

PHOTOCHEMISTRY

The role of light in effecting chemical change has been recognized for many years. Indeed, the connection between solar energy and the biosynthesis of plant carbohydrates from carbon dioxide and water was known by the early 1800's. Yet organic photochemistry was slow to develop as a well-understood and manageable science. Progress only became rapid following the development of spectroscopy and spectroscopic techniques for structure determination and the detection of transient species. For this reason photochemistry for many years was the domain of physical and theoretical chemists. Their work laid the foundation for modern organic photochemistry, which correlates the nature of excited electronic states of molecules with the reactions they undergo.

Quite apart from the unparalleled importance of photosynthesis, photochemical reactions have a great impact on biology and technology, both good and bad. Vision in all animals is triggered by photochemical reactions. The destructive effects of ultraviolet radiation on all forms of life can be traced to photochemical reactions that alter cellular DNA, and the harmful effects of overexposure to sunlight and the resulting incidence of skin cancer are well established. The technical applications of photochemistry are manifold. The dye industry is based on the fact that many organic compounds absorb particular wavelengths of visible light, and the search for better dyes and pigments around the turn of this century was largely responsible for the development of synthetic organic chemistry. Dye chemistry has helped establish the relationship between chemical structure and color, which also is important in color printing and color photography. We cover these important applications of photochemistry only briefly in this chapter, but we hope to convey some understanding of the fundamentals involved.

Most photochemical reactions can be considered to occur in three stages:

1. *Absorption of electromagnetic radiation* to produce electronically excited states.
2. *Primary photochemical reactions* involving excited electronic states.
3. *Secondary or dark reactions* whereby the products of the primary photochemical reaction are converted to stable products.

We shall begin with a closer look at electronic excitation, some aspects of which were discussed in Section 9-9. Because transfer of electronic energy from one molecule to another is a basic process in photochemistry, we will discuss energy transfer also before giving an overview of representative photochemical reactions. The closely related phenomena of chemiluminescence and bioluminescence then will be described. Finally, there will be a discussion of several important applications of photochemistry.

28-1 LIGHT ABSORPTION, FLUORESCENCE, AND PHOSPHORESCENCE

Electromagnetic radiation in the ultraviolet and visible region spans a wavelength range of about 800–100 nm corresponding to energies of 36–286 kcal mole⁻¹. Absorption of such radiation by molecules is not to be regarded as equivalent to simple excitation by thermal energy of 36–286 kcal mole⁻¹. Instead, all the energy of the light quantum is taken up in excitation of an electron to a high-energy, usually antibonding, orbital (Section 9-9). An important point about such processes is that they occur more rapidly than the atoms vibrate in the bonds (**Franck-Condon principle**). The short transition time of an electron between ground and excited states is in complete contrast to what happens during absorption of a quantum of radio-frequency energy in nmr spectroscopy, wherein the absorption process may be slow compared to chemical reactions (Section 27-1). Therefore an electronically excited molecule is, in the first instant that it is produced ($<10^{-13}$ sec), just like the ground-state molecule as far as *positions* and *kinetic energies* of the atoms go, but has a very different electronic configuration. What happens at this point depends on several factors, some of which can be best illustrated by energy diagrams of the type used previously (Section 21-1). We shall consider diatomic molecules, but the argument can be extended to more complicated systems.

Consider Figure 28-1, which shows schematic potential-energy curves for a molecule A—B in the ground state (A—B) and in excited electronic states (A—B)*. We have noted previously (Section 6-1) that in the ground states of most molecules all electrons are *paired*; excited states also can have all electrons paired. Such states with paired electrons are called **singlet** states. But, because the bonding is *weaker* in excited states, the average bond length

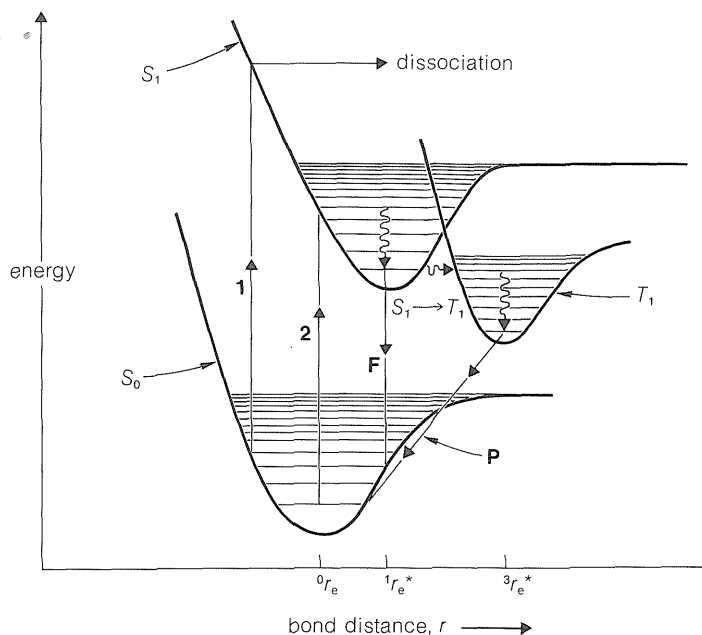


Figure 28-1 Schematic potential-energy diagram for ground and excited electronic states of a diatomic molecule A—B. The horizontal lines represent vibrational energy levels (Section 9-7). Absorption of a photon induces a transition from ground-state singlet to excited singlet ($S_0 \longrightarrow S_1$). Transition 1 leads to dissociation. Transition 2 leads first to *vibrational relaxation* (wavy line) and then to emission ($S_1 \longrightarrow S_0$) corresponding to transition **F** (fluorescence). Alternatively, the excited singlet S_1 may cross over to the triplet state nonradiatively ($S_1 \longrightarrow T_1$, wavy line). Emission from the triplet state to the ground state ($T_1 \longrightarrow S_0$) corresponds to transition **P** (phosphorescence). (In this figure the T_1 curve has been displaced to the right for clarity. In a more accurate drawing the **P** transition would be nearly vertical.)

r_e between the nuclei is *greater* in the excited state than in the ground state. For this reason the upper curve (S_1) in Figure 28-1 is displaced toward a larger average bond length relative to the lower or ground-state curve (S_0).

Excited states also can have *unpaired* electrons. States with two unpaired electrons are called **triplet** states (T) and normally are more stable than the corresponding singlet states because, by Hund's rule, less interelectronic repulsion is expected with unpaired than paired electrons (Sections 6-1 and 21-9A). (For clarity, the potential-energy curve for the excited triplet state (T_1) of A—B is given an unrealistically long equilibrium bond distance, which puts it to the right of the curve for the S_1 state in Figure 28-1.) The electronic configurations for ground singlet (S_0), excited singlet (S_1), and triplet (T_1) states of the σ electrons of a diatomic molecule are shown in Figure 28-2. This diagram will be helpful in interpreting the transitions between S_0 , S_1 , and T_1 states shown in Figure 28-1, and which we will now discuss in more detail.

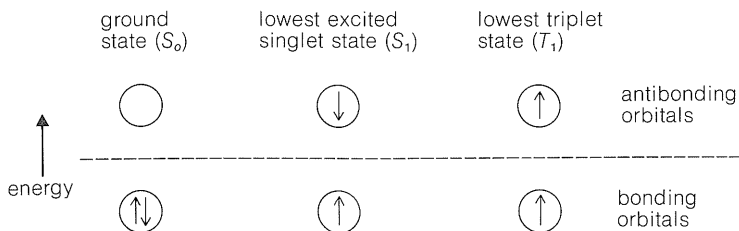


Figure 28-2 Schematic representation of the electronic configurations of ground and lowest excited singlet and triplet states of a diatomic molecule with two σ electrons

When a molecule absorbs sufficient radiant energy to cause electronic excitation, the *spin* of the excited electron remains *unchanged* in the transition. That is to say, ground-state molecules with paired electrons (S_0) give excited states with paired electrons (S_1), not triplet states (T_1). The transition marked **1** in Figure 28-1 corresponds to a singlet-singlet ($S_0 \rightarrow S_1$) transition from a relatively high vibrational level of $A-B$. The energy change occurs with no change in r (Franck-Condon principle), and the electronic energy of the $A-B^*$ molecule so produced is seen to be *above* the level required for dissociation of $A-B^*$. The vibration of the excited molecule therefore has no restoring force and leads to dissociation to A and B atoms. In contrast, the transition marked **2** leads to an excited vibrational state of $A-B^*$, which is not expected to dissociate but can lose vibrational energy to the surroundings and come down to a lower vibrational state. This is called “vibrational relaxation” and usually requires about 10^{-12} sec. The vibrationally “relaxed” excited state can return to ground state with emission of radiation (transition F, $S_1 \rightarrow S_0$); this is known as **fluorescence**, the wavelength of fluorescence being different from that of the original light absorbed. Normally, fluorescence, if it occurs at all, occurs in 10^{-9} to 10^{-7} sec after absorption of the original radiation.

In many cases, the excited state (S_1) can return to the ground state (S_0) by *nonradiative* processes. The most important processes are:

1. By chemical reaction, often with surrounding molecules. This process forms the basis of much organic photochemistry, which will be described in a later section.

2. By transfer of its excess electronic energy to other molecules. This kind of energy transfer also is a very important aspect of photochemistry, and we shall return to it shortly.

3. By decay through a lower energy state. If, for example, the potential-energy curves for the upper and lower singlet states were closer together than shown in Figure 28-1, they may actually cross at some point, thus providing a pathway for S_1 to relax to S_0 without fluorescing. But what about decay of S_1 through the triplet state (T_1)?

Conversion of a singlet excited state to a triplet state ($S_1 \longrightarrow T_1$) is energetically favorable but usually occurs rather slowly, in accord with the spectroscopic selection rules, which predict that spontaneous changes of electron spin should have very low probabilities. Nonetheless, if the singlet state is sufficiently long-lived, the singlet–triplet change, $S_1 \longrightarrow T_1$, (often called **intersystem crossing**) may occur for a very considerable proportion of the excited singlet molecules.

The triplet state, like the singlet state, can return to the ground state by nonradiative processes, but in many cases a radiative transition ($T_1 \longrightarrow S_0$) occurs, even though it has low probability. Such transitions result in emission of light of considerably longer wavelength than either that absorbed originally or resulting from fluorescence. This type of radiative transition is called **phosphorescence** (transition **P** in Figure 28-1). Because phosphorescence is a process with a low probability, the T_1 state may persist from fractions of a second to many seconds. For benzene at -200° , the absorption of light at 254 nm leads to fluorescence centered on 290 nm and phosphorescence at 340 nm. The half-life of the triplet state of benzene at -200° is 7 sec.

28-1A The Carbonyl Group

In previous discussions of electronic absorption spectra (Section 9-9), we have identified two different kinds of transitions in the spectra of simple carbonyl compounds such as 2-propanone or methanal. One involves excitation of an electron in a nonbonding n orbital on oxygen to an antibonding (π^*) orbital of the carbon–oxygen double bond (an $n \longrightarrow \pi^*$ transition), and the other involves excitation of an electron in the bonding (π) orbital to the corresponding antibonding orbital (a $\pi \longrightarrow \pi^*$ transition). These changes are shown for methanal in Figure 28-3. Besides the transitions already discussed, methanal shows strong absorption at 175 nm, which possibly is $n \longrightarrow \sigma^*$, or else $\sigma \longrightarrow \sigma^*$.

