

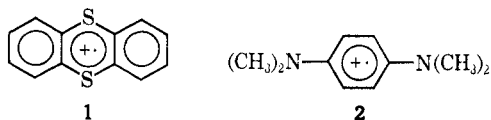
Cation Radicals in Electron Transfer Reactions

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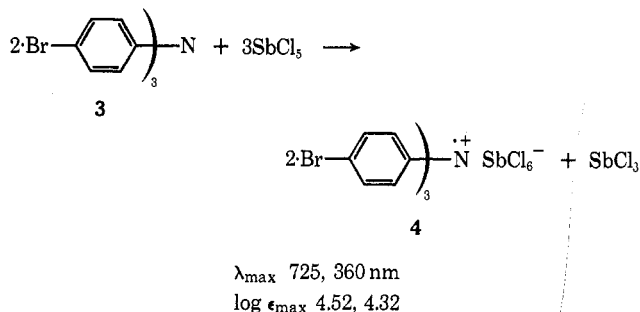
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Cation radicals, symbolized $M^{\cdot+}$, are usually generated by removing an electron from a neutral, electron-paired molecule. Thus they have both a positive charge and an unpaired electron. They are familiar as transient species in mass spectrometry, and they appear as by-products of electron emission in photoelectron spectroscopy. Several rather stable cation radicals, such as that from thianthrene (**1**) and N,N,N',N' -tetramethyl-*p*-phenylenediamine (**2**) have been studied by electron spin resonance spectroscopy.¹ However, the chemical reactions of cation radicals have not, until recently, received much attention.



Cation radicals generated by chemical reactions in solution are normally in a thermally equilibrated condition, whereas those produced in mass spectrometry by high-energy electron impact are in electronically and vibrationally excited states.² Nevertheless, mass spectrometric and photoelectron spectroscopic studies³ teach a lesson that is also relevant to solution chemistry, namely, that molecules containing "lone-pair" atoms such as O, N, or S are particularly prone to lose electrons. Cation radicals in solution are commonly obtained from oxidation of amines, sulfides, or oxygen compounds.

The tris(*p*-bromophenyl)aminium ion **4** played a prominent role in our research, and its synthesis⁴ is illustrative. In 1:1 $\text{CH}_2\text{CN}-\text{CF}_3\text{COOH}$ the oxidation-



reduction potential of the reversible system **3-4** is +0.762 V, vs. $\text{Ag}-\text{AgClO}_4$,⁵ and we have found that hexachloroantimonate ion, which has oxidizing charac-

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ter,⁶ stabilizes the aminium ion against thermal and photochemical decomposition.

While there are obvious thermodynamic limitations on the range of substrates oxidizable by reagents such as **4**, the very rapid rates of electron transfer between ion radicals and neutral molecules⁷ offer a valuable kinetic bonus, as illustrated by the rapid, quantitative oxidations of cycloheptatriene derivatives to tropylium salts⁸ and metalloporphyrins to corresponding cation radicals or dicationic derivatives.⁹

Characterization of an open-chain butane dication (*e.g.*, **6**) was a primary objective¹⁰ of our work with aminium salt oxidants because of its relevance to new initiation processes in cationic polymerization.¹¹ Subsequently, there have been several reports of related oxidative coupling reactions of olefins by both chemical¹² and electrochemical techniques.¹³

The olefin most useful for polymerization studies involving cation radicals is *N*-vinylcarbazole (NVC, **5**), and this monomer gives a quantitative yield of the oxidatively coupled methanolysis product **7** upon reaction with **4** in $\text{CH}_2\text{Cl}_2-\text{CH}_3\text{OH}$ solvent systems.¹⁴ Interestingly the same methanolysis product **7** was obtained,¹⁵ again in quantitative yield, by a similar oxidation of the corresponding cyclobutane dimer **8**, indicating the rapid interconversion of cyclic (**9**) and open-chain (**10**) butane cation radicals (Scheme I), an essential feature of the mechanism proposed¹⁶ (see later discussion) for cycloaddition of certain olefins.

