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Photochemistry of Aryl Diazonium Salts, Triazoles and Tetrazoles

James Grimshaw
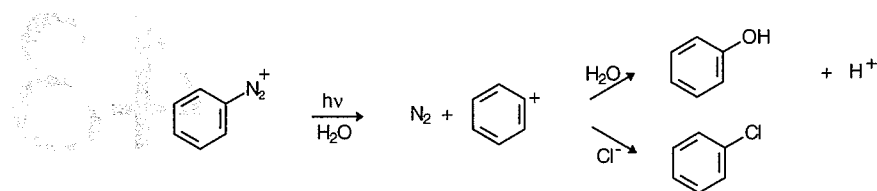*Queen's University of Belfast*

43.1 Introduction

An observation from 1887 noted that solid benzenediazonium nitrate turns rose-red on exposure to sunlight.[1] This sensitivity to light of diazonium salts was exploited in the textile industry as early as 1890 when a process for printing on silk or cotton was devised involving the photo-decomposition, under stencils, of an applied diazonium salt followed by coupling of the residual material with a phenol.[2] Photodecomposition of diazonium salts with loss of nitrogen, followed by coupling of the residual salt with a phenol, forms the basis of the diazo-copying process, which at one time was used extensively for copying large engineering drawings. Some photolithographic processes also utilize the properties of diazonium salts. The research supporting these technical applications led to investigations into the stability to light of aromatic heterocycles having two adjacent nitrogen atoms.[3] From 1959 on, photochemical reactions, which involve the evolution of nitrogen from triazoles, tetrazoles, and related systems began to be examined in detail.
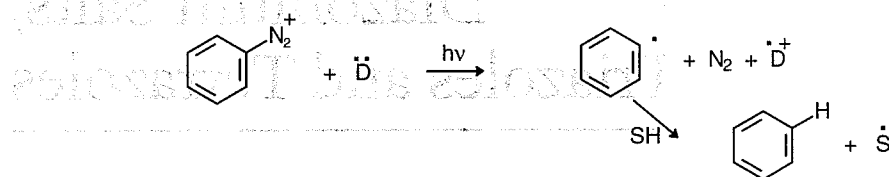
43.2 Arenediazonium Salts

In aqueous solution, diazonium salts show absorption maxima in the ultraviolet (UV) region; benzenediazonium ion has λ_{max} 261 nm (log ε 4.3) and 300 nm (log ε 3.17).[4] Both absorption bands are shifted toward the visible by electron-donating substituents; 4-dimethylaminobenzenediazonium has λ_{max} 382 nm (log ε 4.6).[5] Photolysis in aqueous solution leads to phenol as the main product, according to Scheme 1. Some replacement of the diazonium group by an atom of chlorine or bromine is also found in solutions containing chloride or bromide ions.[6]
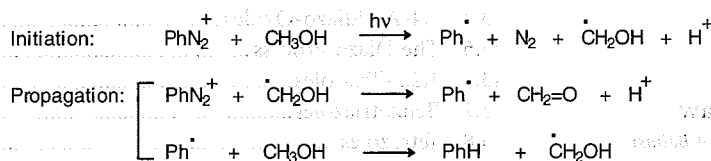
Quantum yields for the photochemical decomposition of aryldiazonium salts in aqueous solution are less than unity. A value of 0.34 has been recorded for decomposition of 4-phenylaminobenzenediazonium
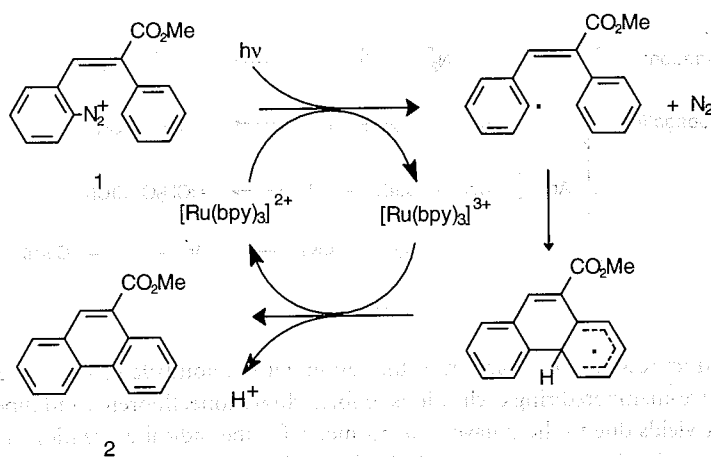
SCHEME 1

SCHEME 2

Initiation: $PhN_2^+ + CH_3OH \xrightarrow{h\nu} Ph^{\bullet} + N_2 + {}^{\bullet}CH_2OH + H^+$

Propagation:
$$\begin{array}{l} PhN_2^+ + {}^{\bullet}CH_2OH \longrightarrow Ph^{\bullet} + CH_2{=}O + H^+ \\ Ph^{\bullet} + CH_3OH \longrightarrow PhH + {}^{\bullet}CH_2OH \end{array}$$

SCHEME 3

on irradiation at 380 nm.[7] Quantum yields of 0.57[8] and 0.97[9] have been noted for the decomposition of 4-dimethylaminobenzenediazonium ions.

The thermal decomposition of aryldiazonium salts also gives phenols, and in a few cases the photochemical processes offer superior yields.[10] Preparation and photodecomposition of diazonium salts in 50% fluoroboric acid has proved useful for the replacement by fluorine in cases where the diazonium salt is exceptionally stable and the usual Schiemann reaction gives poor yields.[11] However the practical problems of avoiding overheating and the eventual screening of light by the reaction product limit the usefulness of these photochemical processes.

The photolysis of benzenediazonium salts in the presence of an electron donor (D) leads to photoelectron transfer according to Scheme 2, followed by carbon–nitrogen bond cleavage to give a phenyl radical. The radical abstracts a hydrogen atom from the solvent (S–H), resulting in overall replacement of the diazonium group by hydrogen. Solvents such as methanol or isopropanol can function as the electron donor but with varying efficiency, depending in the acceptor ability of the diazonium salt.[12] Thus, diazonium salts derived from aminodiphenylamines are decomposed in ethanol to form products derived from the phenyl cation, and photoelectron transfer is not involved.[13] Benzenediazonium salts with less strongly electron-donating substituents (4-methyl or 4-methoxy) afford a mixture of products upon irradiation in methanol because both reaction Schemes 1 and 2 operate. Benzenediazonium salts with electron-withdrawing substituents (4-nitro or 4-chloro) give products only by replacement of the diazonium group by hydrogen.