Although the $n \longrightarrow \pi^*$ and $\pi \longrightarrow \pi^*$ transitions of Figure 28-3 are singlet–singlet transitions, each of the two singlet excited states produced has a corresponding triplet state. Accordingly, there are *four* easily accessible excited states of a carbonyl group—the $n \longrightarrow \pi^*$ singlet (S_1), $n \longrightarrow \pi^*$ triplet (T_1), $\pi \longrightarrow \pi^*$ singlet (S_2), and $\pi \longrightarrow \pi^*$ triplet (T_2). The energies of these electronic states for methanal decrease in the order $S_2 > T_2 > S_1 > T_1$, although this ordering may not hold for all carbonyl compounds.

As we shall see, $n \longrightarrow \pi^*$ singlet and triplet states of carbonyl compounds play an important role in photochemistry. Aldehydes and ketones display all the characteristics of absorption, fluorescence, phosphorescence, and intersystem crossing ($S_1 \longrightarrow T_1$) illustrated in Figure 28-1. Generally, they are more efficient at intersystem crossing than are unsaturated hydrocarbons, perhaps because the energies of the S and T states involved are not widely different.

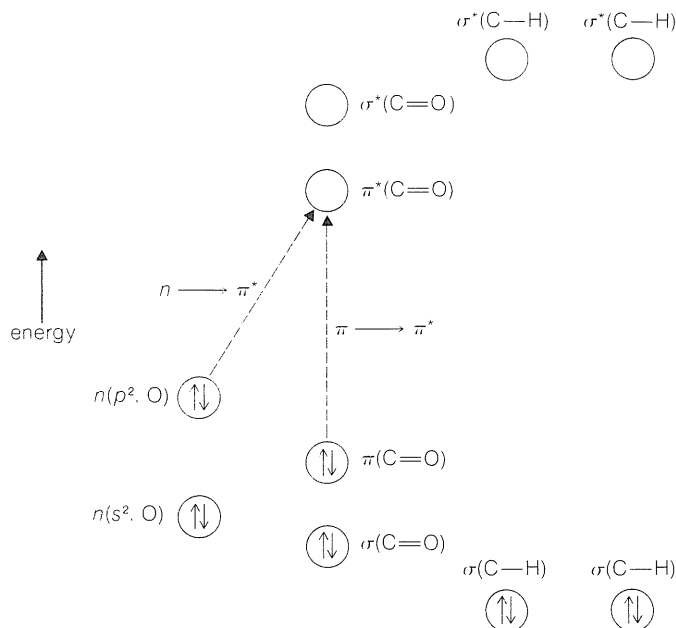
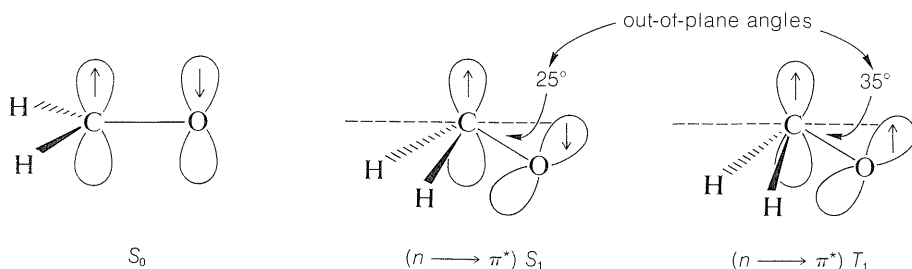


Figure 28-3 Schematic representation of the molecular orbitals and bonding electrons of methanal and the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. Only the outer-shell electrons are shown for carbon and oxygen.

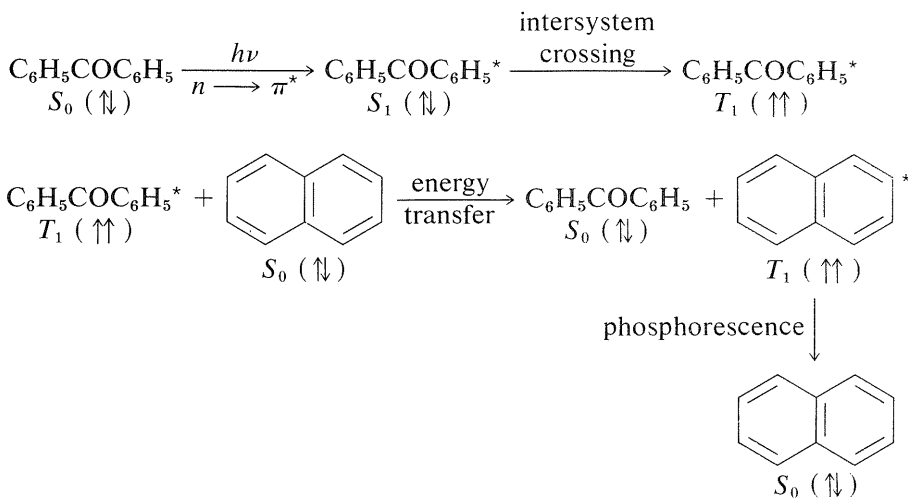
Besides the bond lengths being longer in excited states of molecules, the molecular shapes differ from those of the ground states. Although the Franck-Condon principle requires that absorption produce excited states with the same geometry as the ground states, the excited molecules thereafter can relax to more stable shapes, which may be nonplanar and twisted about the erstwhile π bonds. Methanal is planar with a C–O bond length of 1.21 Å in the ground state, but in the $n \rightarrow \pi^*$ singlet (S_1) state, methanal is pyramidal, with a C–O bond length of 1.32 Å. Methanal is even more distorted in the $n \rightarrow \pi^*$ triplet state, although the bond length remains about the same at 1.32 Å.



28-1B Indirect Electronic Excitation Energy Transfer

It is possible to produce electronic excited states of molecules indirectly by way of energy transfer from other excited molecules. An example is provided

by excitation of naphthalene as the result of energy transfer from excited benzophenone. Benzophenone, $\text{C}_6\text{H}_5\text{COC}_6\text{H}_5$, absorbs ultraviolet light with $\lambda_{\text{max}} = 330 \text{ nm}$ in an $n \rightarrow \pi^*$ transition. Naphthalene does not absorb appreciably in this region. Yet irradiation of a mixture of benzophenone and naphthalene with 330-nm light produces phosphorescent emission from naphthalene. Thus benzophenone absorbs the light and transfers its excess energy to naphthalene, which returns to the ground state by emission. Because the emission is from the triplet state of naphthalene, benzophenone must be involved in exciting the naphthalene to the triplet state. We may write the process as follows:



Energy transfer does not involve a *net* change in electron spin. For this to hold true for excitation of naphthalene from S_0 to T_1 , the energy transfer must come from triplet (not singlet) benzophenone. The process of producing excited states in this way is called **photosensitization**. Singlet–singlet, as well as triplet–triplet, energy transfers are possible, but in all cases there is no net change in spin. Efficient energy transfer will only be possible if ΔG^0 for the transfer is small or negative.

Exercise 28-1 Suppose absorption of light by a diatomic molecule A—B in the lowest vibrational level of the ground state always resulted in dissociation into A and B atoms. Would this necessarily mean that the molecule could not exist in an excited state in which the atoms were bonded together? Explain.

Exercise 28-2 The π -electron system of ethene has one bonding orbital and one antibonding orbital. Using the general approach of Figure 28-2, show the π -electron configurations for the ground state, two different excited singlet states, and a triplet state of ethene. Suppose the bonding energy of one electron in the bonding orbital

is such as to be just canceled by having one electron in the antibonding orbital; would you expect the planar or a nonplanar configuration to be more stable for the excited states of ethene? Explain.

Exercise 28-3 The fluorescence of many substances can be “quenched” (diminished or even prevented) by a variety of means. Explain how concentration, temperature, viscosity, and presence of dissolved oxygen and impurities may affect the degree of fluorescence observed for solutions of a fluorescent material. Would you expect similar effects on phosphorescence? Explain.

Exercise 28-4 Explain qualitatively how temperature could have an effect on the appearance of the absorption spectrum of a diatomic molecule A—B with energy levels such as are shown in Figure 28-1, knowing that most molecules usually are in their lowest vibrational state at room temperature.

Exercise 28-5* Consider a molecule that has a ground state and an excited state which differ from those shown in Figure 28-1 in having potential energy curves with identical shapes, vibrational levels, and r_e values. If we designate the vibrational energy levels of each as 0, 1, 2 \cdots and 0*, 1*, 2*, \cdots (the zeroth level being the lowest), what does the Franck-Condon principle suggest about the relative probabilities of the $0 \longrightarrow 0^*$, $0 \longrightarrow 1^*$, and $0 \longrightarrow 2^*$ transitions? Would the same considerations necessarily hold for the curves of Figure 28-1? Explain.

Exercise 28-6 With reference to the molecular orbital diagram of benzene shown in Figure 21-5, show the electronic configuration of *three* different excited singlet states of benzene corresponding to promotion of an electron from the bonding π orbitals to the antibonding π orbitals. Calculate the energy difference between these states in units of β . Assuming that β is about 20 kcal, calculate the *difference* in λ_{\max} between the three absorption bands corresponding to the three states. How many corresponding triplet states are there?

28-2 ORGANIC PHOTOCHEMISTRY

An extraordinary variety of reactions of organic compounds are known to occur under the influence of visible and ultraviolet light. Some of these, such as the photochemical halogenation of alkanes and photosynthesis in green plants, already have been discussed (see Sections 4-4D and 20-9). It is not our purpose here to review organic photochemistry in detail—rather, we shall mention a few types of important photochemical reactions and show how these can be explained by the principles discussed in the preceding section.

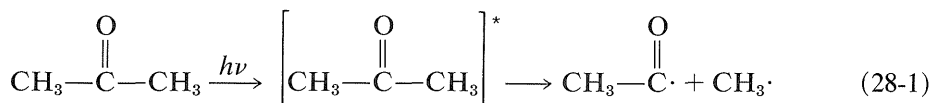
Compounds have very different chemical behavior in their excited states compared to their ground states. Not only is the energy much higher, but the molecular geometry and electronic configurations are different. Intuitively, we

expect that excited states of molecules, in which two electrons occupy *separate unfilled* orbitals, would have substantial diradical character. This is the case, especially for triplet states, as we shall see.

28-2A Photodissociation Reactions

We have mentioned how chlorine molecules dissociate to chlorine atoms on absorption of near-ultraviolet light and thereby cause radical-chain chlorination of saturated hydrocarbons (Section 4-4D). Photochemical chlorination is an example of a photochemical reaction that can have a high *quantum yield*—that is, many molecules of chlorination product can be generated per quantum of light absorbed. The quantum yield of a reaction is said to be unity when 1 mole of reactant is converted to product(s) per einstein¹ of light absorbed. The symbol for quantum yield is usually Φ .

2-Propanone (acetone) vapor undergoes a photodissociation reaction with 313-nm light with Φ somewhat less than unity. Absorption of light by 2-propanone results in the formation of an excited state that has sufficient energy to undergo cleavage of a C–C bond (the weakest bond in the molecule) and form a methyl radical and an ethanoyl radical. This is a *primary* photochemical reaction:



The subsequent steps are dark reactions.