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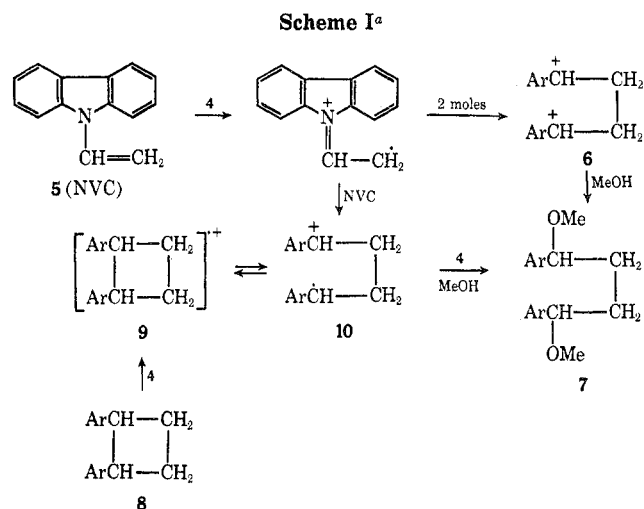
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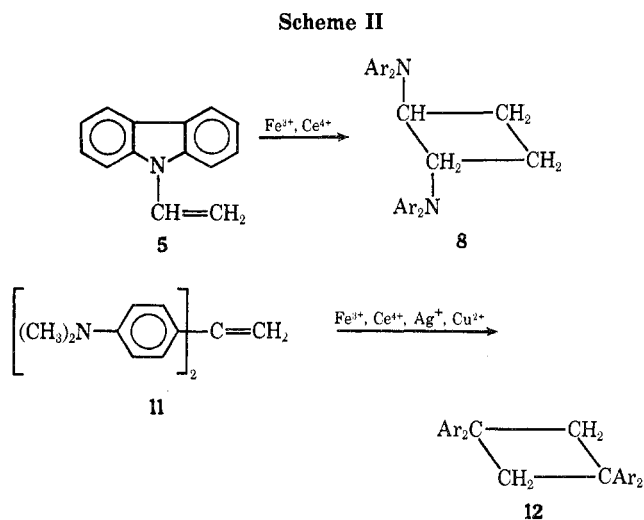
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Cation Radicals in Cycloaddition Reactions

Certain vinyl-substituted aromatic amines¹⁷ (Scheme II) readily undergo cyclodimerization under the catalytic influence of suitable inorganic one-electron oxidants such as Fe(III), Ce(IV), and Cu(II). Of these enamines, *N*-vinylcarbazole (NVC; **5**) and 4,4'-dimethylamino-1,1-diphenylethene (**11**) are most readily available and have been used extensively in our mechanistic studies.



Methanol is the preferred solvent for the metal-catalyzed 2 + 2 cycloadditions; the presence of dissolved air or oxygen is essential for the catalytic action of hydrated cupric nitrate on **11**. Air markedly accelerates the cyclodimerization of NVC catalyzed by hydrated ferric nitrate. Presumably the catalytically active metal derivatives, in both cases, contain methoxide or hydroxide ligands because of facile hydrolysis of the metal nitrates. Addition of other coordinating ligands or anions to the reaction mixtures has a marked effect on reaction rates, especially in cyclodimerization

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Table I
Dimerization of NVC Catalyzed by Ferric Nitrate in Methanol^a

Additive	[Additive], <i>M</i>	10 ⁶ initial rate, <i>M sec</i> ⁻¹	% yield of dimer
None		1.96	80
<i>N</i> -Ethylcarbazole	10 ⁻²	3.66	81
Carbazole	10 ⁻²	16.7	77
(C ₆ H ₅) ₃ N	5 × 10 ⁻⁴	19.4	77
	2 × 10 ⁻³	53.7	76
	10 ⁻²	185	64
Cu(NO ₃) ₂	5 × 10 ⁻³	2.42	77
	10 ⁻²	6.61	77
(C ₆ H ₅) ₃ N	5 × 10 ⁻⁴	75.7	78
Cu(NO ₃) ₂	10 ⁻²		