Quantum yields for the photoelectron transfer process in methanol are generally greater than unity, because the solvent radical takes part in a chain reaction (Scheme 3), the efficiency of which depends on the concentration of the diazonium salt and on the substitution pattern.[14] Quantum yields for decomposition are around 80 for 4-nitrobenzenediazonium (10^{-2} M), 5 for 4-chlorobenzenediazonium (10^{-2} M), and about 2 for 4-methylbenzenediazonium (5×10^{-3} M). Added 2-methyl-2-nitrosopropane acts as a scavenger for phenyl radicals and, under these conditions, the quantum yield for diazonium salt

SCHEME 4

decomposition falls. At the same time, the yield of cation-derived product increases at the expense of radical derived materials. This behavior is probably general but few examples seem to have been recorded.
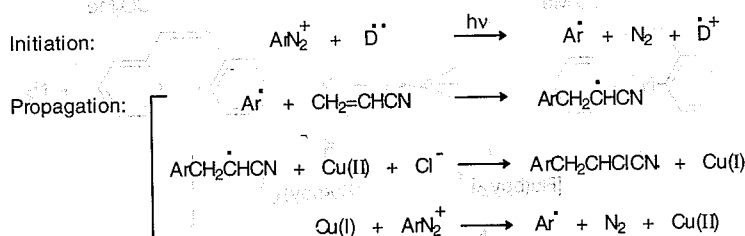
Both the arene cation and the arene radical can be detected using ESR spectroscopy after irradiation of diazonium salts in a glassy matrix at 77 K. The ground state of the phenyl cation bearing an electron donating *para*-substituent is a $(\pi)^5(sp_2)^1$ triplet, and this is easily distinguished from the phenyl radical that may also be formed.[15,16] Phenyl cations in the singlet ground state cannot, of course, be detected by ESR spectroscopy. Irradiation of 4-dimethylaminobenzenediazonium salts at 77 K gives rise to the two reactive intermediates. Warming to 120 K results in gradual decay of the triplet, leaving the radical relatively unaffected. Correlation between the UV and ESR signals allows the absorption at λ_{max} 455 nm to be assigned to the triplet aryl cation.[17]

Other solvents, which lead exclusively to radical derived products from the photolysis of diazonium salts, include formic acid and dimethylformamide. Anions can also act as donors in the photochemical electron transfer process; here, the efficiency increases with decreasing electrochemical oxidation potential of the anion. Tetraphenylboron ion is a good electron donor, while fluoroborate is a poor donor.[18]

Diazonium salts are excellent quenchers of aromatic hydrocarbon triplet states by an electron transfer process. The anthracene radical cation can be detected by UV monitoring as one reaction product after laser flash generation of anthracene triplet in the presence of a diazonium salt.[19] In more concentrated solutions and in the situation where the diazonium and the hydrocarbon are solubilized in aqueous sodium dodecylsulfate micelles, electron transfer occurs from the singlet excited state.[20] A related reaction is electron transfer between the ion pair involving benzenediazonium cation and anthracenesulfonate anion in chloroform, which results in decomposition of the diazonium salt.[21] CIDNP effects during the irradiation of ^{15}N- and ^{13}C-labeled diazonium salts, sensitized by perylene or rubrene, have demonstrated both electron back-transfer within the reaction cage and also escape of both nitrogen and phenyl radicals from the cage.[22,23]

Benzenediazonium salts quench the luminescence of $[Ru(bpy)_3]^{2+}$ by an electron transfer step. The reaction is stoichiometric with no significant back electron transfer from the aryl radical to the resulting Ru(III) complex; however, Ru(III) complexes can be reduced electrochemically to Ru(II). Thus, irradiation of the diazonium salt and $[Ru(bpy)_3]^{2+}$ in the cathode chamber of an electrochemical cell becomes a catalytic process for conversion of the benzenediazonium salt to a phenyl radical.[24]

The photochemical reaction between the diazonium salt **1** and $[Ru(bpy)_3]^{2+}$ produces good yields of the Pschorr-type product **2**, and the process is catalytic; here, the reaction first gives a phenyl radical. This intermediate cyclizes, and then back electron transfer from the cyclized radical to Ru(III) regenerates the catalyst complex (Scheme 4).[25] In contrast, direct photocyclization of **1** in acetonitrile gives poor yields of the phenanthrene. The intermediate in this process now becomes the phenyl cation, and the

Initiation: $ArN_2^+ \;+\; \overset{\cdot\cdot}{D}\; \xrightarrow{\;h\nu\;}\; \overset{\cdot}{Ar} \;+\; N_2 \;+\; \overset{\cdot}{D}{}^+$

Propagation:

$$\overset{\cdot}{Ar} \;+\; CH_2{=}CHCN \;\longrightarrow\; ArCH_2\overset{\cdot}{C}HCN$$

$$ArCH_2\overset{\cdot}{C}HCN \;+\; Cu(II) \;+\; Cl^- \;\longrightarrow\; ArCH_2CHClCN \;+\; Cu(I)$$

$$Cu(I) \;+\; ArN_2^+ \;\longrightarrow\; \overset{\cdot}{Ar} \;+\; N_2 \;+\; Cu(II)$$

SCHEME 5

principal side product results from reaction of the cation with acetonitrile solvent. Attempts to achieve photocatalysis of five-membered ring cyclizations to form fluorenone, fluorene, and dibenzofuran products result in poor yields due to the unfavorable geometry for the radical cyclization step.[26]

The Meerwein reaction between phenyl radicals, thermally generated from arenediazonium salts, and alkenes in the presence of copper(I) ions can also be initiated photochemically. Irradiation of the diazonium salt in the presence of copper(II) ions leads to photoelectron transfer and the generation of phenyl radicals. Addition of the radical to an alkene bond becomes a chain reaction mediated by copper ions according to Scheme 5. Quantum yields for the evolution of nitrogen are in the region of 700.[27]

Photodecomposition of some *ortho*-substituted aryldiazonium ions leads to unusual reaction products due to hydrogen atom transfer between the *ortho*-substituent and the radical center derived by loss of nitrogen from the diazonium ion. Thus, 2-diethylaminobenzenediazonium salts yield *N*-ethylaniline via the intermediate **3**. Deuterium is not incorporated into the benzene ring from either D_2O or CD_3OD.[28] Decomposition of the diazonium salt **4** leads to a benzocyclobutene as the principal product. The influence of the nitro substituent is important, because the un-nitrated diazonium salt is decomposed to give a phenol in the normal manner.[29]
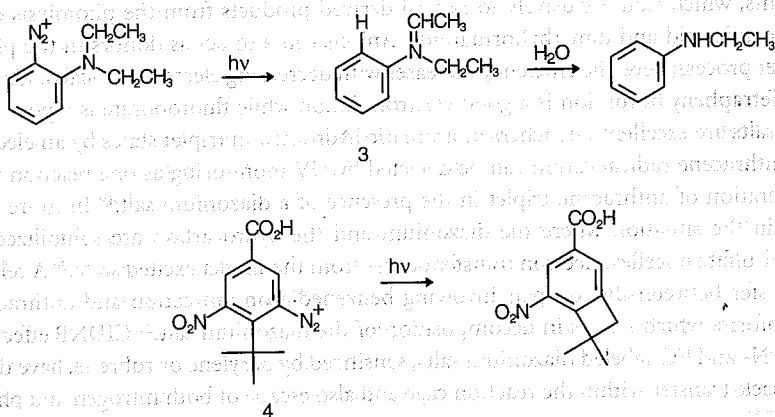