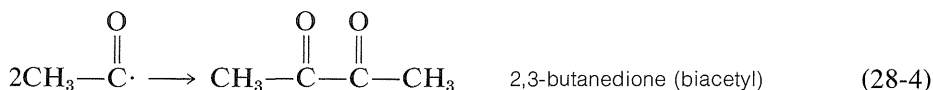
At temperatures much above room temperature, the ethanoyl radical breaks down to give another methyl radical and carbon monoxide:



If this reaction goes to completion, the principal reaction products are ethane and carbon monoxide:

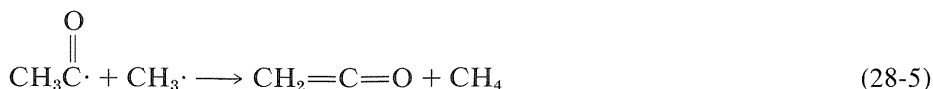


If the ethanoyl radical does not decompose completely, then some 2,3-butanedione also is formed. This reaction is quite important at room temperature or below:

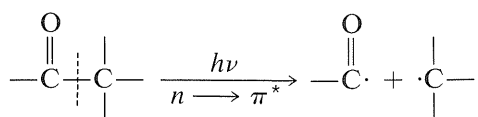


¹The einstein unit is defined in Section 9-4.

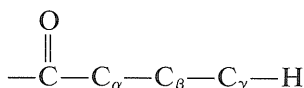
Lesser amounts of methane and ketene also are formed as the result of disproportionation reactions involving hydrogen-atom transfers of the types we have encountered previously in radical reactions (see Section 10-8C):



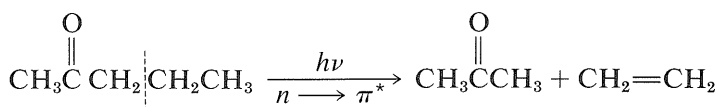
The product-forming reactions, Equations 28-2 through 28-5, all depend on the primary photochemical event, Equation 28-1, which breaks the C–C bond to the carbonyl group. This cleavage has been termed a *Norrish type I process* after the eminent photochemist, R. G. W. Norrish:²



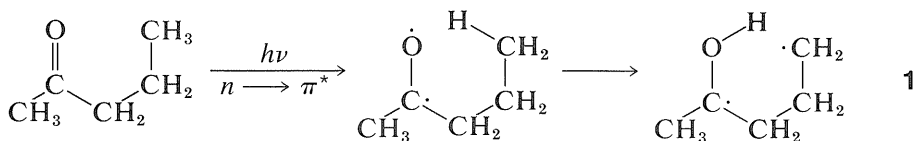
Another photochemical reaction is important for ketones that have at least one γ hydrogen on a chain connected to the carbonyl group, as in



In this pathway (*Norrish type II process*), cleavage occurs at the $\text{C}_\alpha\text{--C}_\beta$ bond to give, as the major product, a ketone of shorter chain length and an alkene. Thus for 2-pentanone:

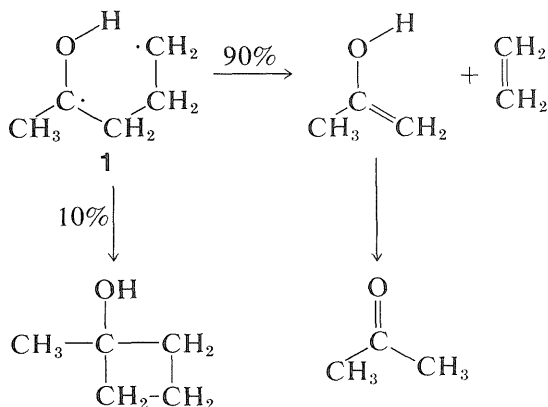


This reaction occurs in an interesting way. Whatever the nature of the $n \longrightarrow \pi^*$ excited state, S_1 or T_1 , the primary photochemical reaction is the abstraction of a hydrogen atom from the γ carbon by the carbonyl oxygen to give the diradical, **1**:

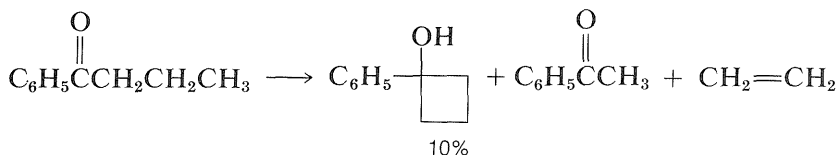
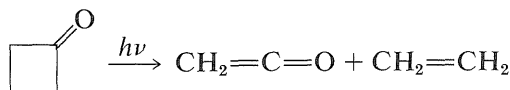
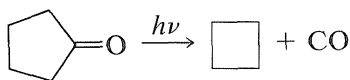
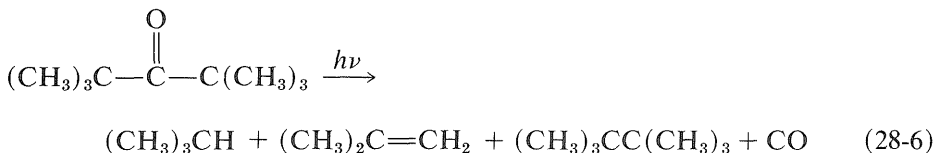


²Recipient with G. Porter of the Nobel Prize in chemistry in 1967 for work on photochemical reactions.

The subsequent dark reactions readily are understood as typical of diradicals. Cleavage of **1** at $C_\alpha-C_\beta$ gives ethene and an enol, which rearranges to the ketone. Alternatively, **1** can cyclize to a cyclobutanol:



A variety of photodissociation reactions have been found to take place with ketones, but the products almost always can be explained as the result of Norrish type I and/or II cleavage. Examples are:



Exercise 28-7 The quantum yield in photochemical chlorination of hydrocarbons such as methane is quite sensitive to the experimental conditions. How would you expect Φ to vary with (a) the *intensity* of the incident light, (b) the *wavelength* of the incident light from 250 nm to 450 nm, (c) the presence of oxygen, and (d) the presence of alkenes? Explain.

Exercise 28-8 The vapor-phase photochemical decomposition of 2-propanone proceeds in the presence of iodine vapor, but the amount of carbon monoxide formed becomes very small. Explain how this result argues against the one-step process,

2-propanone $\xrightarrow{h\nu}$ $2\text{CH}_3\cdot + \text{CO}$. What do you expect the products to be in the presence of iodine?

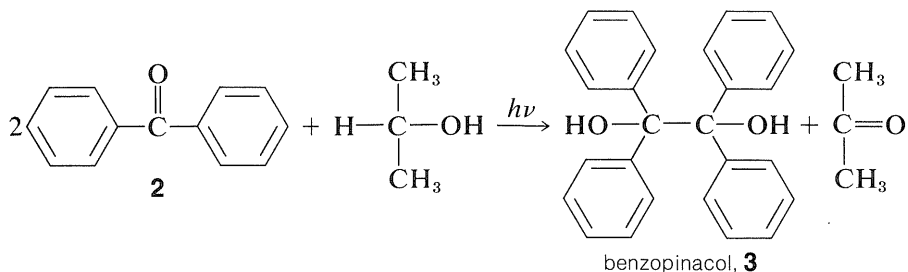
Exercise 28-9 Write a reasonable pathway for the photochemical dissociation shown in Equation 28-6. Explain why this reaction is likely to be favored over Norrish type II reactions for this ketone.

Exercise 28-10 Write a mechanism for formation of cyclobutane from the photolysis of cyclopentanone, and ketene from the photolysis of cyclobutanone.

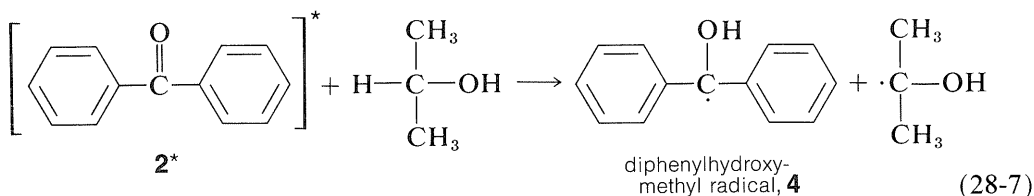
Exercise 28-11 What products would you expect in the photodissociation of 3-methylpentanal?

28-2B Photoreduction of Diaryl Ketones

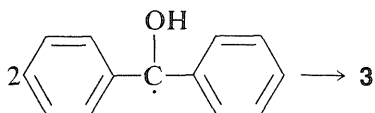
Diaryl ketones do not undergo photodissociation in the same way as alkyl ketones, probably because cleavage to phenyl and other aryl radicals is unfavorable (Table 4-6). Nevertheless, aromatic ketones are photochemically reactive in the presence of compounds that can donate a hydrogen atom, with the result that the carbonyl group is reduced. Indeed, one of the classic photochemical reactions of organic chemistry is the formation of 1,1,2,2-tetraphenyl-1,2-ethanediol (**3**, benzopinacol) by the action of light on a solution of diphenylmethanone (**2**, benzophenone) in isopropyl alcohol. The yield is quantitative.



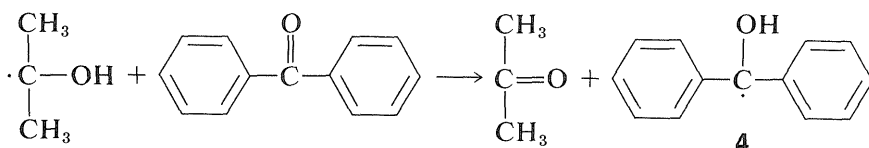
The light is absorbed by **2** and the resulting activated ketone, **2***, removes a hydrogen from isopropyl alcohol:



Benzopinacol results from dimerization of the radicals, **4**:

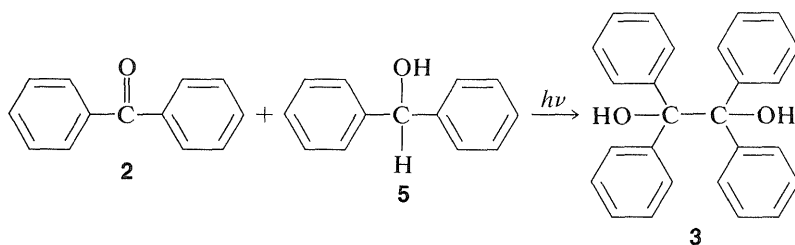


Since the quantum yields of 2-propanone and benzopinacol both are nearly unity when the light intensity is not high, it is clear that two of the radicals, **4**, must be formed for each molecule of **2** that becomes activated by light. This is possible if the 2-hydroxy-2-propyl radical formed by Equation 28-7 reacts with **2** to give a second diphenylhydroxymethyl radical:

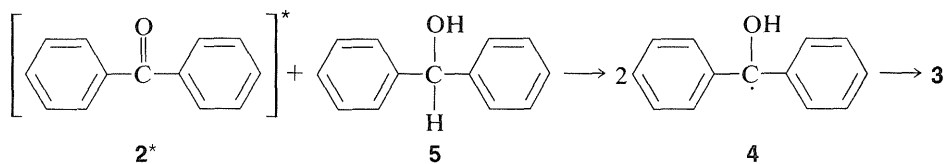


This reaction is energetically favorable because of the greater possibility for delocalization of the odd electron in **4** than in the 2-hydroxy-2-propyl radical.