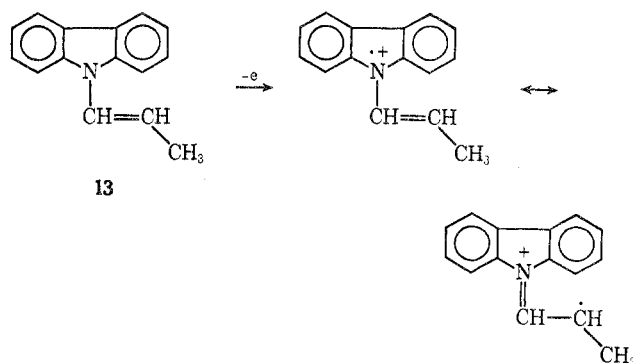
^a [NVC] = 10⁻¹ *M*; [Fe(NO₃)₃·9H₂O] = 2 × 10⁻² *M*; [2,2'-bipyridyl] = 10⁻¹ *M*; temp = 20°.

of NVC by iron(III), where excess 2,2-bipyridyl greatly slows the reaction but eliminates the need for oxygen cocatalysis.¹⁷ Kinetic studies^{17,18} have established the rate expression

$$\frac{d(\text{cyclobutane})}{dt} = k[\text{metal salt}][\text{olefin}]$$

Typical experimental conditions and rate data showing the effect of additives are given in Table I. For given reaction conditions, the rate of cyclodimerization of NVC was always six to seven times greater than concurrent rate of formation of iron(II), although activation energies for both reactions were identical (26 kcal mole⁻¹); these observations are consistent with a chain mechanism for cyclodimerization.

It is not yet clear why NVC yields exclusively the head-to-head trans-1,2-disubstituted cyclobutane dimer **8**, whereas **11** gives exclusively the corresponding head-to-tail 1,3-tetrasubstituted cyclobutane **12**, although obvious steric effects suggest these orientations. Another steric phenomenon in these systems is the complete lack of reactivity of *cis-N*-propenylcarbazole; in contrast, the corresponding trans isomer **13** gives good yields of the head-to-head cyclodimer. Presumably steric interaction between the methyl group and the aromatic rings in the *cis* isomer hinders coplanarity required for resonance delocalization in the cation radical.



Cation Radicals in Photochemical Cyclodimerizations

Aromatic enamines **5** and **11** were also found to

(18) R. A. Crellin, Ph.D. Thesis, University of Liverpool (1970).

undergo photosensitized cyclodimerization,¹⁹ producing cyclobutanes with the same structure as obtained from the metal-catalyzed reactions. The reactions show common features markedly different from those of conventional organic photosensitized reactions.

(a) Sensitizers ranging from benzophenone ($E_T = 69.5$ kcal mole⁻¹) to methylene blue ($E_T = 33$ kcal mole⁻¹) may be used and, since the latter value is much lower than the anticipated triplet-state energies of the reacting olefins (cf. E_T for carbazole = 70 kcal mole⁻¹), energy transfer sensitization is ruled out in many cases.

(b) With all sensitizers (except anthraquinone, fluorenone, and chloranil) and both enamines, cyclodimerization occurs only when oxygen is present in the system. In the absence of oxygen there is essentially no photochemical reaction of the enamine **11**. For NVC, photosensitization in the absence of oxygen leads to slow polymerization.

(c) Yields of cyclobutanes **8** and **12** are essentially quantitative if irradiation is prolonged, and the precipitated dimers are periodically filtered off.

(d) Direct photolysis of the enamines **5** and **11** with, or without, oxygen does not normally produce the cyclobutane dimer. By use of wavelength filters, it was shown that the sensitizer is the primary absorbing species in all cases. In our own work we have noted a nonreproducible rate of formation of **8** by prolonged direct irradiation of NVC in acetone or methanol; this observation has also been made in other laboratories.²⁰ However, while the mechanism of the direct photodimerization remains obscure, reaction rates are orders of magnitude less than those for the corresponding sensitized reactions.

