignard reagents could be cyclized (in 45–75% yield as cyclopropylcarboxylic acids): reaction 37. The lack of

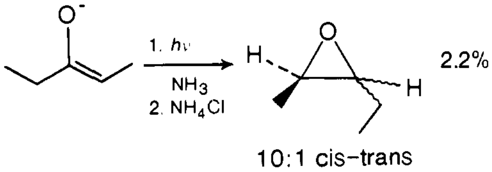


(37)

a. $R_1 = H$; $R_2 = H$
b. $R_1 = D$; $R_2 = D$
c. $R_1 = H$; $R_2 = CH_3$
d. $R_1 = Ph$; $R_2 = H$
e. $R_1 = CH{=}CH_2$; $R_2 = H$

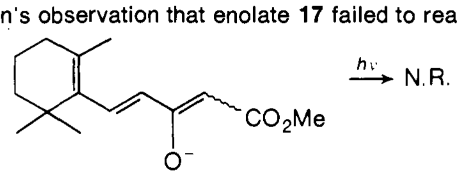
stereospecificity observed was attributed to rapid inversion of the cyclopropyl anion and/or rotation about the allylic system.

Heteroatomic allyl (enolate) anions have also been observed to cyclize inefficiently upon photolysis. When the enolate of 3-pentanone was irradiated in THF, a complex photoreaction ensues in which one cyclized (ca. 2% yield) product is formed (reaction 38).[198] An alternative to concerted cyclization of the enolate to produce the epoxide anion is the possibility, as discussed above, that enhanced basicity may result from photoexcitation. If the carbonyl carbon bears substantial negative charge in the excited state, the excited enolate could be protonated by weak base at that position to yield, with ring closure, the observed epoxide. The reaction could not be sensitized and the predominance of cis product was presumed to be caused by the preferred ground-state conformation of the enolate.



(38)

Recently, the importance of ground-state geometry in directing photochemical cyclizations in oxyanions was affirmed by White and Skeean's observation that enolate **17** failed to react photochemically whereas enolate **18** efficiently cyclized, reactions 39 and 40, respectively.[199] The photochemical cis-trans isomerization of **17** was thus apparently slow. Although the oxygen atom of the enolate is not directly involved in the cyclization, its presence (as an anion) is essential for the observed photoreaction since the protonated precursor reacts by a significantly different photochemical pathway (eq 41). Thus, modification of the charge type for photoreactions of neutral compounds may provide exciting opportunities for the modification of excited-state reactivity. An example of the reverse of this kind of ring closure is found in the photochemical opening of enolate **19** (reaction 42).[200]



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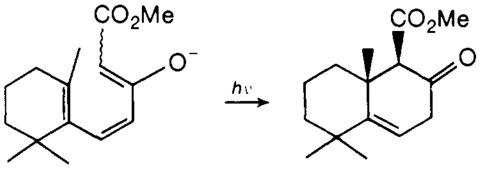

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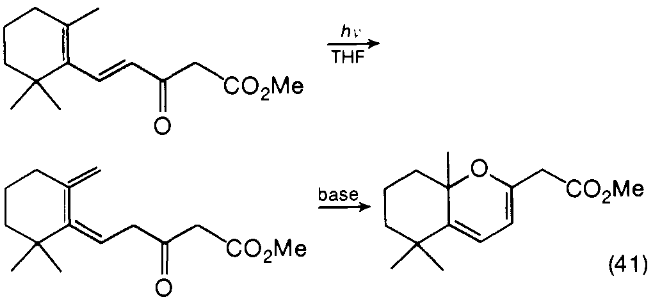

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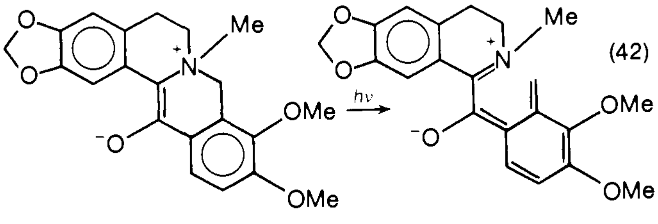

(42)

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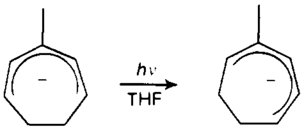
c. Sigmatropic Shifts

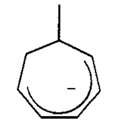
Sigmatropic shifts in neutral compounds occur frequently by photochemical pathways. The recognized photoenolization of aliphatic aldehydes and ketones[201] or the excited-state intramolecular proton transfers in *o*-hydroxybenzoate esters represent common examples. Often the products of such sigmatropic shifts, e.g., enols,[202] display important divergence in photochemical reactivity from that of their precursors.