Photochemical formation of **3** also can be achieved from diphenylmethanone, **2**, and diphenylmethanol, **5**:



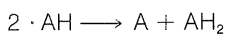
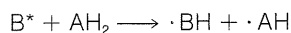
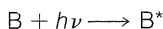
The mechanism is similar to that for isopropyl alcohol as the reducing agent:



This reduction is believed to involve the triplet state of **2** by the following argument: Formation of **3** is reasonably efficient even when the concentration of the alcohol, **5**, is low; therefore, whatever the excited state of the ketone, **2***, that accepts a hydrogen atom from **5**, it must be a fairly long-lived one. Because solutions of **2** show no visible fluorescence, they must be converted rapidly to another state of longer life than the singlet (S_1). The long-lived state is then most reasonably a triplet state. In fact, if naphthalene is added to the reaction mixture, formation of benzopinacol, **3**, is drastically inhibited because the benzophenone triplet transfers energy to naphthalene more rapidly than it reacts with the alcohol, **5** (see Section 28-1A).

Exercise 28-12 Irradiation of benzophenone in isopropyl alcohol in the presence of oxygen gives no benzopinacol (the benzophenone is not consumed), but does give 2-propanone (with Φ equal to unity) and hydrogen peroxide (with Φ nearly unity). The reaction does not occur readily in the absence of benzophenone. Explain how benzophenone acts as a *photosensitizer* for the oxidation of isopropyl alcohol by oxygen.

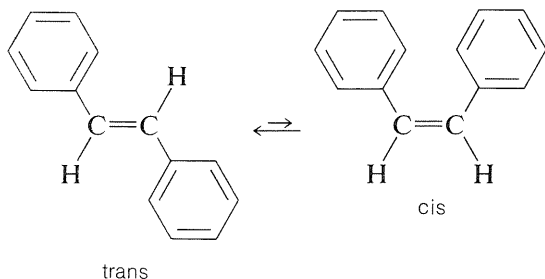
Exercise 28-13 What would you expect to be the quantum yield of 2-propanone in the following sequence of reactions for benzopinacol formation, where B = diphenylmethanone, **2**; $\cdot\text{BH}$ = diphenylhydroxymethyl radical, **4**; $(\text{BH})_2$ = benzopinacol, **3**; A = 2-propanone; $\cdot\text{AH}$ = 2-hydroxy-2-propyl radical; and AH_2 = 2-propanol?



How could this sequence be ruled out if formation of benzopinacol, **3**, in the presence of an excess of optically active 2-butanol gave no racemized alcohol?

28-2C Photochemical Isomerization of Cis and Trans Alkenes

An important problem in many syntheses is to produce the desired isomer of a cis-trans pair of alkenes. The problem would not arise if it were possible to isomerize the undesired isomer to the desired isomer. In many cases such isomerizations can be carried out photochemically. A typical example is afforded by *cis*- and *trans*-1,2-diphenylethene (stilbene):



Here the trans form is easily available by a variety of reactions and is more stable than the cis isomer because it is less sterically hindered. However, it is possible to produce a mixture containing mostly cis isomer by irradiating a solution of the trans isomer in the presence of a suitable photosensitizer. This process in no way contravenes the laws of thermodynamics because the input of radiant energy permits the equilibrium point to be shifted from what it would be normally.

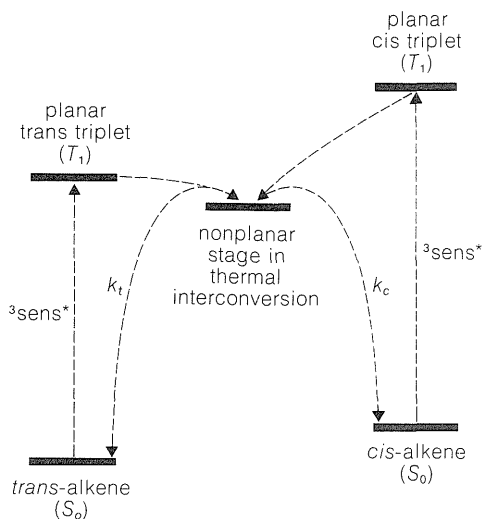
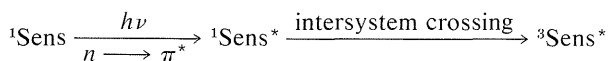


Figure 28-4 Schematic energy levels for *cis*- and *trans*-1,2-diphenylethene. The upward transitions are achieved by transfer of energy from triplet sensitizer. The downward transitions from the nonplanar stage marked with the rate constants k_t and k_c involve loss of thermal energy to the solvent, or phosphorescence. The lower energies assigned to the S_0 and T_1 states of *trans*-1,2-diphenylethene relative to the S_0 and T_1 states of the *cis* isomer reflect steric hindrance between the phenyl groups of the *cis* isomer.

Isomerization appears to occur by the following sequence: The sensitizer, usually a ketone such as benzophenone or 1-(2-naphthyl)ethanone, is raised by an $n \rightarrow \pi^*$ transition from the singlet ground state (S_0) to an excited state (S_1) by absorption of light. Intersystem crossing then occurs rapidly to give the triplet state (T_1) of the sensitizer:



(Sens = $\text{C}_6\text{H}_5\text{C}(=\text{O})\text{C}_6\text{H}_5$; $^1\text{Sens}$ = singlet state; $^3\text{Sens}^*$ = triplet state)

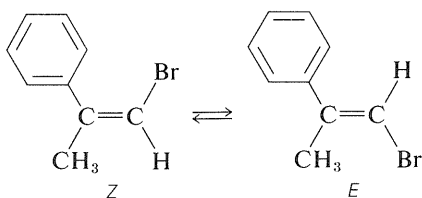
The next step is excitation of the alkene by energy transfer from the triplet state of the sensitizer. Remember, the net electron spin is conserved during energy transfer, which means that the alkene will be excited to the triplet state:



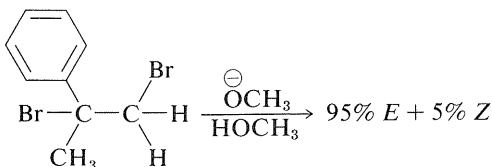
The triplet state of the alkene is most stable when the p orbitals, which make up the normal π system of the double bond, are not parallel to one another (Figure 6-17). Therefore, if the energy-transfer process leads initially to a planar triplet, this is converted rapidly to the more stable nonplanar form. The excitation of either the *cis* or the *trans* isomer of the alkene appears to lead to a common triplet state, as shown in Figure 28-4.

The final step in the isomerization is decay of the alkene triplet to the ground state. This happens either by emission of light (phosphorescence) or by having the triplet energy converted to thermal energy without emission of light. Either way, the *cis* or *trans* isomer could be formed and, as can be seen from Figure 28-4, the ratio of isomers produced depends on the relative rates of decay of the alkene triplet to the ground-state isomers, k_c/k_t . This ratio turns out to favor formation of the *less stable* isomer. Therefore, provided both isomers can be photosensitized efficiently, sensitized irradiation of either one will lead ultimately to a mixture of both, in which the thermochemically less stable isomer predominates. The sensitizer must have a triplet energy in excess of the triplet energy of the alkene for energy transfer to occur, and the **photostationary** or equilibrium point is independent of the nature of the sensitizer when the latter transfers energy efficiently to *both* *cis* and *trans* isomers. In the practical use of the sensitized photochemical equilibrium of *cis* and *trans* isomers, it is normally necessary to carry out pilot experiments to determine what sensitizers are useful.

Another example of how photochemical isomerization can be used is provided by the equilibration of the *E* and *Z* form of 1-bromo-2-phenyl-1-propene:



The *E* isomer is formed to the extent of 95% in the dehydrohalogenation of 1,2-dibromo-2-phenylpropane:

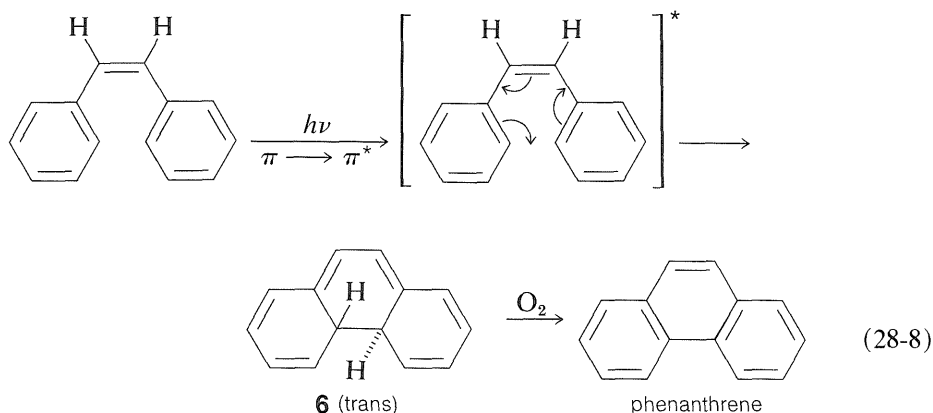


Photoisomerization of the elimination product with 1-(2-naphthyl)ethanone as sensitizer produces a mixture containing 85% of the *Z* isomer.

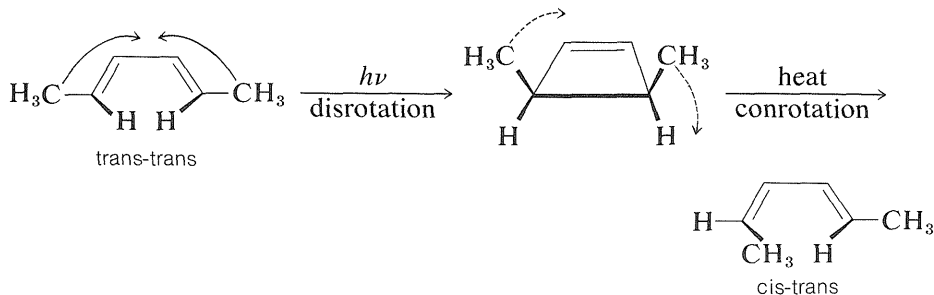
Exercise 28-14* Suppose the rates of the processes marked k_c and k_t in Figure 28-4 were the same. Which isomer would be favored at photoequilibrium if the rate of the reaction represented by k_t^* were greater than the rate represented by k_c^* ? On the basis of steric hindrance, would you expect the rate of the k_t^* process or the k_c^* process to be greater, using benzophenone as sensitizer? Explain.