Detailed kinetic studies on the dimerization of NVC have been carried out with rhodamine 6G as sensitizer. For sensitizer concentrations $<10^{-5}$ M the rate of dimerization was first order in sensitizer and first order in NVC, with an activation energy of 4 kcal mole⁻¹, and rates of dimerization were not increased by the use of pure oxygen, instead of air, to saturate the solutions. Therefore, oxygen must play a catalytic function. This is borne out by the complete absence of products containing oxygen.

Quantum yields (ϕ_d) for photosensitized cyclodimerization of *N*-vinylcarbazole (NVC) were measured^{16,21} under a variety of experimental conditions for several sensitizers. In all cases, $\phi_d \geq 1$. In fact, for sensitization by chloranil, quantum yields as high as 14 were observed, leaving little doubt that a chain mechanism operates. Another interesting feature of these photodimerizations is that the olefins **5** and **11** were extremely efficient quenchers for the fluorescence of fluorenone and rhodamine 6G. Taken with the comparatively high quantum yields, this suggests that the primary photochemical processes involve singlet

Table II
Retardation of Cyclodimerization of NVC and Fluorescence Quenching at 25°

Quencher	Fluorenone (acetone)		Rhodamine 6G (methanol)	
	K_q , M^{-1}	Rel rate of dimerization	K_q , M^{-1}	Rel rate of dimerization
NVC	88	1.00	23.0	1.00
DABCO	171	0.10 ^a	8.0	1.00 ^a
Ferrocene	268	0 ^a	88.1	0.04 ^a

^a Reaction mixture contained 10^{-3} M (quencher).

excited states of these sensitizers, a conclusion strongly supported by parallel quantitative studies of quenching effects and sensitization (Table II).

Photosensitized cyclodimerization of NVC by fluorenone was rapid and efficient in acetone (more rapid in the presence of oxygen), and ferrocene was found to retard the cyclodimerizations in both solvents. The reacting enamines were effective quenchers for fluorenone fluorescence in a manner similar to that reported for other amines,^{22,23} as were ferrocene and diazabicyclooctane (Dabco).

Electron transfer mechanisms are responsible for fluorescence quenching of fluorenone by several aromatic and aliphatic amines.²²⁻²⁴ The close agreement with quenching constants for the present systems argues strongly in favor of a similar mechanism for the enamines **5** and **11**. Additional evidence for electron transfer mechanisms in the present work is provided by the quenching efficiency of ferrocene, which readily undergoes electron transfer reactions. Quenching rate coefficients (k_q) approach diffusion-limiting values in the solvents employed, and the retarding effect of ferrocene on the dimerization of NVC is a consequence of its greater quenching ability. It is noteworthy that Dabco, a more efficient quencher of fluorescence from fluorenone than NVC in acetone, retards photodimerization of the latter, whereas with rhodamine 6G in methanol, in which Dabco is a less efficient quencher than NVC, there is no effect on rate of photodimerization.

A Cation-Radical Chain Mechanism for 2 + 2 Cycloaddition

A plausible chain reaction mechanism accounting for most of the experimental observations is shown in Scheme III. The initiation reaction applies equally well to singlet or triplet excited states, although the former are thought to be primarily involved. Equilibria between open-chain and cyclized cation radicals such as **16** and **17** will obviously be affected by the steric and electronic nature of substituents and may be diverted to open-chain dicationic species in the presence of excess oxidant,^{10,17} as discussed earlier (Scheme