Diazonium salts, relatively stable to heat, have been used as photoinitiators in polymerization processes. Both phenyl cations and radicals generated during the illumination stage will initiate polymerization of vinyl ethers and the crosslinking of low-molecular-weight polymers with reactive alkene substituents.[30]
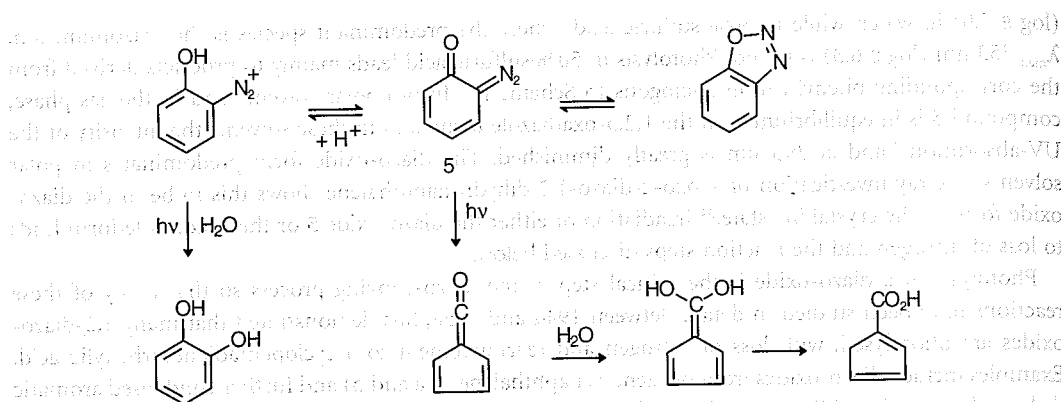
43.3   1,2-Arenediazo-Oxides

The 2-hydroxybenzenediazonium ion is in acid-base equilibrium ($pK_a = 1.14$)[31] with 2-diazocyclohexa-3,5-dien-1-one **5** (the diazo-oxide form). Diazo-oxides show absorption maxima at longer wavelengths than the corresponding diazonium salt form. Thus, 1-diazo-2-oxo-1,2-dihydrobenzene has λ_{max} 395 nm

(log ε 7.0) in water, while in 50% sulfuric acid, where the predominant species is the diazonium ion, λ_{max} 353 nm (log ε 6.3) is found. Photolysis in 50% sulfuric acid leads mainly to products derived from the corresponding phenyl cation analogous to Scheme 1.[32] In nonpolar solvents and in the gas phase, compound **5** is in equilibrium with the 1,2,3-oxadiazole form, and in these solvents the intensity of the UV-absorption band at 395 nm is greatly diminished. The diazo-oxide form predominates in polar solvents.[33] X-ray investigation of 1-oxo-2-diazo-1,2 dihydronaphthalene shows this to be in the diazo-oxide form in the crystalline state.[34] Irradiation of either the diazo-oxide **5** or the oxadiazole form leads to loss of nitrogen and the reaction steps discussed below.

Photolysis of a diazo-oxide is the critical step in the diazo-copying process so that many of these reactions have been studied in detail. Between 1944 and 1958, Süs demonstrated that many 1,2-diazo-oxides are photolysed, with loss of nitrogen and rearrangement to a cyclopentadienecarboxylic acid. Examples include diazo-oxides from benzene **5**, naphthalene **6** (a and b) and further condensed aromatic hydrocarbons,[35–38] pyridine, quinoline **8**, benzotriazole and benzimidazole derivatives.[36,39] Süs ascribed structures to the products in which the alkene bond was not conjugated to the carboxyl group. Modern work with benzene and naphthalene derivatives indicates that the products have the conjugated enecarboxylic acid form. The conversions proceed with high quantum yield for the naphthalene diazo-oxides where $\Phi = 0.72$.[40] In an acidic pH range, some diazonium salts can couple rapidly with the corresponding cyclopentadienecarboxylic acid, leading to products such as **9**.
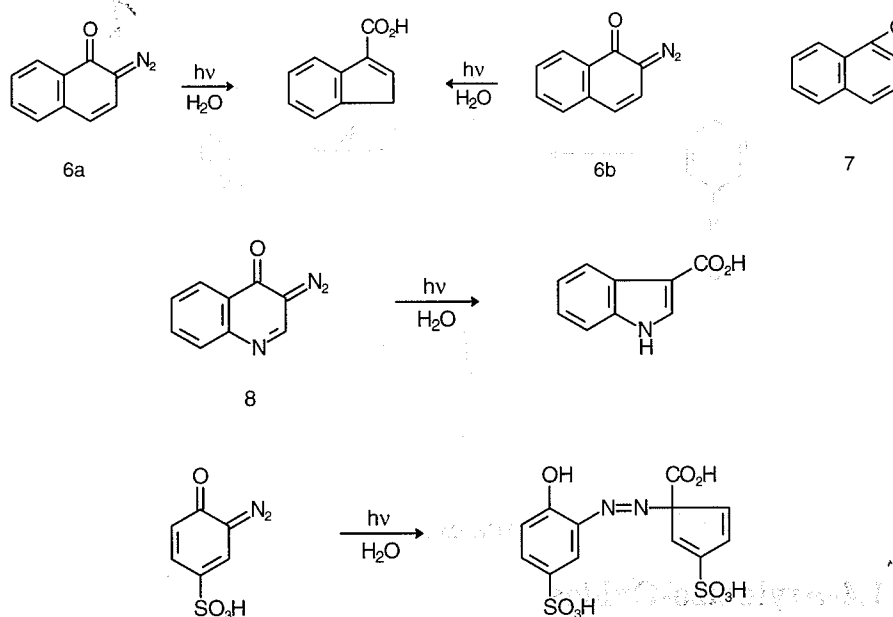
Fast-reaction techniques, employing laser flash excitation followed by UV monitoring of the reaction, show that photolysis of diazo-oxides derived from benzene[41] and naphthalene[42] follows the course illustrated in Scheme 6 for the benzene series. In aqueous solution, only the ketene and the ketene hydrate are observed as short-lived intermediates.[43] Rates of the intermediate reactions have been followed over a large pH range and show the expected profiles due to acid-base catalysis. Photolysis within a film of Novolak-resin shows evidence for the short-lived carbene intermediate, and it has been proposed that this species is stabilized as the oxirene form.[44] However, photolysis of the ¹³C-labeled naphthalene derivatives cannot involve an oxirene intermediate **7** as no scrambling of the ¹³C label is observed in the products.[45]
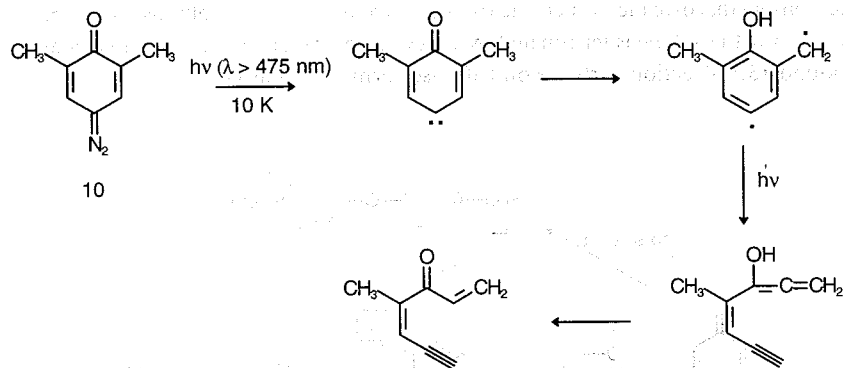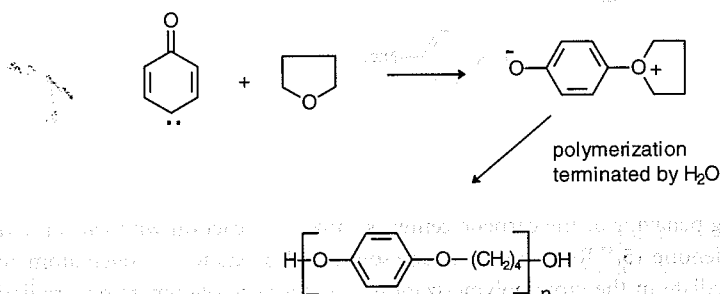
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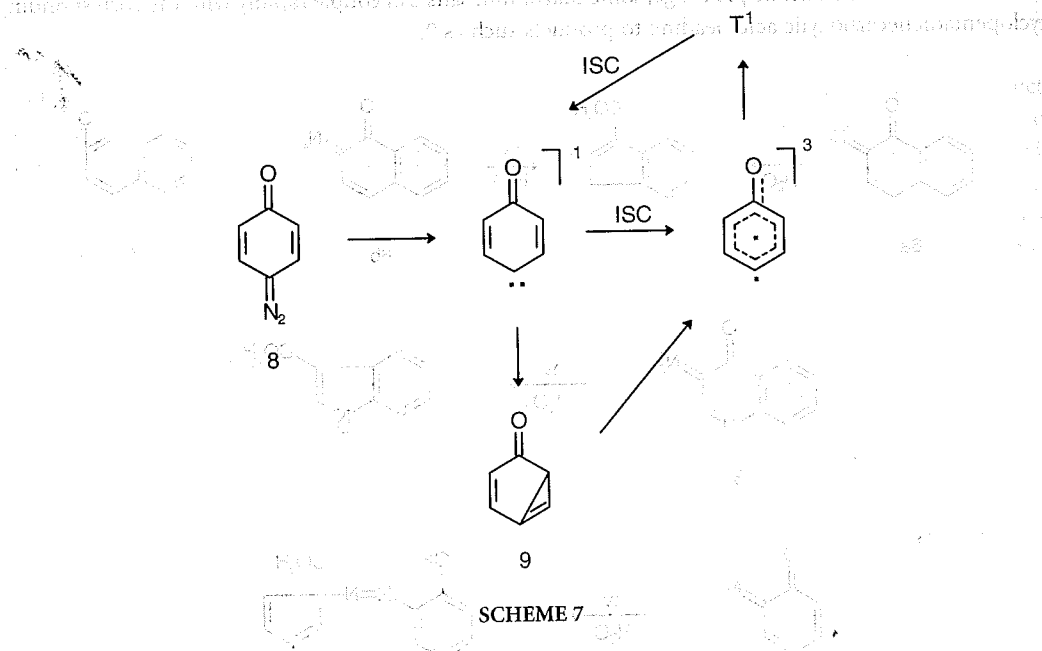
SCHEME 7