28-2D Photochemical Cyclization Reactions

One may well ask why the isomerization of alkenes discussed in the preceding section requires a sensitizer. Why cannot the same result be achieved by direct irradiation? One reason is that a $\pi \longrightarrow \pi^*$ singlet excited state (S_1) produced by direct irradiation of an alkene or arene crosses over to the triplet state (T_1) inefficiently (compared to $n \longrightarrow \pi^*$ excitation of ketones). Also, the S_1 state leads to *other* reactions beside isomerization which, in the case of 1,2-diphenylethene and other conjugated hydrocarbons, produce cyclic products. For example, *cis*-1,2-diphenylethene irradiated in the presence of oxygen gives phenanthrene by the sequence of Equation 28-8. The primary photoreaction is cyclization to a dihydrophenanthrene intermediate, **6**, which, in the presence of oxygen, is converted to phenanthrene:



The cyclization step of Equation 28-8 is a photochemical counterpart of the electrocyclic reactions discussed in Section 21-10D. Many similar photochemical reactions of conjugated dienes and trienes are known, and they are of great interest because, like their thermal relatives, they often are stereospecific but tend to exhibit stereochemistry opposite to what is observed for formally similar thermal reactions. For example,

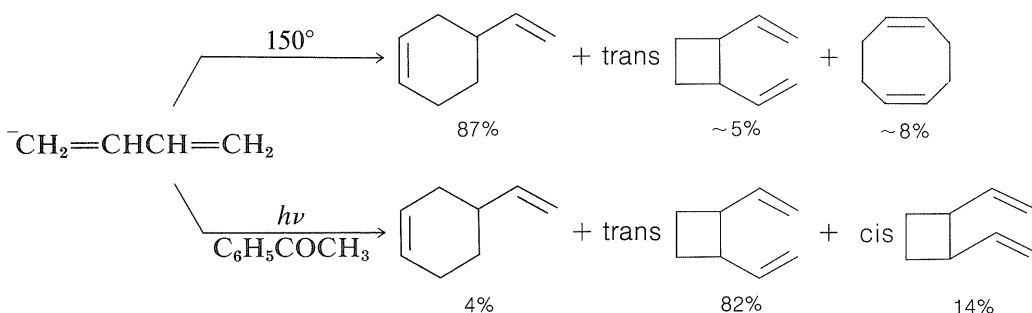


These reactions are $4n$ -electron concerted processes controlled by the symmetry of the reacting orbitals. The thermal reaction is most favorable with a

Möbius transition state (achieved by conrotation), whereas the photochemical reaction is most favorable with a Hückel transition state (achieved by disrotation).

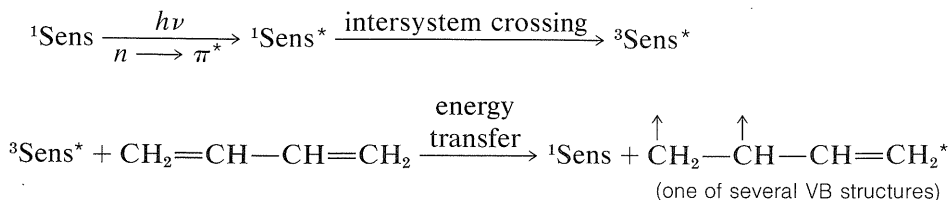
- Exercise 28-15 a.** Account for the formation of the *trans*-dihydrophenanthrene, **6**, in the cyclization of Equation 28-8.
- b.** Both *cis*- and *trans*-1,2-diphenylethene isomers can be cyclized to phenanthrene. Explain how this is possible for the *trans* isomer.

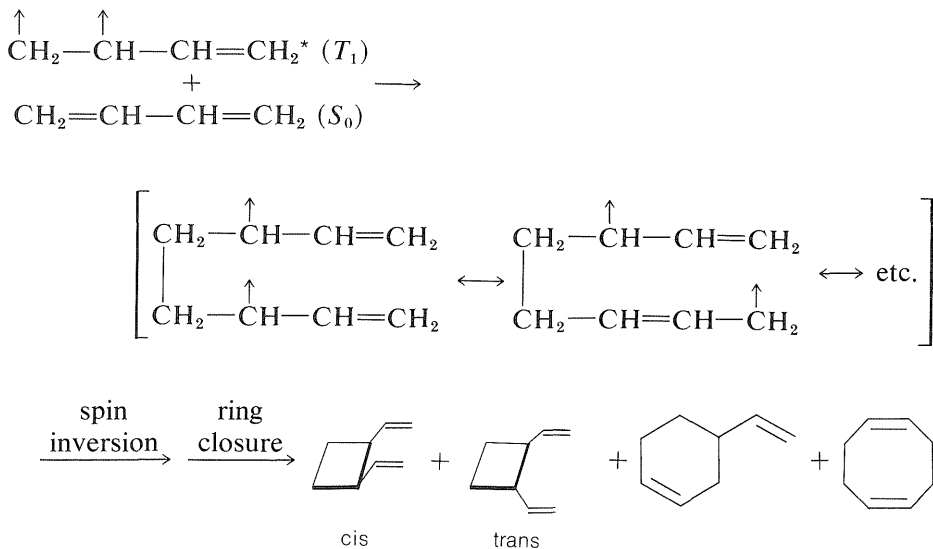
Conjugated dienes also undergo photochemical cycloaddition reactions. Related thermal cycloadditions of alkadienes have been discussed in Sections 13-3A, 21-10A, and 21-10D, but the thermal and photochemical reactions frequently give different cyclic products. Butadiene provides an excellent example of the differences:



In the thermal reaction the $[4 + 2]$ or Diels–Alder adduct is the major product, whereas in the photochemical reaction $[2 + 2]$ cycloadditions dominate. Because the photochemical additions are sensitized by a ketone, $\text{C}_6\text{H}_5\text{COCH}_3$, these cycloadditions occur through the triplet state of 1,3-butadiene and, as a result, it is not surprising that these cycloadditions are stepwise, nonstereospecific, and involve diradical intermediates.

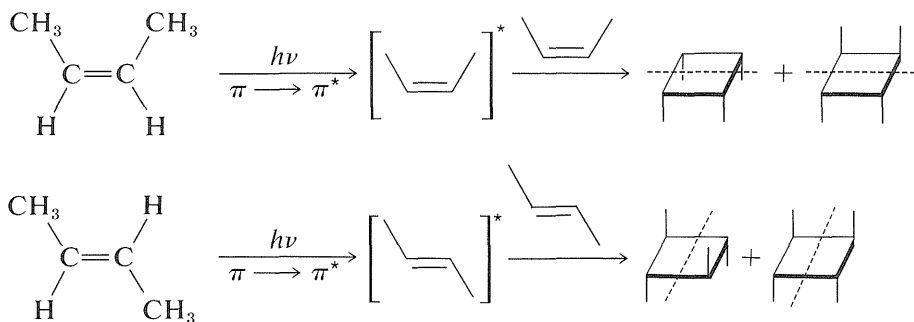
Excitation:



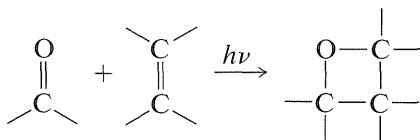
Cycloaddition:

Direct irradiation of 1,3-butadiene with 254-nm light produces cyclobutene and small amounts of bicyclo[1.1.0]butane along with dimers.

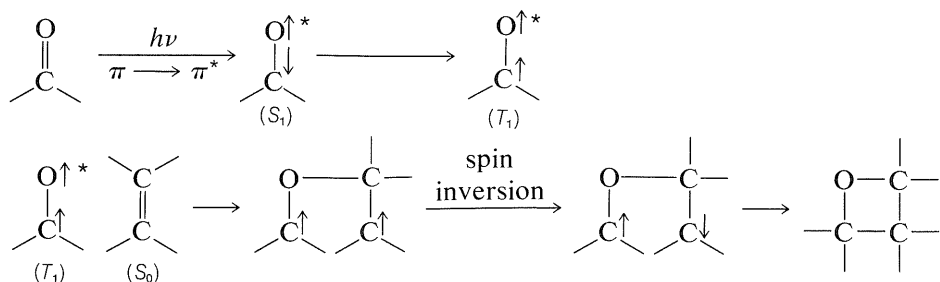
In contrast to conjugated dienes, simple alkenes such as 2-butene do not react easily by photosensitized cycloaddition. But they will form [2 + 2] cycloadducts on direct irradiation. These additions occur by way of a singlet excited state and are stereospecific:



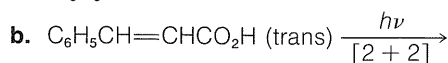
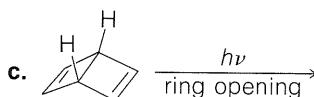
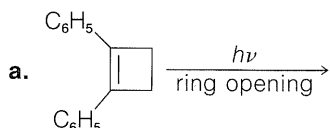
A related reaction, which has no precedent in thermal chemistry, is the cycloaddition of an alkene and an aldehyde or ketone to form an oxacyclobutane:



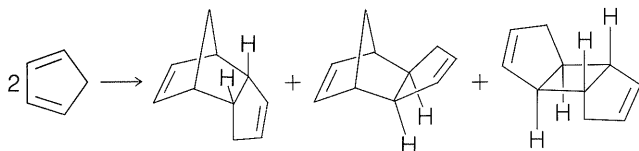
In this kind of addition the ground-state alkene (S_0) reacts with an excited state (usually T_1) of the carbonyl compound by way of a diradical intermediate:



Exercise 28-16 Draw structures for the products expected from the following reactions. Be sure to indicate stereochemistry.

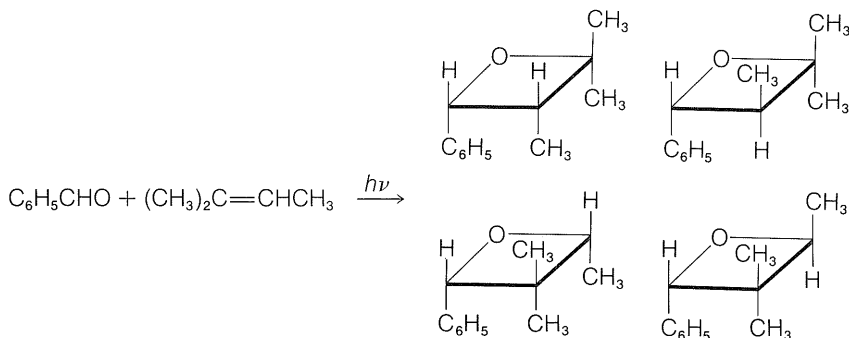


Exercise 28-17 1,3-Cyclopentadiene gives the following substances on irradiation in the presence of a ketone sensitizer:



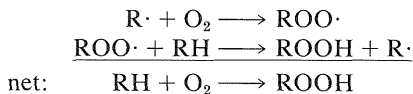
Write reasonable mechanisms for the formation of these substances.

Exercise 28-18 Show the mechanistic steps by which formation of the following reaction products can be explained:

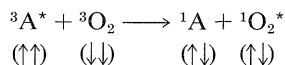


28-2E Singlet Oxygen Reactions

The ground state of molecular oxygen is unusual because it is a triplet state. Two electrons of parallel spin occupy separate π orbitals of equal energy (degenerate), as shown schematically in Figure 28-5.³ The next two higher electronic states both are singlet states and lie respectively 24 and 37 kcal mole⁻¹ above the ground state. From this we can understand why ordinary oxygen has the properties of a diradical and reacts rapidly with many radicals, as in the radical-chain oxidation of hydrocarbons (autoxidation; Sections 15-10 and 16-9E and Exercise 4-33):



Oxygen also efficiently quenches excited triplet states of other molecules ($^3\text{A}^*$) and, in accepting triplet energy, is itself promoted to an excited *singlet* state. Notice that the total spin orientation is conserved:



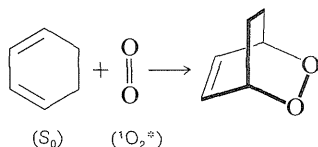
Singlet oxygen is highly reactive toward many organic molecules and will form oxygenated addition or substitution products. As one example, conjugated dienes react with singlet oxygen to give peroxides by [4 + 2] cyclo-



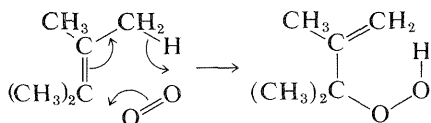
Figure 28-5 Electronic configurations of the two highest occupied (degenerate) π orbitals of oxygen (O_2) in the ground and excited states

³For a more detailed account of the electronic configuration of molecular oxygen, see M. Orchin and H. H. Jaffé, *The Importance of Antibonding Orbitals*, Houghton Mifflin Co., Boston, 1967; or H. B. Gray, *Chemical Bonds*, W. A. Benjamin, Inc., Menlo Park, Calif., 1973.