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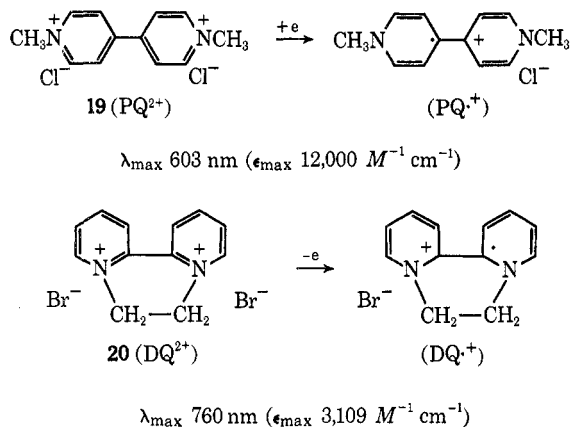
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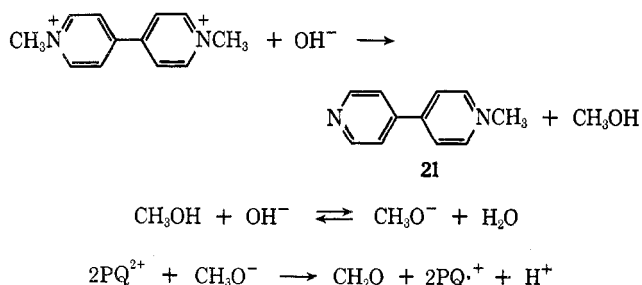
lar oxygen. One-electron reductions of 1,1'-dimethyl-4,4'-bipyridylium dichloride (paraquat dichloride; **19**) and 1,1'-ethylene-2,2'-bipyridylium dibromide (diquat dibromide; **20**) are of considerable interest because of the correlation between ease of reduction, cation radical stability, and herbicidal activity, in a range of bipyridylium salts.³²



Paraquat (PQ^{2+}) and diquat (DQ^{2+}) are useful oxidants in aqueous solution ($E_0 = -446$ and -349 mV, respectively). Our interest in these compounds was further stimulated by the observation that their respective cation radicals were readily produced by reaction of the salts with aqueous alkali.³³

Under high vacuum the reaction between sodium hydroxide and paraquat dichloride in water was highly reproducible. The final yield of cation radical (based on paraquat) approached a limiting value of 66% and, after admission of air to the systems, reaction products were identified as paraquat dichloride, 1-methyl-4-(4-pyridyl)pyridinium chloride (**21**), and formaldehyde.

The reaction sequence shown below accounts for the experimental observations and is substantiated by the observations that, on addition of methanol to aqueous systems or working in methanol solvent, yields of $\text{PQ}^{\cdot+}$ were quantitative. Oxidation of methoxide ion by the paraquat ion is essentially instantaneous in methanol or aqueous methanol when $[\text{MeO}^-] \geq 0.1 \text{ M}$ and is in marked contrast to the more usual ring substitution which occurs when pyridinium ions interact with bases.³⁴ Other alcohols with α -hydrogen atoms will

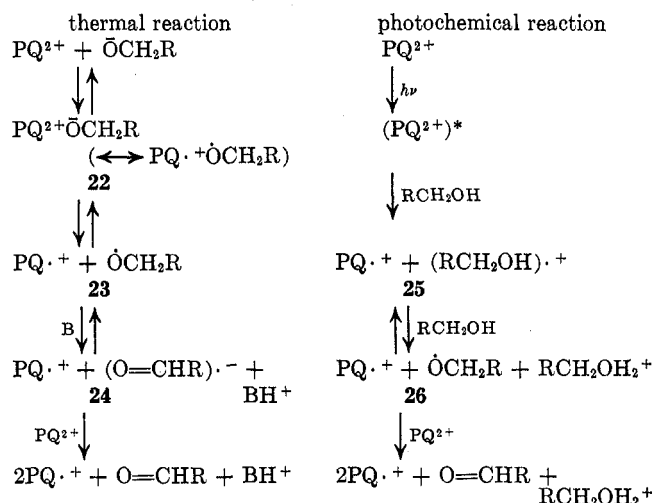


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(33) J. A. Farrington, A. Ledwith, and M. F. Stam, *Chem. Commun.*, 259 (1969).

(34) D. Bruck and D. E. Guttman, *J. Amer. Chem. Soc.*, **90**, 4964 (1968); E. M. Kosower and J. W. Patton, *Tetrahedron*, **22**, 2081 (1966); R. E. Lyle, *Angew. Chem., Int. Ed. Engl.*, **6**, 973 (1966).

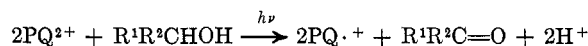
Scheme IV



also reduce paraquat in basic media, but solutions of potassium *tert*-butoxide in *tert*-butyl alcohol are inactive.