Anionic, intramolecular, thermal sigmatropic rearrangements are relatively rare, and only a single clear example of a photochemical, anionic shift is available.[203] It is possible, of course, that a number of more complex bond-forming reactions may proceed by such rearrangements without being explicitly recognized. Upon photolysis, the methylcycloheptadienyl anion **20** was converted to its isomer **21** (reaction 43). The analogous reaction in **22** failed, and **22** could be recovered essentially unchanged even after 1 week of irradiation with a high-pressure mercury arc at 0 °C.[203] These results suggest the importance of the destabilizing effect of alkyl groups (presumably steric hindrance to solution) at the centers of greatest electron density in conjugated anions in solution. The observation that anions **20** and **22** are stable thermally (30 min at 150 °C)[203] suggests the importance of orbital topology in determining the course of such hydrogen shifts. The application of symmetry rules predicts a suprafacial 1,6-hydrogen shift in these photochemical rearrangements (which is geometrically possible in these anions) and a geometrically difficult antarafacial 1,6-shift for the thermal process.



(43)

20 **21**



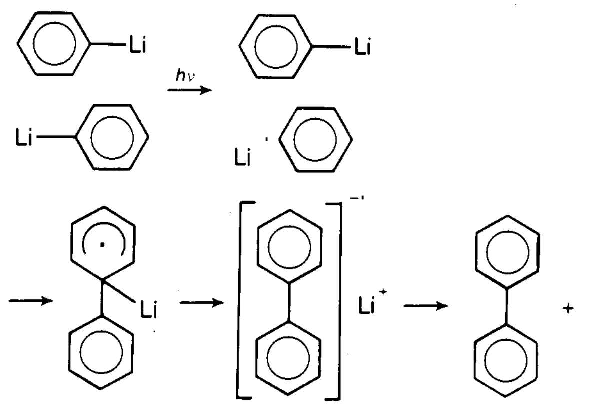
22

D. Intermolecular Bond-Forming Reactions

The formation of *meso*- and *d,l*-3-(3-cyclopentenyl)cyclopentenes by the photolysis of cyclopentadienide (reaction 26), discussed earlier, represents a method in which anion photolysis results in carbon-carbon bond formation by routes unavailable to the neutral precursors.[204] Insufficient work is available to enable more extensive generalization about the synthetic utility of this kind of reaction, but a number of novel photochemical reactions have been reported in which C–C bond formation is observed.

Ultraviolet irradiation of phenyllithiums, for example, gives coupling products and, apparently, metallic lithium in high yield (reaction 44).[205] Although the reaction product is the same as that obtained by photolysis of aryl mercury, bismuth, aluminum, and lead compounds,[206] where free metal is liberated and organic products form by radical coupling, the coupled product obtained in (44) probably arises from a biaryl radical anion. This mechanism, shown in reaction 45, recognizes that phenyllithium

$$\mathrm{PhLi} \xrightarrow[\text{ether}]{h\nu} \mathrm{Ph{-}Ph} + \mathrm{Li}^+ \qquad (44)$$

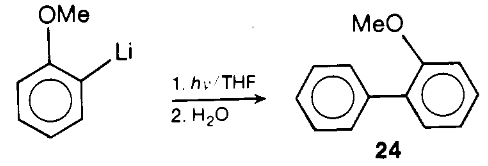


(45)

is dimeric in ether solution and that the biphenyl radical anion decomposes gradually in ether to biphenyl and lithium. Thus, the primary photoprocess can be considered a C–Li homolytic fission or a photoinduced electron transfer to Li^+ in the highly polarized C–Li bond. This phenyl radical attack apparently competes with electron transfer since phenyllithium is known to act as a photochemical electron source if a reasonable acceptor (an aromatic hydrocarbon) is present[154,207] (reaction 46).

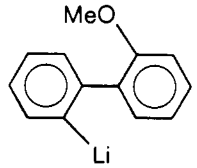
$$PhLi + ArH \xrightarrow{h\nu} Ph\cdot + Ar^- \cdot Li^+ \qquad (46)$$

The products which resulted from irradiation of *o*-methoxyphenyllithium also suggest that simple aryl radical coupling cannot solely account for the observed products (reaction 47).[208]



+ others (47)

In addition to major formation of anisole (63%) and a trace amount of 2,2′-dimethoxybiphenyl (**23**), a conceivable synchronous coupling product, a significant amount (17%) of 2-methoxybiphenyl (**24**) was isolated after aqueous workup. Since it could be demonstrated that **23** did not photoconvert to **24** on photolysis in the presence of lithium, two alternate mechanisms for the coupling were envisioned: (a) photochemical loss of lithium methoxide to give a benzyne which upon capture by aryllithium gave **25**, a precursor to the observed **24**, or (b) formation of **25** by the intermediacy of a species formed by aryl radical attack on a ground-state molecule of 2-methoxyphenyllithium present within the solvent cage. (The starting material is again dimeric in ether.) The importance of synchronous coupling as a competitive pathway is shown in the production of 3,3′-dimethoxybiphenyl (19%) in the photolysis of *m*-methoxyphenyllithium, where loss of LiOMe to form benzyne is rendered impossible. It is apparently also possible to couple aryl- and alkyllithiums photochemically since photolysis of **26** in the presence of *n*-butyllithium gives, after water workup, *n*-butylbenzene (reaction 48),[208] possibly through a benzyne intermediate.