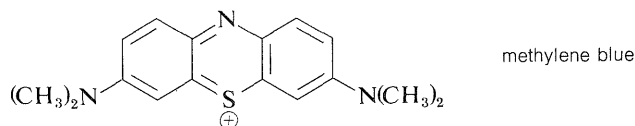
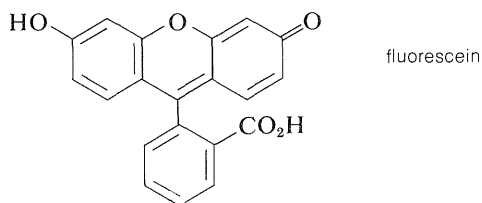
addition. Because only singlet states are involved, this addition is quite analogous to thermal Diels–Alder reactions (Section 21-10A):



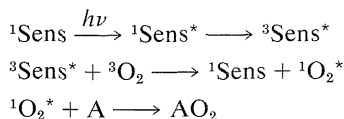
If the alkene or alkadiene has at least one hydrogen on the carbon adjacent to the double bond, reaction with singlet oxygen may give hydroperoxides. The mechanism of this reaction is related to [4 + 2] cycloadditions and is presumed to occur through a Hückel pericyclic transition state (see Section 21-10D):



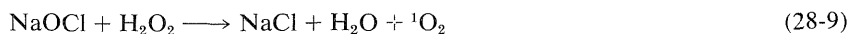
Many reactions of this type can be achieved by allowing the hydrocarbon to react with oxygen in the presence of a sensitizing dye that strongly absorbs visible light. The dyes most commonly used for this purpose include fluorescein (and its chlorinated analogs, eosin and rose bengal), methylene blue, and porphyrin pigments (such as chlorophyll).



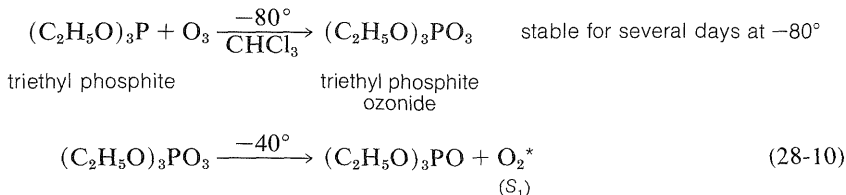
The overall process of photosensitized oxygenation of a substrate (A) proceeds by the following steps:



Singlet oxygen can be produced chemically as well as by photochemical sensitization. There are several chemical methods available, one of the best known being the reaction of sodium hypochlorite with peroxide:

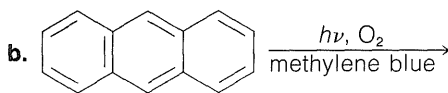
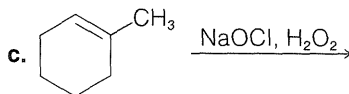
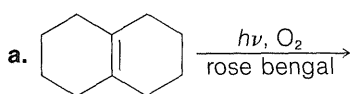


An alternative method of formation, which can be used in organic solvents at low temperatures, involves the thermal decomposition of triethyl phosphite ozonide (Equation 28-10):



Regardless of whether singlet oxygen is formed chemically or photochemically, it gives similar products in reactions with alkenes.

Exercise 28-19 Write structures expected for the products of the following reactions:



28-2F Photobiology

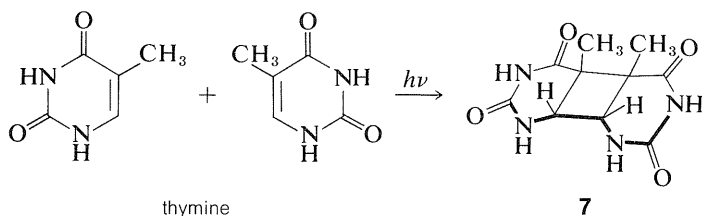
Photosensitized reactions of oxygen are largely damaging to living organisms. Indeed, singlet oxygen reacts destructively with amino acids, proteins, and nucleic acids. How does an organism protect itself against the damaging effects of oxygen? There are no simple answers, but green plants provide a clue. Chlorophyll is an excellent sensitizing dye for singlet oxygen; yet green plants evidently are not harmed because of it. A reason may be that singlet oxygen is quenched very efficiently by other plant pigments, especially the carotenoid pigments such as β -carotene (Section 2-1). That this is the case is indicated by the fact that mutant plants unable to synthesize carotene are killed rapidly by oxygen and light.

Exercise 28-20* Write at least three possible reactions that β -carotene could undergo as a result of energy transfer from $^1\text{O}_2$.

That direct irradiation with ultraviolet light is damaging to single-cell organisms is well known. It also is known that the nucleic acids, DNA and RNA, are the important targets of photochemical damage, and this knowledge has stimulated

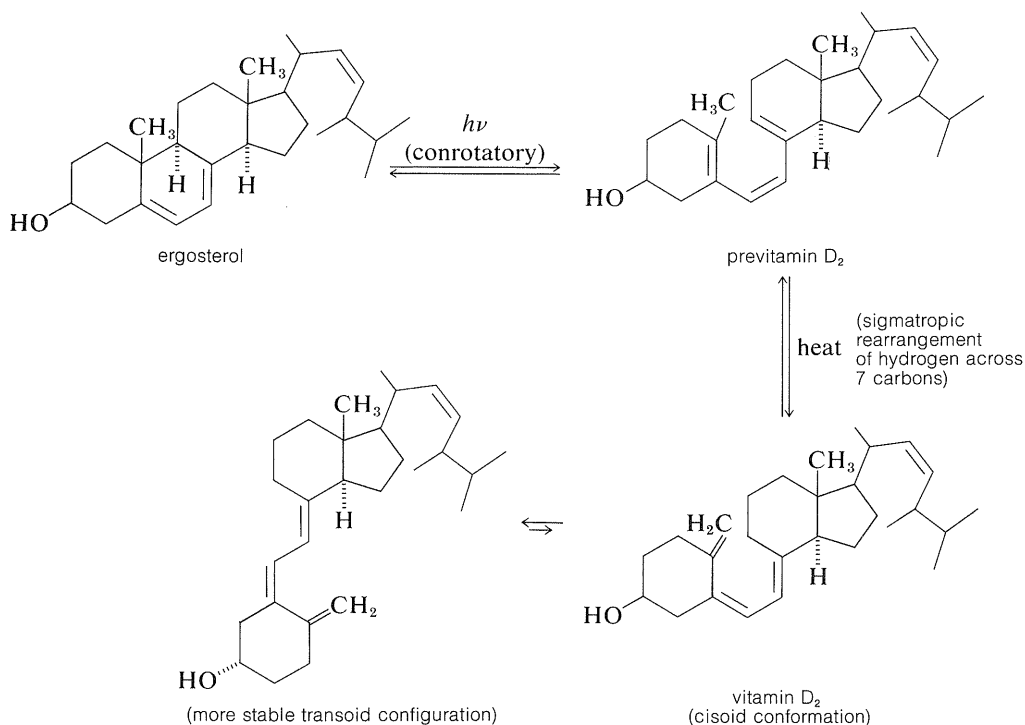
much research in the field of photobiology in the hope of unravelling the chemistry involved.

An interesting and significant outcome is the finding that the pyrimidine bases of nucleic acids (uracil, thymine, and cytosine) are photoreactive and undergo $[2 + 2]$ cycloadditions on irradiation with ultraviolet light. Thymine, for example, gives a dimer of structure 7:



Comparable experiments with the nucleic acids have confirmed that cycloaddition of their pyrimidine bases also occurs with ultraviolet light and effectively cross-links the chains, a process obviously quite inimical to the functioning of the DNA (see Section 25-13B). A remarkable and not well understood aspect of photobiology is the repair and defense mechanism both plants and animals possess to minimize the damaging effects of radiation.

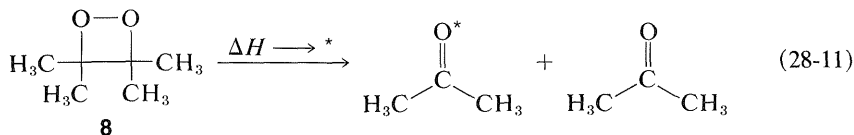
On the positive side, there are photochemical reactions that are essential for human health. One of these is the formation of vitamin D (the antirachitic vitamin) by irradiation of ergosterol. This photochemical reaction is an electrocyclic ring opening of the cyclohexadiene ring of ergosterol of the type described in Section 28-2D. The product, previtamin D₂, subsequently rearranges thermally to vitamin D₂:



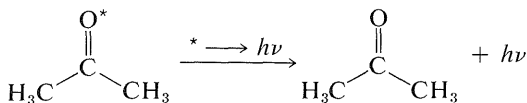
28-3 CHEMILUMINESCENCE

The most common means of generating electronically excited states of molecules is by the absorption of electromagnetic radiation. But excited states are accessible by other routes. Indeed, as shown in Section 28-2E, the excited singlet state of molecular oxygen can be produced by chemical reactions (Equations 28-9 and 28-10). Many other reactions are known that generate products in electronically excited states, and this is especially evident when the electronically excited products go to the ground state by the emission of visible light. This behavior is known as **chemiluminescence** and is transduction of chemical energy (ΔH) into radiant energy ($h\nu$). Chemiluminescence is possible only when the ΔH of the reaction is sufficiently large to allow for production of at least one of the products in an electronically excited state (*). Chemiluminescence amounts to $\Delta H \longrightarrow * \longrightarrow h\nu$, which is opposite to most photochemistry which involves $h\nu \longrightarrow * \longrightarrow \Delta H$.

A beautiful example of a chemiluminescent reaction is the thermal dissociation of the cyclic peroxide, **8**, into two molecules of 2-propanone:



The energy of the transition state for this reaction is about 90 kcal mole⁻¹ *above* the level of the ground-state ketone. This makes it possible for the transition state to lead to either excited singlet or triplet ketone, which have energies of 85 and 78 kcal mole⁻¹, respectively, relative to the ground-state ketone (see Figure 28-6). Accordingly, half of the 2-propanone molecules can be produced in an excited state and may decay to the ground state by visible emission (luminescence):⁴



We should not be surprised at the high exothermicity of Reaction 28-11. The peroxide is of high energy (thermochemically unstable) because it combines the strain-energy characteristics of small rings with the weakness of O–O bonds, whereas the product is a stable substance with a strong carbonyl bond.

Chemiluminescence in many reactions is hard to detect because the efficiency of light emission is low. Thus, even though the excited state may be formed in high yield, it may be quenched by other species more efficiently than it loses energy by emission. This fact can be used to advantage by adding a substance

⁴Production of two molecules of excited 2-propanone per molecule of **8** is not possible under the same conditions because this would correspond to a reaction with ΔH° of at least 156 kcal above formation of two moles of ground-state ketone.