Reaction rates for reduction of PQ^{2+} by CH_3O^- and CD_3O^- were shown to be almost identical; the absence of kinetic isotope effect eliminates hydrogen or hydride abstraction as the likely rate-determining step in oxidation of methoxide ion. It seems reasonable, therefore, to assume that primary electron transfer between CH_3O^- and PQ^{2+} is rate determining (see Scheme IV). Before discussing the mechanism of these reactions in more detail, it is relevant to consider the related photochemical oxidation of neutral alcohols by PQ^{2+} and DQ^{2+} .

Paraquat dichloride is reduced to the cation radical $\text{PQ}^{\cdot+}$ by uv irradiation of aqueous solutions containing primary or secondary alcohols.^{35,36} There was no reaction on irradiation in pure water or aqueous *tert*-butyl alcohol. Rates were retarded by added halide ion in the sequence of increasing quenching ability $\text{Cl}^- < \text{Br}^- \ll \text{I}^-$. Similar results were observed for diquat salts (DQ^{2+} , 2Cl^-), except that in this case halide ion quenching was so effective that the commercially important diquat dibromide could not be photoreduced in 0.1 M solutions. For all alcohols, stoichiometric amounts (gle) of corresponding carbonyl compounds were produced according to the following overall equation and reaction rates were proportional to the first power of the light intensity.



Reaction could be activated using 313 or 334 nm (but not 366 nm) irradiation, consistent with excitation *via* the long-wavelength tail of the absorption spectrum of paraquat, and quantum efficiencies lie in the range 10–40%.

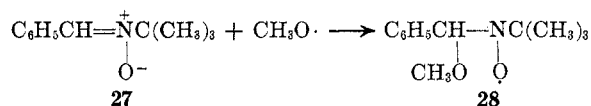
A striking feature of the photoreduction of PQ^{2+} was the rapid decay in rate as reaction proceeded ascribed

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to the cation-radical product. $\text{PQ}\cdot^+$ has a convenient "window" at 310–340 nm in its absorption spectrum,³⁷ and this rate retardation must therefore involve genuine quenching of excited states or reversibility of the redox processes. Paraquat does not luminesce at room temperature, whereas diquat dichloride fluoresces in water ($\phi_F = 0.04 \pm 0.02$) but not at all in alcohols (including *tert*-butyl alcohol) or in ~20% aqueous alcoholic solutions. The observed quenching of photoreduction of paraquat ($E_T = 71.5$ kcal³⁸) by phenol ($E_T = 82$ kcal³⁹) is unlikely to involve triplet energy transfer. Also the comparable, mild, quenching efficiency of ferrocene, normally a very efficient quencher for triplet states,⁴⁰ argues against triplet intermediates. k_H/k_D kinetic isotope effects for $\text{CH}_3\text{-OH-CD}_3\text{OH}$ and $\text{CH}_3\text{OH-CH}_3\text{OD}$ are approximately 1.4, suggesting strongly that hydrogen abstraction is not a rate-determining process. Rather, these isotope effects are similar to those reported²⁴ for electron transfer quenching of biacetyl fluorescence by amines, phenols, and alcohols and support a similar mechanism for the present case (Scheme IV). Electron transfer quenching of fluorescence has also been reported for pyridinium ions⁴¹ and other organic cations.⁴²

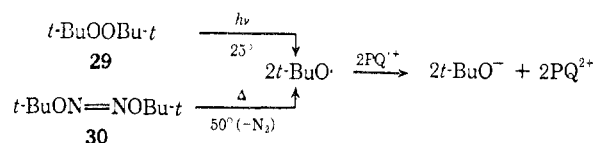
An important step in the suggested mechanism is the oxidation of alcohols to alkoxy radicals by singlet excited paraquat. Only when the alkoxy radical has an α -hydrogen atom is the product $\text{PQ}\cdot^+$ observed experimentally; otherwise intermediate stages **25** and **26** revert back to ground-state reactants, with apparent fluorescence quenching in the case of diquat. By this mechanism *tert*-butyl alcohol should be effective as a quencher for diquat fluorescence, as observed experimentally, but cannot produce $\text{PQ}\cdot^+$. Unambiguous confirmation of the intermediacy of alkoxy radicals was provided by spin-trapping experiments with benzylidene *N-tert*-butyl nitron (**27**). Continuous photolysis of paraquat in methanol containing the latter gives rise to a long-lived free radical having nitrogen and β -hydrogen hyperfine coupling constants⁴³ identical with those of the nitroxide radical **28**.