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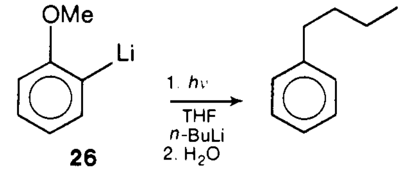
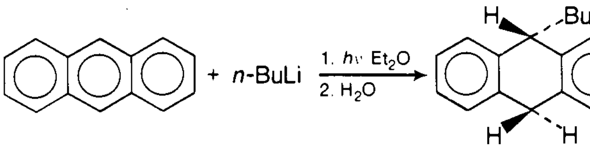
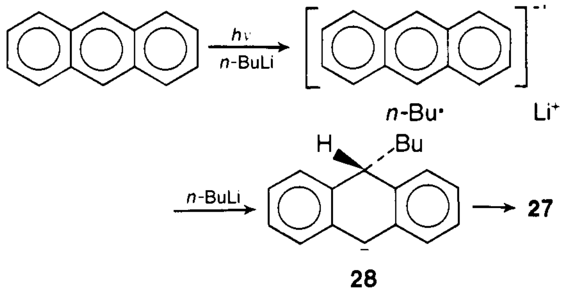


(48)

In fact, a variety of alkyllithiums add to aromatic systems. *n*-Alkyllithiums containing two of ten carbon atoms react with anthracene to form 9-alkyl-9,10-dihydroanthracene (reaction 49).[209] Methyl-, vinyl-, and phenyllithium cause only partial reduction of the hydrocarbon. *sec*-Butyllithium alkylates without photochemical activation. The possibility that this reaction occurred by primary photochemical electron transfer followed by dark capture of the anthracene radical anion by alkyllithium (reaction 50) could be discounted by the observation that the rate of attack by radical anion of anthracene on alkyllithiums in the dark is much lower than the rate of the photochemical reaction.



27 (49)



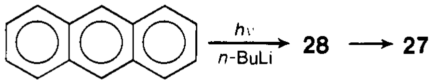
(50)

Two alternate mechanisms (reactions 51 and 52) were proposed. In the first, electron transfer occurs as in (50), but instead of attack by alkyllithium, coupling of the caged butyl radical with the anthracene anion radical ensues (reaction 51). In the second,

$$C_{14}H_{10} + BuLi \xrightarrow{h\nu} [C_{14}H_{10}]^{\cdot-} + Bu\cdot$$

$$\mathbf{28} \rightarrow \rightarrow \mathbf{27} \qquad (51)$$

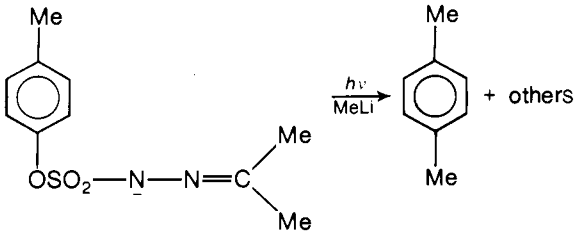
reaction 52, direct attack of the excited state of butyllithium on ground-state anthracene to form anion **28** occurs. This reaction assigns the primary photoprocess as involving enhanced nucleophilicity in the excited state of the anion.



(52)

It is clear that more mechanistic work on the details and scope of this reaction are warranted. Preliminary work in our laboratory[196] indicates that such alkylations may have fair generality and that the mechanism followed by a given carbanion or alkyllithium can differ within a family of anions.

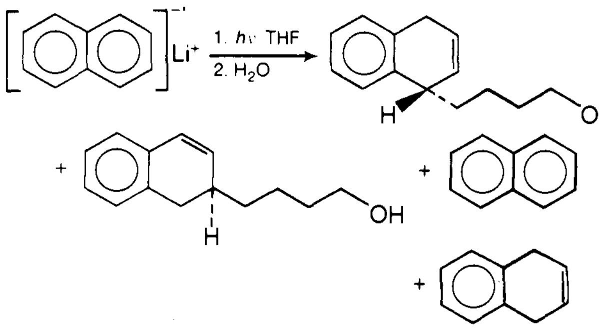
The possibility that some alkylations may be accomplished by nucleophilic substitution is supported by the observation that upon irradiation in the presence of alkyllithiums the tosyl hydrazones of camphor and acetone alkylate on the ring (reaction



(53)

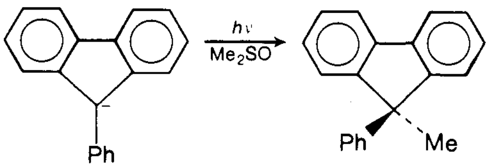
53).[210] Analogous reactions could be observed with the sodium salts of sulfinate and toluene-*p*-sulfonate. Butyllithium was similarly reactive, but by a lower yield process.