43.4   1,4-Aryldiazo-Oxides

The 4-hydroxybenzenediazonium ion is a strong acid that exists in polar and nonpolar solvents as the conjugate base form, 4-diazocyclohexa-2,5-dienone (the 1,4-diazo-oxide) with λ_{max} 342 nm (log ε 4.47) and 448 nm (log ε 1.80).[46] The 1,4-naphthalenediazo-oxides are also well known. Spectroscopic data indicate considerable interaction between the carbonyl and diazo functions in these molecules.[47] Irradiation of 1,4-diazo-oxides follows the course indicated in Scheme 7 for 1,4-benzenediazo-oxide **8**. Loss of nitrogen affords a singlet carbene, which is transformed by ISC into the more stable triplet form. These triplet carbenes have been characterized by spectroscopy in an argon matrix[48] and show an infrared (IR) carbonyl stretching frequency in the range 1550 to 1518 cm^{-1}, indicating considerable delocalization of one electron into the carbonyl function. The triplet has an adsorption maximum in the UV close to that of the parent diazo-oxide. Further irradiation to the T^1 state is followed by ISC and collapse to the short-lived singlet state. The singlet converts either to the triplet or to the bicyclohexadienone **9**. Thus, a photostationary state is established between the triplet and **9**. Isomer **9** can be isolated in an argon matrix

SCHEME 8

SCHEME 9

and on warming collapses to the triplet carbene.[48,49] Exceptions to this scheme are found with diazo-oxides having a methyl group adjacent to the carbonyl function. Within an argon matrix, the triplet carbene from **10** reacts by hydrogen atom transfer and collapse of the resulting biradical to an open chain structure (Scheme 8).[50]

Preparative scale photochemical reactions of 1,4-diazo-oxides yield products expected from an electrophilic carbene intermediate. The singlet carbene is stabilized in polar solvents.[51] It reacts with primary alcohols as an electrophile, giving the corresponding hydroquinone mono-ether.[52] With isopropanol, and probably other secondary alcohols, hydrogen atom abstraction occurs, giving the phenoxyl radical.[53]
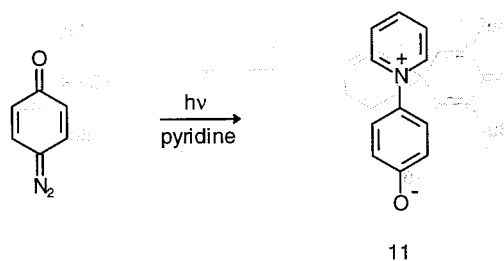
The electrophilic behavior of these carbene intermediates is also shown by their reactions with pyridine and with cyclic ethers as electron donors. Pyridine forms betaines of the type **11**, which are strongly colored.[54] In 1956, Süs noted the formation of strongly colored photoproducts with pyridine but assumed these to be C-substituted rather than N-substituted pyridines. Reaction with tetrahydrofuran produces a 1:1 copolymer, which probably arises by the mechanism shown in Scheme 9.[55] The photopolymerization