Electron Transfer Scavenging of Alkoxy and Hydroxyalkyl Radicals

Examination of the reactions outlined in Scheme IV shows that alkoxy radicals ($\text{RCH}_2\text{O}\cdot$) should be pro-

duced *via* both thermal (alkoxide ion) and photochemical (neutral alcohol) routes. For the former, the initial reactant pair **22** is analogous to pyridinium ion-iodide ion pairs, in which charge transfer forces are known to be important.⁴⁴ A necessary corollary of these processes is that *tert*-alkoxy radicals, generated in the presence of paraquat cation radical, should immediately undergo electron transfer reduction forming *tert*-alkoxide ion and paraquat. This has been confirmed⁴⁴ unambiguously for *tert*-butoxy radicals and paraquat cation radical, the former being generated photochemically from di-*tert*-butyl peroxide (**29**) and thermally from di-*tert*-butyl hyponitrite (**30**).



Photolysis of di-*tert*-butyl peroxide in 1:1 water-*tert*-butyl alcohol, containing independently generated paraquat cation radical, resulted in steady decoloration of the solution. Kinetic measurements established that the rate of disappearance of $\text{PQ}\cdot^+$ was independent of $[\text{PQ}\cdot^+]$ but first order in [di-*tert*-butyl peroxide]. Thermal decomposition of di-*tert*-butyl hyponitrite in 1:1 water-*tert*-butyl alcohol was an even more convenient source of *tert*-butoxy radicals, and kinetic studies gave comparable results.⁴⁵ Rate coefficients for thermal decomposition of di-*tert*-butyl hyponitrite at 65° obtained in the present work ($k = (3.5 \pm 0.2) \times 10^{-4} \text{ sec}^{-1}$) compare very well with those extrapolated from data of Traylor and Keifer⁴⁶ ($k = 3.7 \times 10^{-4} \text{ sec}^{-1}$) and Neuman and Bussey⁴⁷ ($k = 3.6 \times 10^{-4} \text{ sec}^{-1}$), obtained by very different techniques in different solvents. Reaction products contained 1 mole of base for each mole of $\text{PQ}\cdot^+$ consumed, strongly supporting the proposed electron transfer mechanism. It follows that, in 1:1 *tert*-butyl alcohol- H_2O , *tert*-butoxy radical must possess oxidizing power in excess of that of PQ^{2+} , for which $E_0 = -446$ mV, and may, therefore, function as a primary one-electron oxidant in reactions presently interpreted in other ways.

The reaction sequence (Scheme IV) for thermal reactions of alkoxide ion with PQ^{2+} assumes that alkoxy radicals react rapidly with base to give corresponding anion radicals of the appropriate carbonyl compound (*i.e.*, conversion of **23** to **24**). This idea, first proposed by Bunnett and his collaborators⁴⁸ to explain details of related, reductive dediazonation processes involving methoxide ion, is supported⁴⁹ by the increasing acidity

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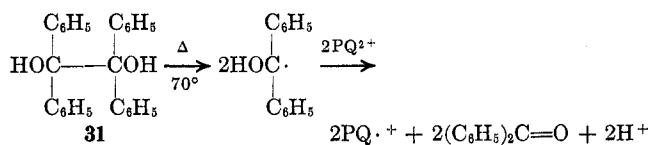
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of $\text{Ph}_2\dot{\text{C}}\text{OH}$ over its parent alcohol Ph_2CHOH . Interconversion of alkoxy radicals ($\text{RCH}_2\text{O}\cdot$) and corresponding hydroxyalkyl radicals ($\text{R}\dot{\text{C}}\text{HOH}$) is known to be extremely rapid,⁵⁰ and generation of the former, in basic media, would rapidly yield $(\text{RCH}=\text{O})\cdot^-$, as indicated in Scheme IV.