Alkylation products have also been observed if aromatic radical anions are irradiated. Attack on the solvent (THF) occurs if lithium naphthalenide is excited in THF (reaction 54).[211] Reduction products, possibly formed via photoinduced disproportionation (i.e., electron transfer), can also be found.

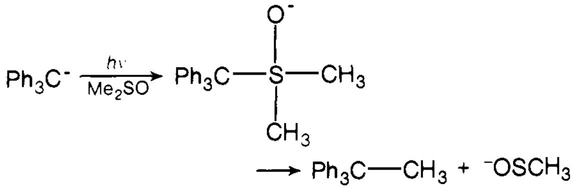


(54)

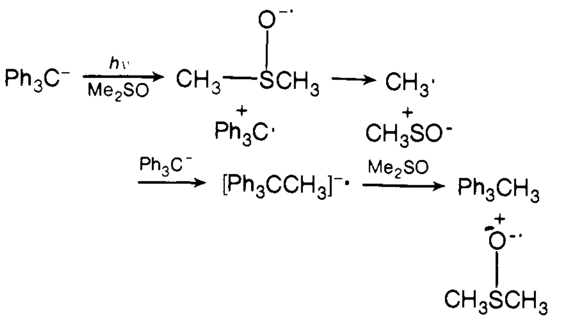
An interesting recently identified photoalkylation involves the irradiation of carbanions in dimethyl sulfoxide (Me_2SO).[212] When several triaryl carbanions were irradiated with visible light in Me_2SO, reasonable yields (52–82%) of alkylated products could be isolated (reaction 55). The possibility of direct S_N2 nucleophilic attack on the methyl group of Me_2SO by the anion excited state was excluded on theoretical grounds since a simple Hückel calculation shows that the alkylation site should have greatly reduced charge density in the excited state. Nonetheless, excited-state nucleophilic attack at sulfur was considered (reaction 56). The tetrahedral intermediate formed conceivably could fragment to the observed products. The more attractive possibility that alkylation was acheived via alkyl radicals participating in a reaction chain (reaction 57) analogous to that of the photoinduced $S_{RN}1$ reactions discussed earlier was examined by adding methyl radical scavengers. Such interceptors failed to alter product yields, but the inability to exclude cage processes makes exclusion of this mechanism risky.



(55)

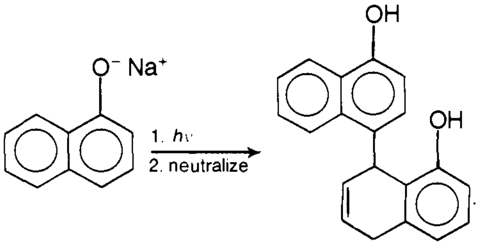


$$\mathrm{Ph_3C^-} \xrightarrow[\mathrm{Me_2SO}]{h\nu} \mathrm{Ph_3C{-}\overset{O^-}{\underset{CH_3}{S}}{-}CH_3} \longrightarrow \mathrm{Ph_3C{-}CH_3} + {}^-\mathrm{OSCH_3} \qquad (56)$$



$$\begin{gathered} \mathrm{Ph_3C^-} \xrightarrow[\mathrm{Me_2SO}]{h\nu} \mathrm{CH_3{-}\overset{O^{-\cdot}}{S}CH_3} \longrightarrow \mathrm{CH_3\cdot} \\ + \qquad\qquad + \\ \mathrm{Ph_3C\cdot} \qquad \mathrm{CH_3SO^-} \\ \xrightarrow{\mathrm{Ph_3C^-}} [\mathrm{Ph_3CCH_3}]^{-\cdot} \xrightarrow{\mathrm{Me_2SO}} \mathrm{Ph_3CH_3} + \mathrm{CH_3\overset{O^{-\cdot}}{S}CH_3} \qquad (57) \end{gathered}$$

The photoexcitation of phenolate anions can also lead to new bond formation. The photolysis of sodium 1-naphthoxide, for example, leads to a dimeric product (reaction 58).[213] Although the mechanism for the photocoupling is still unknown, initial electron ejection is unlikely since a different dimeric product results from the generation of phenoxy radical. Enhanced excited-state nucleophilicity (at C-8) can better accommodate formation of the observed product. Phenoxide and 2-naphthoxide fail to undergo analogous photodimerization.