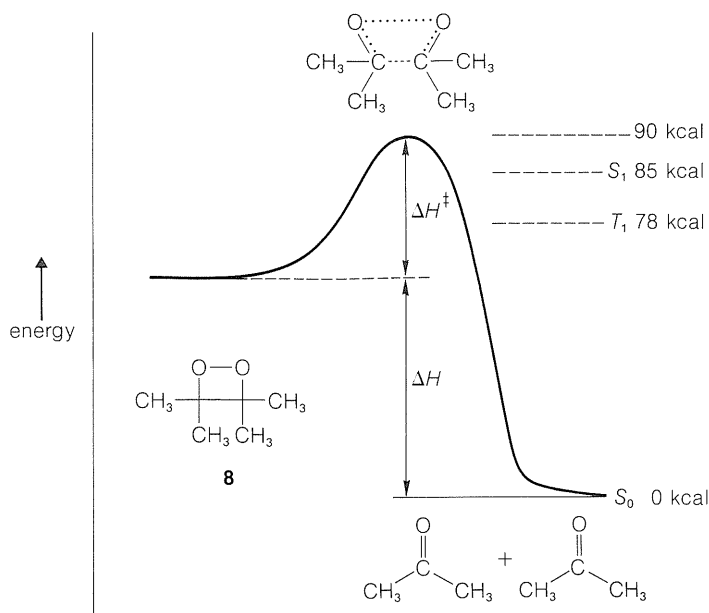
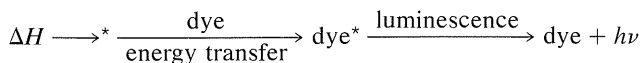
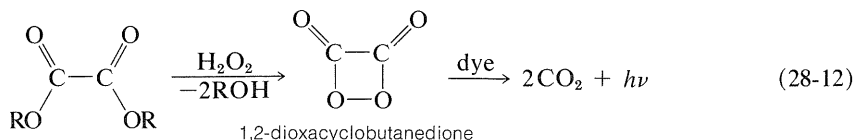


Figure 28-6 Energy profile for the thermal dissociation of 3,3,4,4-tetramethyldioxacyclobutane, **8**, to acetone, showing that the transition state is above the threshold required to produce either excited singlet (S_1) or triplet (T_1) acetone.

that quenches the excited state efficiently and, after energy transfer, gives bright fluorescence or phosphorescence:



Chemiluminescence can be greatly amplified by this process and it forms the basis of spectacular demonstrations of “cold light.” An example is the *per*-hydrolysis of ethanedioic (oxalic) esters with hydrogen peroxide in the presence of a fluorescent substance (Equation 28-12). The reaction is believed to pass through the highly unstable dioxacyclobutanedione, which dissociates into two moles of carbon dioxide with such exothermicity that electronic excitation occurs, as evident from the intense light produced in the presence of fluorescent dyes:



This reaction has been developed into a commercial product, marketed under the trade name “Coolite,” which can be used as an emergency light source by simply shaking a tube to bring the reactants in contact with one another.

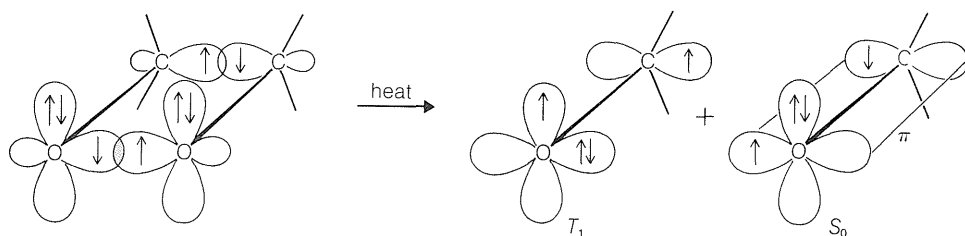


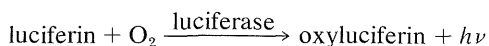
Figure 28-7 Representation of electron configuration changes in dissociation of tetramethyldioxacyclobutane, **8**, to T_1 and S_0 2-propanone. Spin-orbit coupling of the nonbonding and the σ -bonding orbital on oxygen (shaded) produces one molecule of ketone in the triplet (T_1) state.

Of major interest is the identity of the excited state (singlet or triplet) produced by chemiluminescent reactions. Little is known about excited states produced chemically except in a few cases, as in Reaction 28-11. Here the chemiluminescence dissociation gives a ratio of triplet 2-propanone to excited singlet 2-propanone of 100:1. This is a surprising result because it means that that spectroscopic selection rules of electron-spin conservation are not followed in this chemiexcitation. The reaction has generated a triplet state from a singlet state. How can this be? Some idea of what is involved can be obtained from Figure 28-7, in which we see that breaking of the two sigma C–C and O–O bonds gives directly one molecule of ground-state ketone (all spins paired) and one molecule of triplet ketone. In this process, the electrons associated with the orbitals on one of the oxygen atoms appear to interact in such a way as to interchange electrons between orbitals *on the same atoms* with a spin inversion. This is called **spin-orbit coupling**.

28-3A Bioluminescence

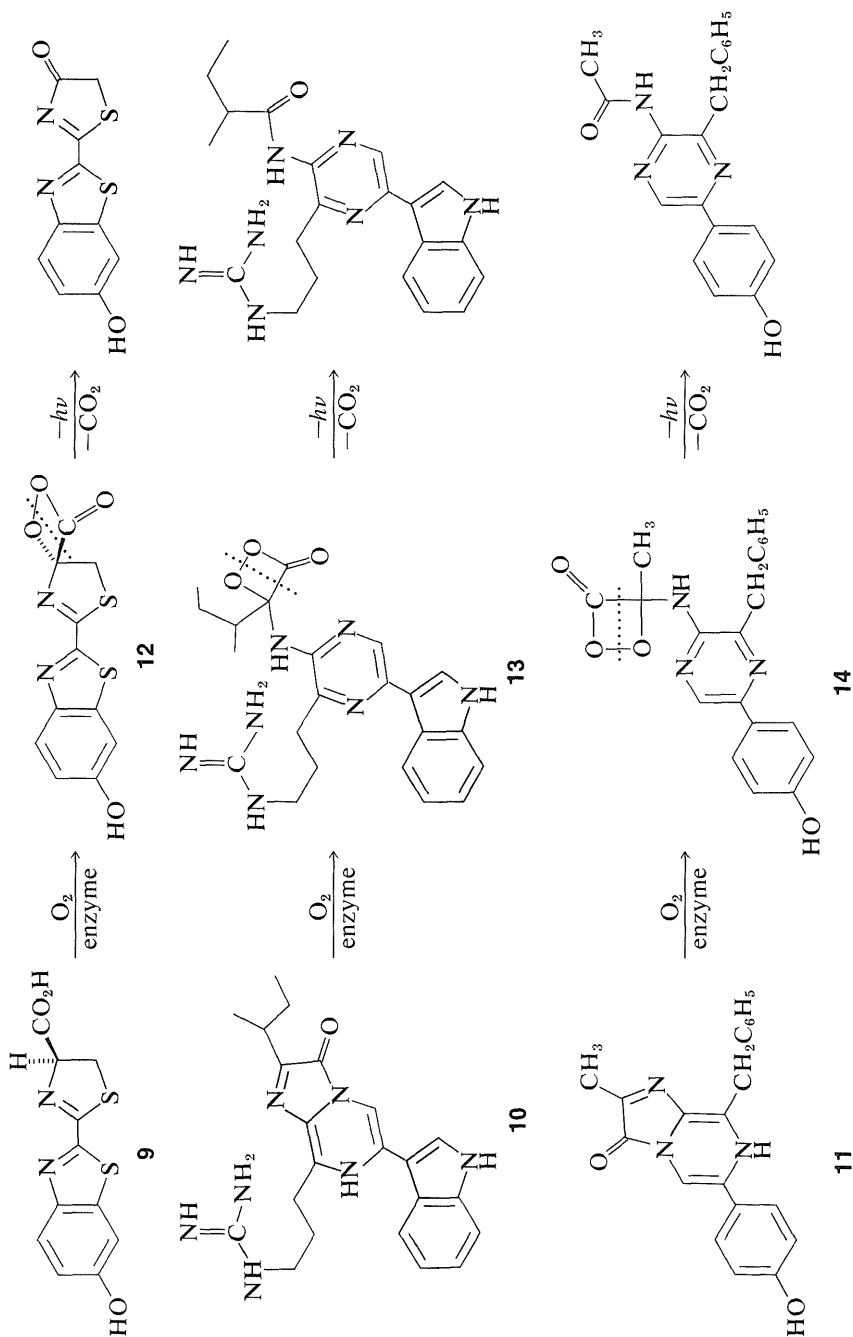
The emission of visible light by living organisms is a mysterious and fascinating phenomenon. The magical glow of the firefly and of certain plants and marine animals is a familiar sight and one that has stimulated man's curiosity and imagination for centuries. Despite intense interest in bioluminescence, it is only recently that substantial progress has been made in our understanding of how it occurs.

One of the earliest studies of bioluminescence was made by the French scientist R. Dubois toward the end of the nineteenth century. He demonstrated that bioluminescent organisms emitted light as a consequence of chemical change. He succeeded in isolating the active chemical from fireflies (luciferin) and the activating enzyme (luciferase, named by Dubois from the Latin *lucifer*, meaning light bearer). Luciferin and the enzyme in the presence of oxygen were found to reproduce the natural bioluminescence:

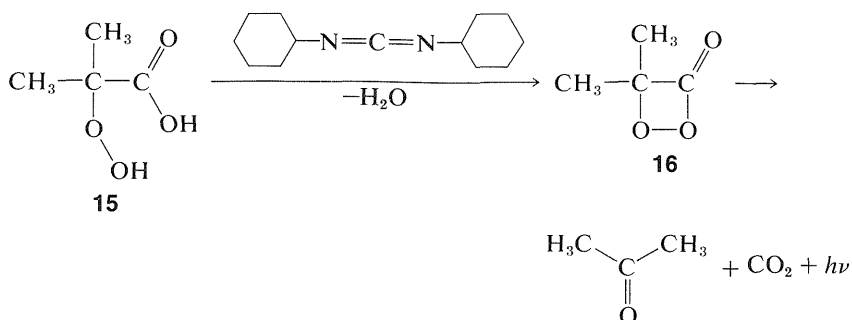


Further progress required elucidation of the structures of luciferin and its oxidation product. It turned out that there are several luciferins, depending

on the organism. Firefly luciferin has the benzothiazol structure, **9**; the luciferins from the marine crustacean *Cypridina hilgendorfi* and the sea pansy *Renilla reformis* have structures **10** and **11**, respectively. Their oxidation products **12**, **13**, and **14** also are shown:



Although the luciferins **9–11** may not seem closely related, each appears to react with oxygen (at the direction of the appropriate enzyme) to give cyclic peroxy lactone intermediates **12–14**. Luminescence is the consequence of the energetically favorable dissociation of the dioxacyclobutanone ring system to carbon dioxide and a carbonyl component. This mechanism is suggested by experiments with the peroxy acid, **15**, which with *N,N*-dicyclohexylcarbodiimide gives a very reactive compound presumed to be the peroxy lactone, **16**. This substance liberates CO_2 rapidly at room temperature with luminescence:



28-4 COLOR AND CONSTITUTION

Visible light is electromagnetic radiation having a rather narrow range of wavelengths (400–800 nm). A black substance absorbs *all* wavelengths of visible light. Selective absorption of visible light by a substance imparts color, but the color is not that of the light absorbed but instead of the residual light that the substance transmits or reflects. For example, a compound that absorbs in the region 435–480 nm removes blue light from the visible spectrum, and the residual light is recognized by the eye as being yellow. The relationship of the observed color to wavelength of light absorbed is shown in Table 28-1. It is customary to call the color observed the **complementary color** or the **subtraction color** to that absorbed.