A similarly rapid interconversion of $\text{RCH}_2\text{O}\cdot$ and $\text{R}\dot{\text{C}}\text{HOH}$ will be likely in the photochemical oxidation of alcohols by PQ^{2+} . In this case, $\text{R}\dot{\text{C}}\text{HOH}$ radicals must then be further oxidized by ground-state paraquat. Independent evidence for the latter process was obtained by studying thermal decomposition of benzpinacol (**31**) in methanol containing paraquat dichloride.⁵¹



Paraquat oxidation of semipinacol radicals ($\text{Ph}_2\dot{\text{C}}\text{OH}$)

(50) F. S. Dainton, I. V. Janovsky, and G. A. Salmon, *Chem. Commun.*, 335 (1969).

(51) K. Brown, A. S. Hopkins, and A. Ledwith, manuscript in preparation.

formed by unimolecular thermolysis of **31** was apparently very efficient. Reaction rates, monitored by observing the appearance of $\text{PQ}\cdot^+$, indicated an apparent activation energy of 28 kcal mole⁻¹ for decomposition of benzpinacol ($k = 2.5 \times 10^{-6}$ sec⁻¹ at 64°); these figures are in good agreement with data extrapolated from those of Neckers and Colenbrander⁵² for thermal decomposition of benzpinacol in the presence of oxygen.

It seems reasonable to conclude, therefore, that these preliminary experiments with paraquat cation radical and paraquat establish a potentially useful, and extremely convenient, new technique for quantitative scavenging of organic radicals by clearly defined electron transfer reactions. Cation radicals are likely to be increasingly recognized as intermediates in many well-known organic processes. Moreover, highly colored, stable cation radicals offer convenient tools for quantitative studies in suitable systems.

It is a pleasure to acknowledge the stimulus provided by Professor C. E. H. Bawn, F.R.S., and the invaluable help of the collaborators listed in the references, in the development of this work.

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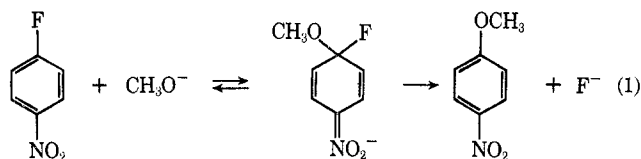
The Base-Catalyzed Halogen Dance, and Other Reactions of Aryl Halides

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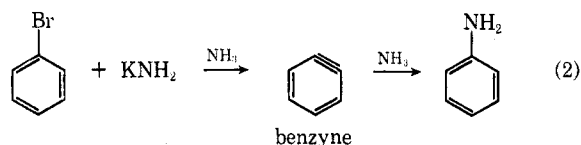
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From textbooks one might conclude that reactions of aryl halides with basic or nucleophilic reagents are relatively few and relatively straightforward. They say that unsubstituted aryl halides are unreactive with nucleophiles under ordinary conditions, which is true. They point out that certain electron-attracting substituents, especially when ortho or para to halogen, greatly facilitate displacement of halogens by the $\text{S}_{\text{N}}\text{Ar}$ mechanism¹ (cf. eq 1). They also teach that with very



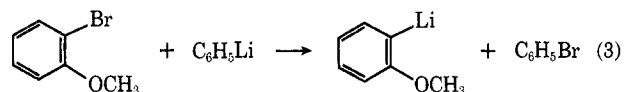
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strong bases aryl halides may react by the aryne mechanism,² as exemplified in eq 2. But that is about all



most have to say.

Presentations which are more advanced and more current also describe the halogen-metal interconversion reaction³ (cf. eq 3), the remarkably facile $\text{S}_{\text{N}}\text{Ar}$ reactions



of hexafluorobenzene and related compounds,⁴ the anal-

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(2) J. D. Roberts, D. A. Semenow, H. E. Simmons, Jr., and L. A. Carlsmith, *J. Amer. Chem. Soc.*, **78**, 601 (1956).

(3) R. G. Jones and H. Gilman, *Org. React.*, **6**, 339 (1951).

(4) J. Burdon, *Tetrahedron*, **21**, 3373 (1965).