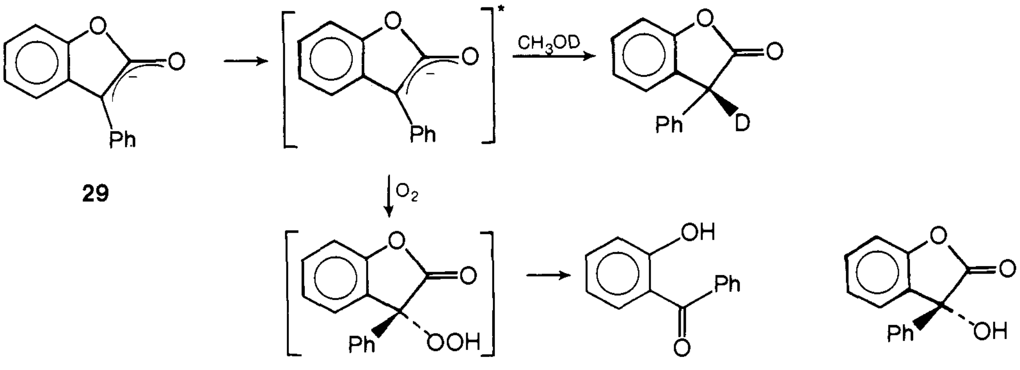


(58)

Photoxidation of the enolate **29** of 3-phenylisocoumaranone[214] occurs if the enolate chromophore is excited with long-wavelength UV light in the presence of oxygen (reaction 59). In degassed CH_3OD, rapid deuterium incorporation occurs photochemically when the conjugate acid of **29** is irradiated at 3130 Å. Since dark deuterium exchange is slow, the intermediacy of the anionic excited state (from excitation of the conjugate acid) is implied. The oxidation resembles the photosensitized oxidation of alkoxides by singlet oxygen,[215] a mechanistically very different reaction where the anion ground state intercepts an oxygen excited state.

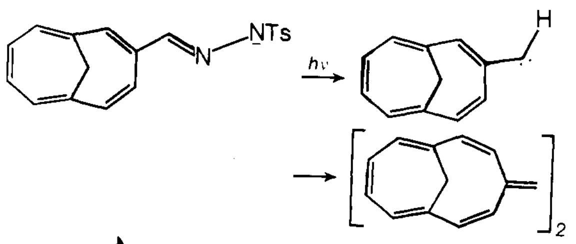
E. Photofragmentations

Like neutral molecules, anions often fragment upon photoexcitation. Particularly facile are such reactions where a small stable molecule is eliminated by successive bond cleavages. A common photochemical anionic fragmentation involves the photodecomposition of sodium salts of tosylhydrazones.[216] To illustrate the reaction, two recent examples of such cleavage reactions are shown in reactions 60 and 61 in which, respectively, carbene dimers[217] and diazo compounds[218] can be prepared by the fragmentation. Thermolysis of tosylhydrazone salts may also lead to fragmentation so that the photochemical pathway is significantly more useful than the thermal pathway

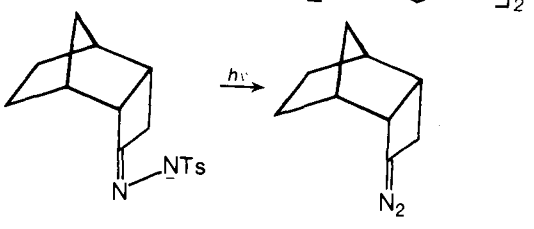


29

(59)



(60)



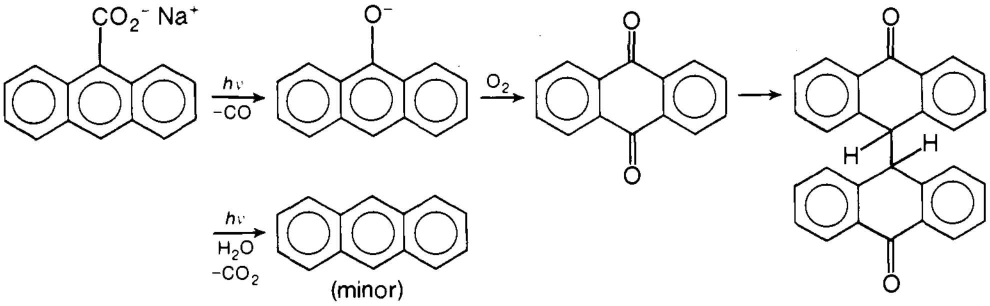
(61)

only if it is desirable to avoid secondary thermal reactions.