of solid 1,4-benzenediazo-oxide, which yields the polyether **12**, probably also proceeds in a similar manner. Reaction with oxetane is terminated by a Stevens rearrangement of the intermediate ylide to the spiro-compound **13**.[56] Reaction with acetonitrile also forms an ylide **14**.
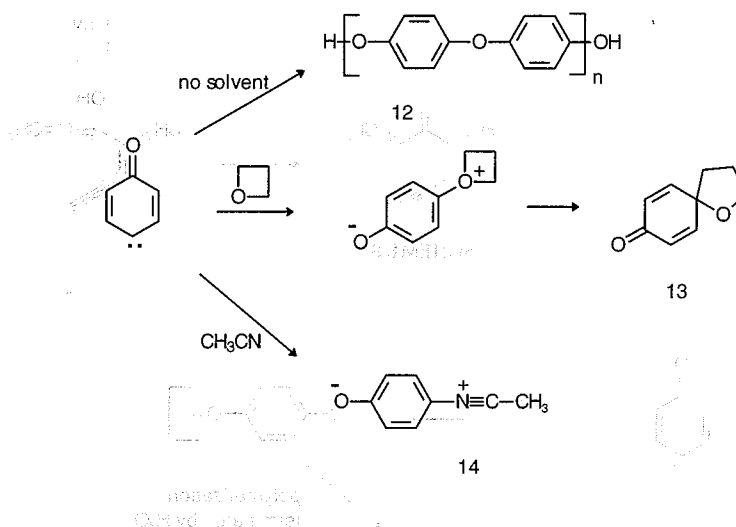
The atom abstracting behavior of the carbene center is shown by reaction with carbon tetrachloride to form the cyclohexadienone **15**.[57] Reactions in alkane solvents also lead to hydrogen atom abstraction, and this step is intermediate in the cross polymerization of piperylene oligomers by irradiation in the presence of 1,4-benzenediazo-oxide.[58]
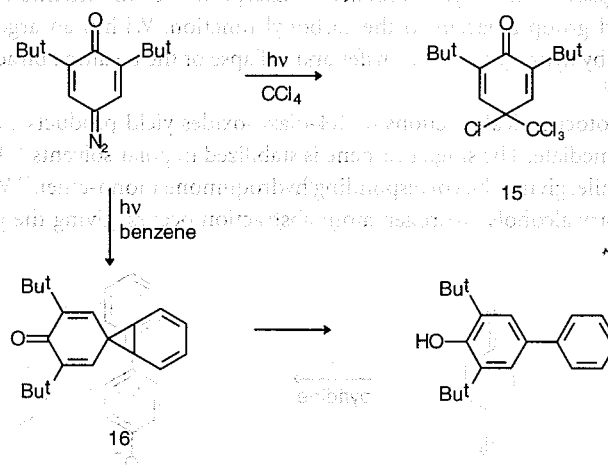
Photodecomposition of 1,4-benzenediazo-oxides in benzene or toluene leads to diphenyl derivatives. Reaction with benzene and with perdeuteriobenzene has been shown to proceed via a tricyclic intermediate **16**.[59] Preparative scale reaction between benzene-1,4-diazo-oxide and toluene led to the isolation of only two products, 4-hydroxy-2′-methyl- and 4-hydroxy-4′-methyl-biphenyl. Presumably the presence of a third isomer was not recognized at the time.

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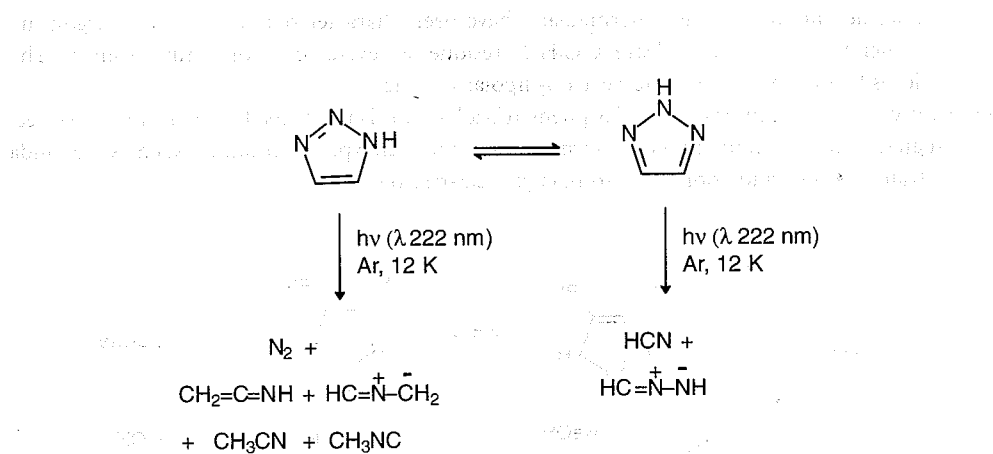
43.5 The Diazo Process

Photochemical decomposition of diazonium salts is the key step in a reprographic process once much used with large-scale engineering drawings. Both the Xerox reprographic systems and computer drawing programs have rendered the diazo process much less important than it formally was. Photoresist lacquers used in the manufacture of printed circuit boards employ variations of the diazo process. The earliest process, developed in 1890, used primuline as the source of the diazonium salt.[2] Cloth or paper was coated with primuline and then diazotized *in situ*. Exposure to light through a stencil left a positive image in the undecomposed diazonium compound. This image was developed in an alkaline phenol solution.

Kalle A-G of Wiesbaden developed the first commercially successful process.[60] It is often referred to as the Kögel process (from the author's name attached to the U.S. patent).[61] The Kögel process uses paper coated with both a diazo-oxide and a phenolic component, and the coating is made faintly acidic to slow down coupling of the two components while increasing the shelf life of the material. After exposure to a strong light, a positive image forms by decomposition of the diazo component, and development is achieved by exposing the paper to ammonia vapor when the remaining diazo component couples with the phenol. The usual diazo-oxide employed is a 2-diazo-1-oxo-1,2-dihydronaphthalene bearing a sulfonic acid substituent. Various phenols have been used to give images of different colors. This process has the great advantage that it requires no aqueous solutions; the final prints are dry and are immediately usable.

The Chemische Fabrick L. van der Grinten, of Venlo devised an alternative system,[62] known as a one-component system, that uses paper coated with a stabilized diazonium salt, but no phenol. Coupling is achieved after exposure by developing the paper in an alkaline solution of a phenol. The original diazonium salt used was 4-diethylaminobenzenediazonium associated with a complex anion. Choice of the phenolic component allowed modification of the color of the final image.