Carboxylate anions may fragment if the anion formed is stable. For example, sodium 9-anthroate loses CO (or, in a minor pathway, CO_2) upon photoexcitation (reaction 62).[219] The formation of the anthrol anion is analogous to the photochemical nitro-to-nitrate rearrangement observed in the photolysis of aryl nitro compounds.[220]

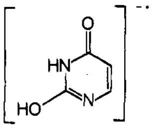
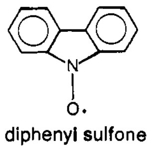
Photoinduced decarboxylation can be observed in sodium glycidates[221] (reaction 63) but other photoreactions apparently intervene with aliphatic[221] or less complex arylcarboxylic acids.

These cleavages can also be observed in sodium salts of sulfonic acids. With sodium 9-anthracenylsulfonate loss of SO_2 occurs upon irradiation of the n,π* bond whereas loss of $SO_3^-\cdot$ occurs with π,π* excitation (reaction 64).[222] The initial rearrangement in the formation of anthrolate parallels that discussed



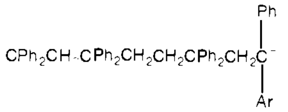
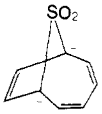
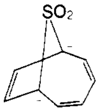
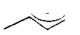
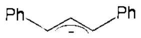
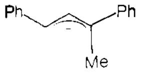
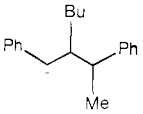
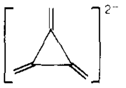
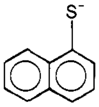
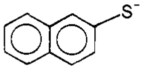
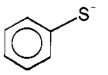
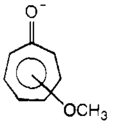
(62)

TABLE A.I. Absorption Maxima of Some Recently Prepared Radical Anions ($M^+A^-\cdot$)[a]

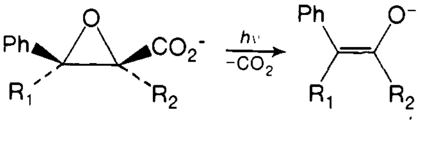
anion ($A^-\cdot$)	M^+	solvent	λ_{max}, nm	ref
benzenide	—		~387	228
naphthalenide	CTA	H_2O/1% MeOH	324, 365, 775, 850	229, 230
biphenylide	CTA	1% MeOH/H_2O	405, 635	229
2,2-paracyclophanide	—	MTHF	~830	231
fluorenide	CTA	1% MeOH/H_2O	380, 395, 660, 695	229
anthracenide	—	MTHF	~327, 357, 400, 714	231
dianthracenide	—	MTHF	~800	231
9,10-diphenylanthracenide	TBA	CH_3CN	~560, 600, 670	232
	TBA	DMF	645, 709, 724	233
9,10-biphenylylanthracenide	TBA	DMF	826, 1001	233
phenanthrenide	CTA	1% MeOH/H_2O	420, 450, 650, 975, 1125	229
tetracenide	Li	THF	402, 486	234
azulenide	—	2-propanol	~440	235
1,3-di-*tert*-butylazulenide	TBA	HMPA	454	235
	TBA	CH_2Cl_2	454	235
1,1-phenyl-4-nitrophenylethylenide	TEA	CH_3CN	340, 387, 610, 660	236
(*E*)-2-bromo-	TEA	CH_3CN	280, 585, 645	236
(*Z*)-2-bromo-	TEA	CH_3CN	420, 560, 680	236
(*E*)-2-chloro-	TEA	CH_3CN	340, 390, 590, 630	236
(*Z*)-2-chloro-	TEA	CH_3CN	315, 383, 590, 650	236
$TCNQ^-\cdot$	TBA	DME/CH_3CN	~410, 750, 880	237
acetophenone ketyl	—	H_2O	314, 445	238
benzophenone ketyl	—	H_2O	339, 615	238
4-hydroxybenzophenone ketyl	—	EtOH	540	239
benzenide ketyl	—	H_2O	320, 440	238
benzil ketyl	—	H_2O	362, 545	238
	Na	EtOH	550	240
	Na	DMSO	620, 650, 720	240
benzoin ketyl	—	H_2O	312, 460	238
fluorenone ketyl	—	H_2O	360, 450	238
	Na	MTHF	455, 490, 513, 529	241
	K	MTHF	458, 500, 520, 535	241
	Sr	MTHF	455, 510	241
fluorenone ketyl	Li	THF	452	242
1-NH_2-	Li	THF	446	242
2-NH_2-	Li	THF	472	242
3-NH_2-	Li	THF	510	242
4-NH_2-	Li	THF	460	242
2,7-$(NH_2)_2$-	Li	THF	474	242
1,8-diaza-	Li	THF	437	242
dimethyl maleate ketyl	—	MeOH	345	243
dimethyl fumarate ketyl	—	MeOH	335	243
1,3-dibenzoylbenzene ketyl	Na	HMPA	760	244
camphorquinone ketyl	—	H_2O	305	245
9,10-anthraquinone-2-sulfonate ketyl	—	H_2O	398, 465, 496	238
	—	H_2O	310	246
	TPA	DMF	320–382, 614, 761	247
diphenyl sulfone ketyl		MTHF	360, 1030	248
phenyl methyl sulfone ketyl		MTHF	385	248
diphenyl disulfone ketyl		MTHF	368, 695	249
bacteriochlorophyll$^-$		DMF	~380, 580, 770	250

[a] Abbreviations are listed at the end of Table A.II.

TABLE A.II. Absorption Maxima of Some Recently Prepared Closed-Shell Anions (M^+ A^-)[a]

anion (A^-)	M^+	solvent	λ_{max}, nm	ref
$Ph_2\overline{C}C_3H_7$	Li	THF	490	251
 $\mathrm{CPh_2CH{-}CPh_2CH_2CH_2CPh_2CH_2\overset{Ph}{\underset{Ar}{C}}{}^-}$				
Ar = 2-pyridyl	2Li	THF	443	252
	2Li	toluene	435	252
	2Na	THF	444	252
	2Cs	THF	441	252
Ar = 3-pyridyl	Li	THF	483	252
	Li	tetraglyme	481	252
	Na	THF	475	252
Ar = 4-pyridyl	Li	THF	436	252
	Li	THF	442, 550, 605	253
	Li	THF	545	253
	Li	hexane	194, 215, 235, 260 (hexamer)	254
	Li	hexane	450	255
	Li	Et_2O	476	255
	Li	THF	564	255
	Na	THF	523, 564	255
	K	THF	537	255
	Li	hexane	445	255
	Li	Et_2O	484	255
	Li	THF	565	255
	Na	THF	525, 565	255
	K	THF	535	255
	Li	cyclohexane	442	256
polyisoprenyl	Li	THF	287, 305, 335	257
$PhCH_2^-$	—	THF	362	258
	Na	THF	355	258
	Ba	THF	345	259
	Sr	THF	322	259
	Ca	THF	332	259
				
hexacyano	Na	glyme	222, 285, 315	260
hexakis(carbo-*m*ethoxy)	Na	glyme	264, 306	260
cyclopentadienide	Na	H_2O	<225	261
	K	Et_2O	<225	262
indenide	Li	Et_2O	213, 250, 288, 350	263
	Li	$C\text{-}C_6H_{11}\text{-}NH_2/Et_2NH$	340, 370, 400	264
fluorenide	Li	$C\text{-}C_6H_{11}\text{-}NH_2/EtNH$	340, 370, 400	263
	Li	(solid)	355, 420, 460, 490	265
	Li	TMEDA/solid	345, 410, 433, 460	265
fluorenide	K	TMEDA/solid	320, 380, 460, 490, 515	265
	K	THF/poly(ethyleneoxide	381	266
	Li	$C\text{-}C_6H_{11}\text{-}NH_2/Et_2NH$	452, 480, 512	264
	Li	DME/PhH	352, 373	267
	Na	DME/PhH	358, 373	267
	Na	$EtNH_2$	362, 438, 469, 499	268
	Cs	$EtNH_2$	365, 447, 472, 505	268
	Ba	$EtNH_2$	352, 426, 452, 476	268
9-butyl-	Li	THF	385	269
9-(2-*m*ethoxyethyl)-	Li	THF	360	269
9-(3-dimethylaminopropyl)-	Li	THF	385	269
cyclononatetraenide	Li	THF	250, 320	263
tetraphenylethylene dianion	2Li	THF	385, 495	270
	2Na	THF	495	270
dihydronaphthalenide	Na	THF	435	271
1-naphthoxide	—	PVA sheets	250, 335, 354	272
2-naphthoxide	—	PVA sheets	230, 245, 284, 349	272
	Na	H_2O	333	273
	Na	H_2O	293, 347	273
	Li	THF	285	274
	Li	DMF	308	274
	Cs	THF	299	274
	Cs	DMF	308	274
 (σ adduct)	K	Me_2SO	335	275
quinoline-2-carboxylate	Na	H_2O	265, 305	276
quinoline-8-carboxylate	Na	H_2O	286, 315	276
1-pyrenesulfonate	Na	H_2O/PhH	303, 317, 333, 347	277
triphenylsilyl	Li	THF	335	278
	Cs	THF	376	278
	Li	DME	331	278
	Li	dioxane	329	278
methyldiphenylsilyl	Li	THF	335	278
	Cs	THF	380	278
	Li	dioxane	329	278
naphthalene dianion	2Li	Et_2O	530	279
anthracene dianion	2Li	Et_2O	554	279
tetracene dianion	2Li	Et_2O	580	279
perylene dianion	2Li	Et_2O	552	279
pyrene dianion	2Li	$2Et_2O$	569	279