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43.6 1,2,3-Triazoles

1,2,3-Triazoles with no substituent on nitrogen exist in a rapid tautomeric equilibrium between the *1H* and *2H* forms (Scheme 10). An independent photolysis pathway exists for each tautomer. For the parent

triazole molecule, the first formed intermediates have been characterized at 12 K in an argon matrix. The *1H* isomer loses nitrogen to leave a C_2H_3N residue as several interconverting isomers. The *2H* tautomer loses hydrogen cyanide to leave a 1,3-dipolar residue.[63]

Preparative-scale photolysis of 4- and 5-phenyltriazoles affords products derived from related reactive intermediates.[64] The recombination of intermediates to form unexpected products such as the imidazole 17 is illustrated by the irradiation of 4,5-diphenyl-1,2,3-triazole.
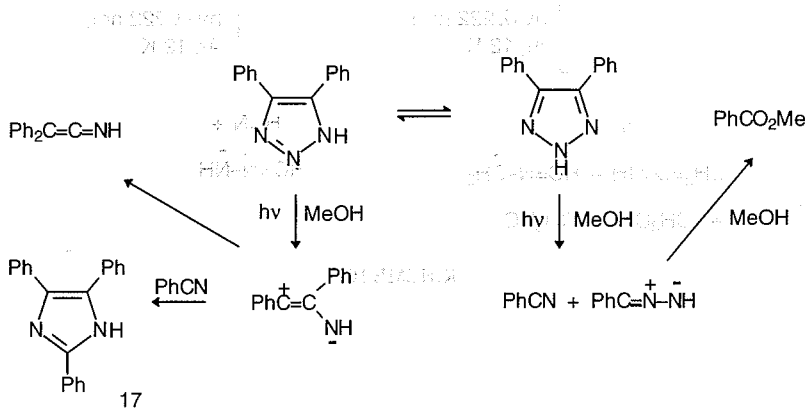
1-Phenyl-1,2,3-triazoles **18** do not show this tautomeric equilibrium, and photolysis leads only to the loss of nitrogen. The residual biradical is usually represented as a carbene. It is in equilibrium with an aziridine form, and the reverse equilibrium leads to a mixture of two isomeric carbenes. Two competing reactions then lead to the stable products. First, Wolff rearrangement of the carbene yields a ketene imide. Second, cyclization of the carbene center onto the phenyl group leads to an indole. Two isomeric indoles may be isolated because of rearrangement of the carbene via the aziridine.[65] Ring opening of the aziridine reactive intermediate favors formation of a carbene with an electron-withdrawing group on the carbene carbon center; thus, whereas photolysis of **19** gives two indoles via this carbene rearrangement, reaction of **20** leads to only one indole product. Photolysis of 1,5-diphenyl-1,2,3-triazole gives both 2- and 3-phenylindoles due to interconversion of the carbene intermediates via an aziridine.[66]

19

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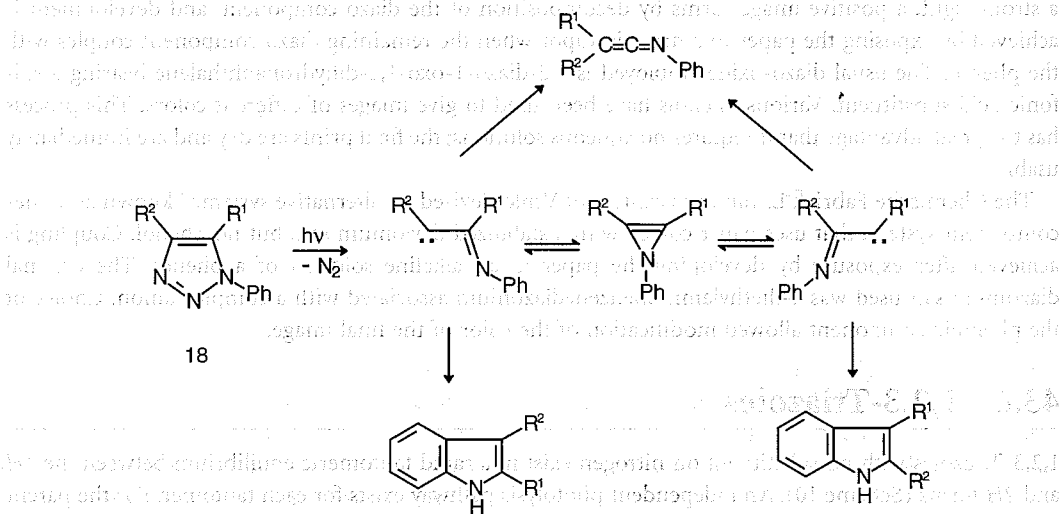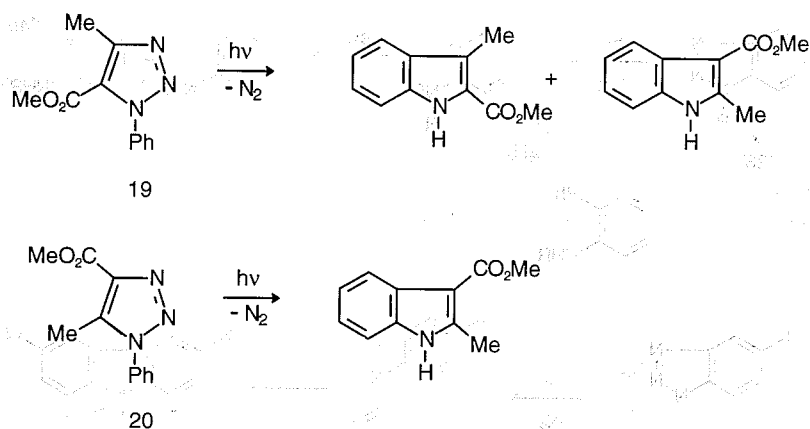
The relative rates of Wolff rearrangement and cyclization to the indole depend on the substituent pattern. Fast rearrangement of hydrogen and trimethylsilyl groups in position 5 of the triazole ring is observed so that no indole product can be detected in these reactions. With a phenyl substituent in position 5, both the Wolff rearrangement and cyclization to the indole are observed.[66,67] Photolysis of **21** gives products mainly via the Wolff rearrangement.[68]

Photolysis of 1-tosylamino-1,2,3-triazole anions leads to loss of two molecules of nitrogen and the generation of an alkyne. Strained cycloalkynes, for example **22**, have been generated in this way and trapped as Diels–Alder type adducts.[69]

21

22
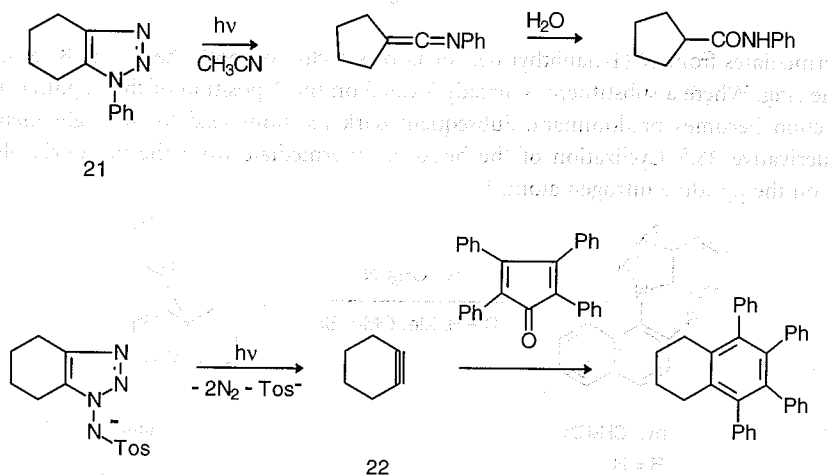
43.7   Benzotriazoles

Photolysis of benzotriazoles **23** leads to loss of nitrogen and generation of a 1,3-biradical intermediate. When R = H or alkyl, the intermediate attacks a solvent molecule as shown.[70,71] Photolysis of 1-phenyl-benzotriazoles at room temperature takes a different course. An intramolecular radical insertion step leads to a carbazole in good yields.[67,71] Reaction of the dichloro compound **24** gives only one dichloro-carbazole, indicating that the intermediate biradical does not undergo rapid ring closure to give **25** followed by three-membered ring opening. The ESR spectrum of the biradical from 1-phenylbenzotri-azole at 77 K is consistent with a triplet ground state, which converts to the singlet and then rapidly cyclizes to carbazole.[72]
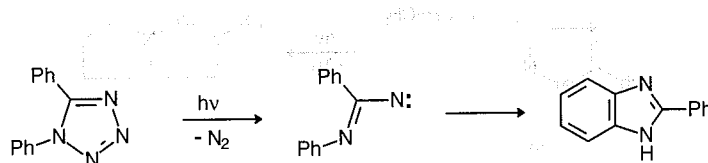
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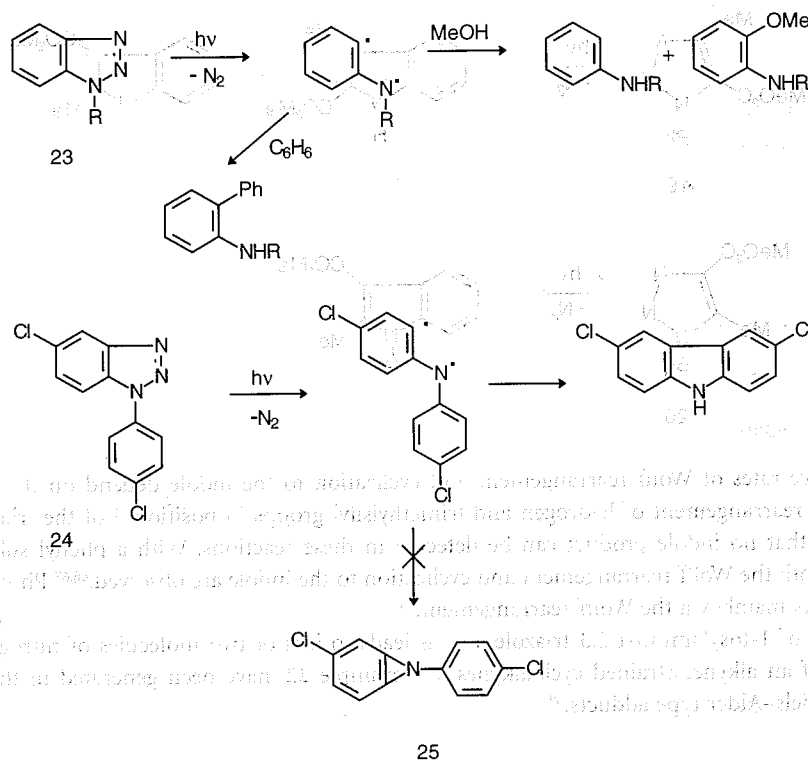
The intermediates from *N*-(1-naphthyl)benzotriazoles cyclize on both the 2- and 8ª-positions of the naphthalene ring. Where a substituent is already located on the 2-position of the naphthalene ring, this second reaction becomes predominant. Subsequent dark reactions lead to the eight-membered ring carbazole derivative **26**.[73] Cyclization of the biradical intermediate from the benzotriazole **27** occurs principally on the pyridine nitrogen atom.[74]


26

27   70%   10% yield
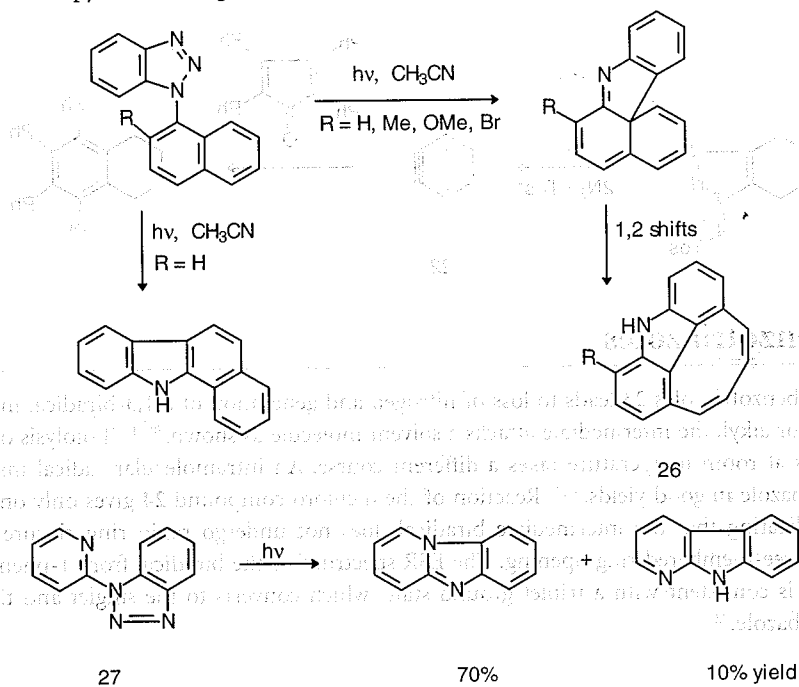
43.8 Tetrazoles

1,5-Disubstituted tetrazoles lose nitrogen on photolysis to generate a biradical intermediate, usually formulated as the nitrene (for example, **28**). Benzimidazoles are formed from 1-phenyltetrazoles by cyclization of the intermediate onto the *N*-phenyl ring.[75,76] Where an *N*-vinyl group is present, cyclization occurs on the vinyl group to form an imidazole. Photoreaction of **29** shows a competition between expulsion of a molecule of nitrogen and electrocyclization to **30**, which generates a new six-membered ring.[77]
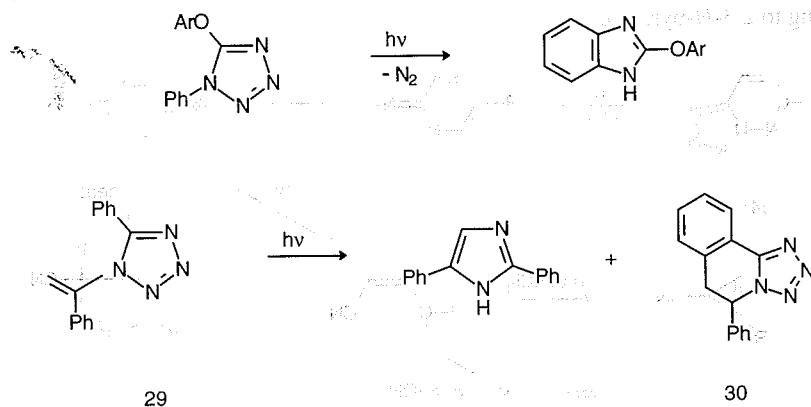