[a] Abbreviations used in Tables A.I and A.II: CTA, hexadecyltrimethylammonium; MTHF, 2-methyltetrahydrofuran; TBA, tetrabutyla*mm*onium; DMF, dimethylforma*m*ide; THF, tetrahydrofuran; TEA, tetraethyla*mm*onium; DME, dimethoxyethane; HMPA, hexamethylphosphora*m*ide; TPA, tetrapropylammonium; PVA, poly(vinylanthracene).



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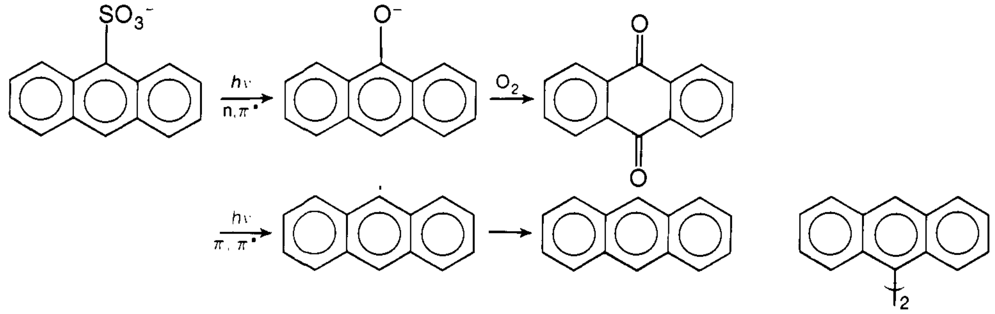
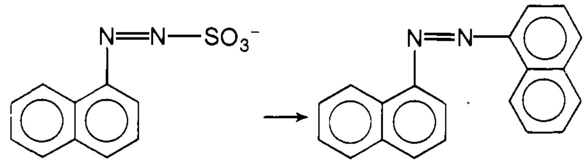


(64)

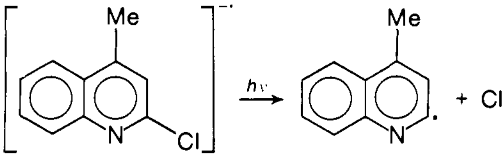
earlier for carboxylic acids. Azo coupling products are observed when **30** is irradiated (reaction 65).



30

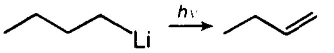
(65)

Low-temperature ESR spectroscopy implicates $C_{10}H_7N{=}N\cdot$, as a primary photoproduct.[223] Radicals can also be observed from photofragmentation of the radical anions of aryl chlorides, e.g., reaction 66.[224]

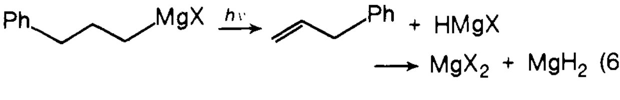


(66)

Photofragmentation is relatively rare in hydrocarbon anions. The photoinduced elimination of LiH from butyl- or ethyllithium[225] (reaction 67) and the loss of HMgX in the photolysis of 3-phenylpropylmagnesium bromide[226] (reaction 68), and the lack of comparable reactivity in benzylmagnesium bromide, however, suggest that photochemical elimination reactions may be important processes.



(67)



(68)

IV. Conclusions

Although anions exhibit a rich variety of photochemistry and their absorption spectra allow the possibility of visible light excitation, the studies of anion photochemistry are still in an exploratory stage. The common observation of divergent photochemical courses in anionic and neutral excited molecules predicts novel mechanistic and synthetic possibilities in the characterization of these photoexcited states. The association of anions with metal cations, along with the recent observation of alkali metal catalysis of some photochemical reactions,[227] suggests that photochemical investigations of anions and their ion pairs will be a most fruitful area of photochemical research.

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V. Appendix

Many excellent detailed spectroscopic studies of closed- and open-shell anions were omitted from the above discussions for reasons of brevity. Tables A.I and A.II are offered as an overview of anions whose spectral properties have been examined and as a source for leading references for anion absorption spectra.

The coverage in the tables is not completely comprehensive, and, in order to keep the data presented concise, no descriptive comments on the transitions are included. Studies included in the table were limited to those which are recent (since 1970), which had spectroscopic characterization as a major goal of the study, and which appeared in widely accessible journals. As such, the choice of which data to exclude is somewhat arbitrary. Many of the reviews cited earlier contain partial listings of anion absorption spectra.[3,17,18,34,48,50-52] In general, studies cited in the text are omitted here.

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