3,5-Disubstituted tetrazoles are photolysed to nitrilimines with loss of nitrogen. Nitrilimines are short lived at room temperature and can be trapped by 1,3-dipolar addition to an alkene or alkyne.[78] 1,3-Diphenylnitrilimine **31** has been characterized by matrix isolation at 10 K.[79] Prolonged irradiation of the nitrilimine under these conditions leads to conversion to diphenylcarbodiimide and benzonitrile. Intramolecular addition of nitrilimines to an alkene bond in **32** or the alkyne bond in **33** has been used to generate five- and six-membered rings.[80,81]

32

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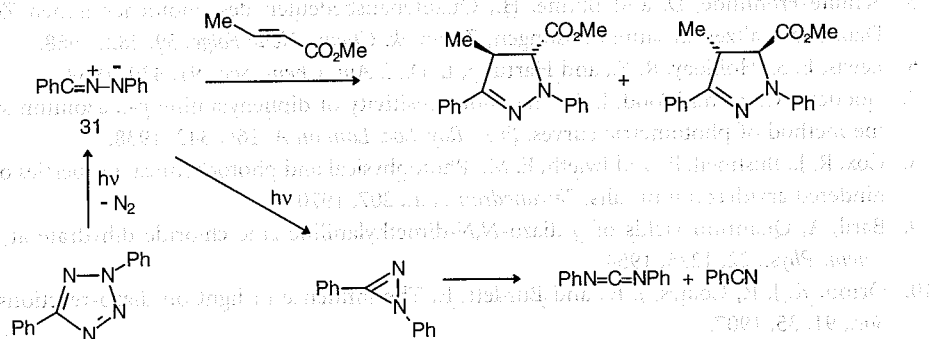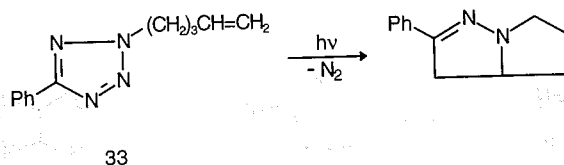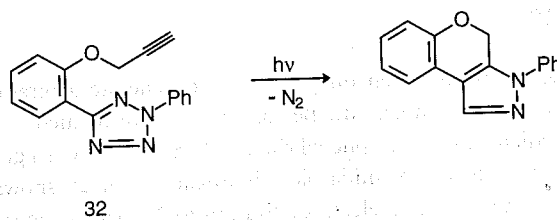
Tetrazolo[1,5-*b*]pyridazines **34** also lose nitrogen on photolysis. In these cases, the intermediate biradical rearranges to a diazonitrile. This molecule also loses nitrogen on exposure to light to leave a carbene from which the final stable products are generated. Electrocyclization of the diazonitrile is a competing reaction leading to a 3-*H*-pyrazole **35**:[82]

34   **35**
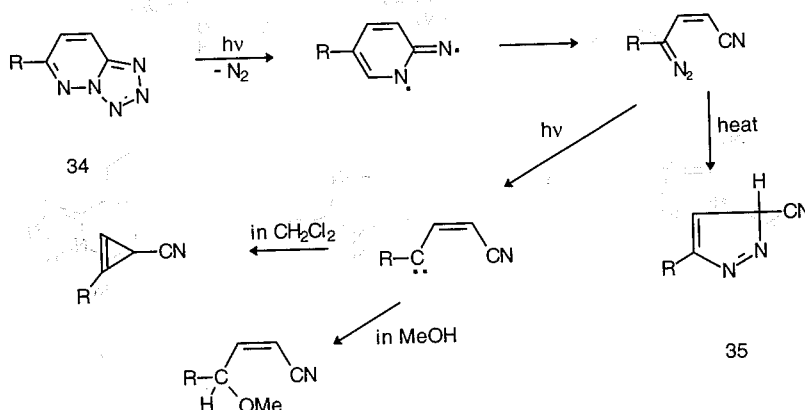
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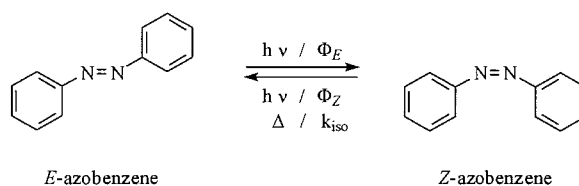
FIGURE 89.1 $E \rightarrow Z$ and $Z \rightarrow E$ isomerization of azobenzene by light (hv) with quantum yields Φ_E and Φ_Z, respectively, and $Z \rightarrow E$ isomerization by heat (Δ) with the rate constant k_{iso}.
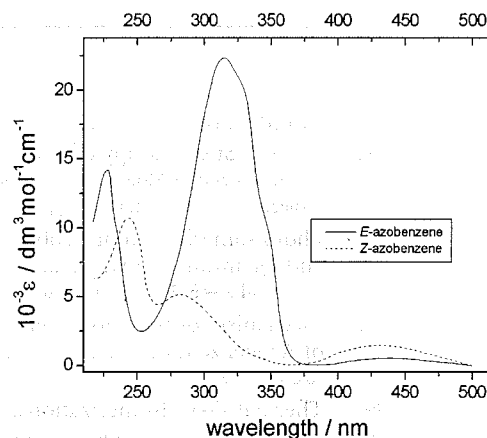

FIGURE 89.2 Absorption spectra of E- and Z-azobenzene in ethanol. (Adapted from Jaffé, H.H. and Orchin, M., *Theory and Applications of Ultraviolet Spectroscopy*, John Wiley & Sons, New York, 1962.)

In the following section, the UV/VIS spectroscopy of azobenzenes, the knowledge of which is a prerequisite for photochemical isomerization reactions, is described. Conditions and quantum yields of the photoisomerization will be dealt with in Section 89.3 for the azobenzene molecule and some of its derivatives. The mechanism of these simple light-induced unimolecular reactions (i.e., the dynamics of molecular changes) has only recently been studied directly by means of experimental laser spectroscopy methods. The results obtained thus far are summarized and compared with conclusions from quantum chemical calculations in Section 89.4. Thermal $Z \rightarrow E$ isomerization reactions influence the concentration ratio of E- and Z-isomers in the photostationary state on irradiation of azobenzenes. They are described separately in Section 89.5. Finally, a selection of interesting prospective applications of the photoisomerism of azobenzenes is presented in Section 89.6.

89.2 UV/VIS Spectroscopy of Azobenzenes

Rau classified azobenzenes as azobenzene-type, aminobenzene-type, and pseudostilbene-type molecules according to their UV/VIS spectra, based on different energies for the transitions of n- and π-electrons into the π^*-obitals.[2,3]

Azobenzene-Type Molecules

The stable E-isomer of the parent molecule azobenzene shows a low-intensity n$\rightarrow$$\pi^*$ band (λ_{max} = 444nm/ $\varepsilon \approx 440$ dm^{3}mol^{-1}cm^{-1}) in the visible (VIS) and a high-intensity $\pi \rightarrow \pi^*$ band (λ_{max} = 316 nm/$\varepsilon \approx 22\,000$) in the UV[5] (see Figure 89.2). The bands are well separated. Changes in the substitution on azobenzene by various groups, except for an amino group, and changing the solvent have only minor effects.

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