It is important to recognize that visible color will not necessarily depend on having the wavelength for maximum absorption (λ_{max}) in the visible region. Many substances with broad absorption bands will have λ_{max} below 400 nm and yet appear strongly colored because their absorption bands extend into the visible spectrum. This is illustrated in Figure 28-8.

Exercise 28-21 What color would you expect to perceive if white light were passed through a solution containing a substance that absorbed very strongly but only within the specified wavelength ranges?

- a. 660 ± 30 nm b. 530 ± 30 nm c.* 560 ± 300 nm d.* 480 ± 0.1 nm

Table 28-1
Color and Wavelength

Light absorbed		Complementary (subtraction) color seen
Wavelength (nm)	Color	
400–435	violet	green-yellow
435–480	blue	yellow
480–490	green-blue	orange
490–500	blue-green (cyan)	red
500–560	green	purple (magenta)
560–580	yellow-green	violet
580–595	yellow	blue
595–605	orange	green-blue
605–750	red	blue-green (cyan)

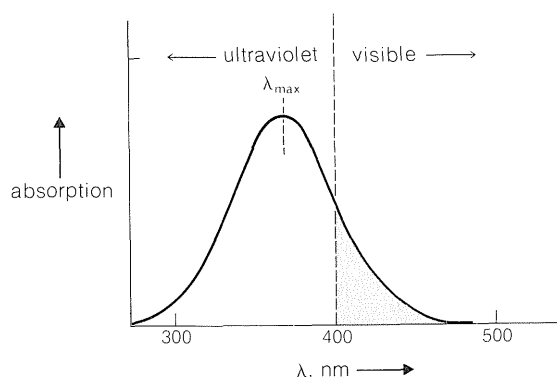


Figure 28-8 Absorption in the visible region by a colored substance that has λ_{\max} in the ultraviolet

Exercise 28-22 What visible color would you expect of the substance having the spectrum shown in Figure 28-8?

Clearly, the color perceived, its brightness and its intensity, depends on the shape of the electronic spectral curve of the absorbing substance, which in turn depends on the chemical structure of the substance. A change in absorption from the blue to the red end of the spectrum corresponds to a *decrease*

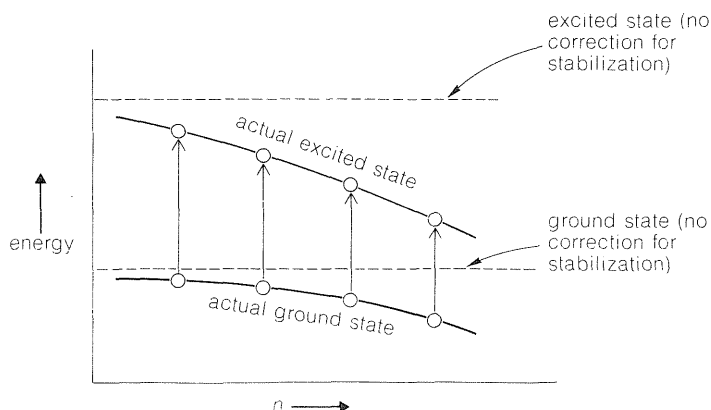
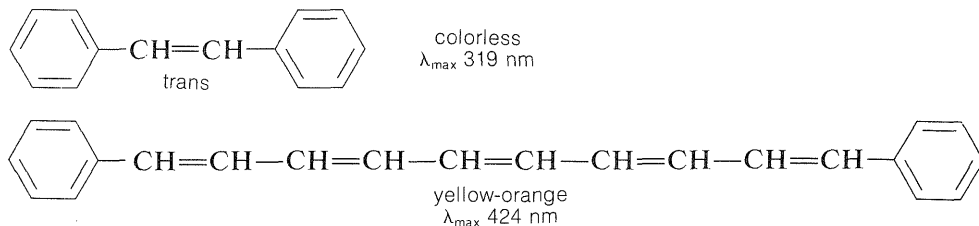


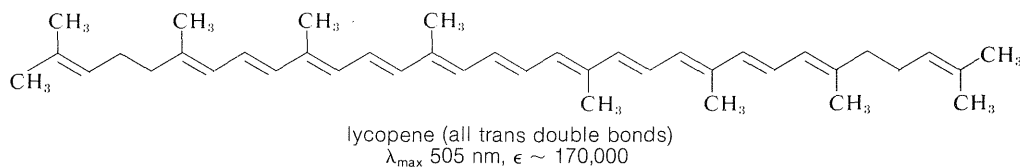
Figure 28-9 Schematic relationship between stabilization of ground and excited states of systems with n conjugated double bonds

in the energy of the associated electronic transitions. We know also that this trend is associated with increasing conjugation of multiple bonds. For instance, 1,2-diphenylethene is colorless, whereas 1,10-diphenyl-1,3,5,7,9-decapentaene is yellow-orange:

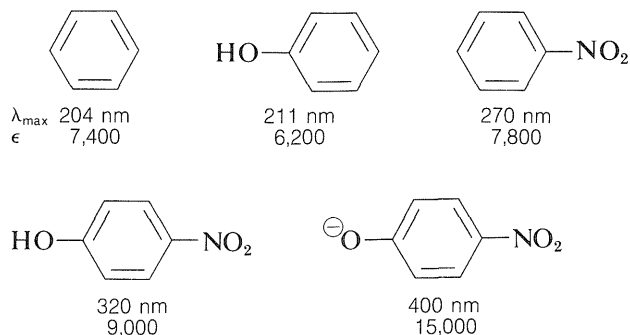


Generally, the more extended a planar system of conjugated bonds is, the smaller is the energy difference between the ground and excited states. This effect is shown schematically in Figure 28-9, from which you can see that conjugation stabilizes *both* the ground state and the excited state but relatively more so the excited state. Thus the gap between the states narrows with increasing conjugation, and absorption shifts to longer wavelengths (also see Section 9-9B and 21-5C).

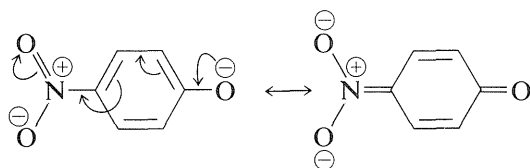
The effect of substituents on colors associated with conjugated systems is of particular interest in the study of dyes, because most dyes have relatively short conjugated systems and would not be intensely colored in the absence of substituent groups. (The plant pigments β -carotene, Section 2-1, and lycopene, often used as food coloring, are exceptions.)



To clarify the effect of substituents we will discuss the spectrum of 4-nitrobenzenol, even though the compound has no value as a dye. It is a pale yellow compound (λ_{\max} 320 nm) with an ultraviolet absorption band tailing into the visible, as in Figure 28-8. Its close relatives are benzene, benzenol, and nitrobenzene:

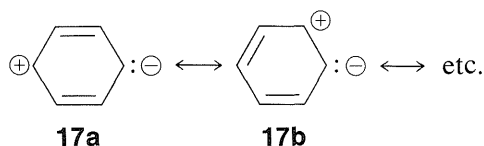


The conjugated π system common to all four compounds is that of the benzenoid ring, which is described as the absorbing **chromophore** (Section 22-3B). The hydroxyl and nitro substituents can be seen individually to shift the λ_{\max} of the chromophore to longer wavelengths. However, the combined effect of the two substituents is much more dramatic, especially if the OH group is converted to the corresponding anion, 4-nitrobenzenolate. Now λ_{\max} is shifted into the visible region, giving a yellow color, and because ϵ is large, the color is intense. Thus, properly chosen substituents can shift the main benzenoid absorption band from the ultraviolet into the visible region of the spectrum. Such substituents are often called **auxochromes**. They act by extending the conjugation of the chromophore and are particularly effective in causing large shifts towards the visible when one substituent is a π -electron donor and the other a π -electron acceptor. Thus, with the 4-nitrobenzenolate ion, interaction between the strongly electron-donating —O^\ominus group and the strongly electron-accepting —NO_2 group provides significant stabilization:



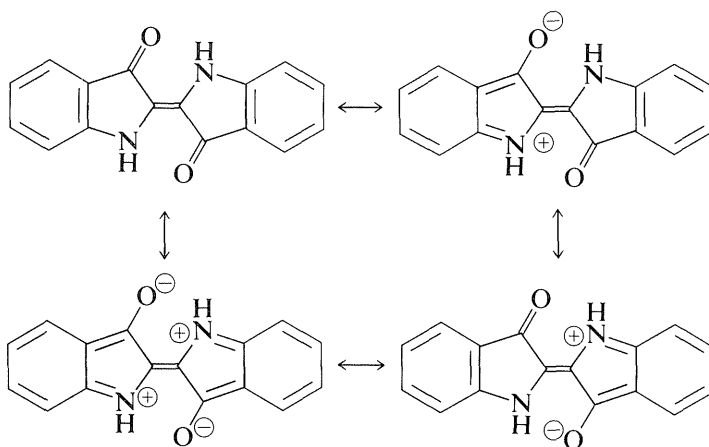
Resonance stabilization of this kind must be more important in the excited state than in the ground state if it is to narrow the energy gap between them (Figure 28-9). The narrowing of the energy gap is expected because excited electronic states have hybrid structures with much more important contributions from dipolar valence-bond forms than does the ground state (see Section 9-9B). Another way to look at the effect of substituents is to recall that excited singlet states of benzene will be stabilized by important

contributions from resonance structures such as **17a** and **17b**:

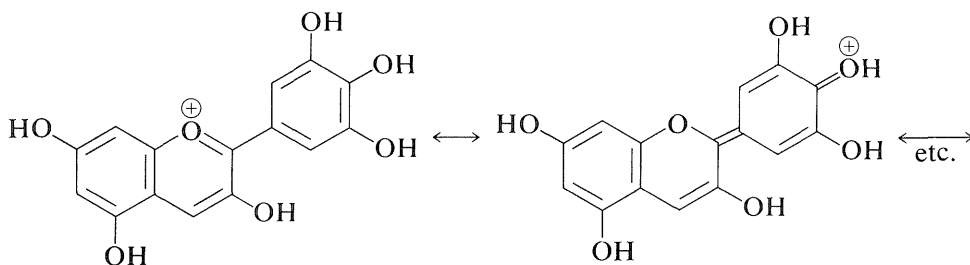


Hence, substitution of an electron-attracting group (such as NO_2) at one end of such a system and an electron-donating group (such as O^-) at the other end should be particularly favorable for stabilization of the excited state (relative to the ground state, where **17a**, **17b**, etc., are of lesser importance). At the same time, we should *not* expect that two electron-attracting (or two electron-donating) groups at opposite ends would be nearly as effective.

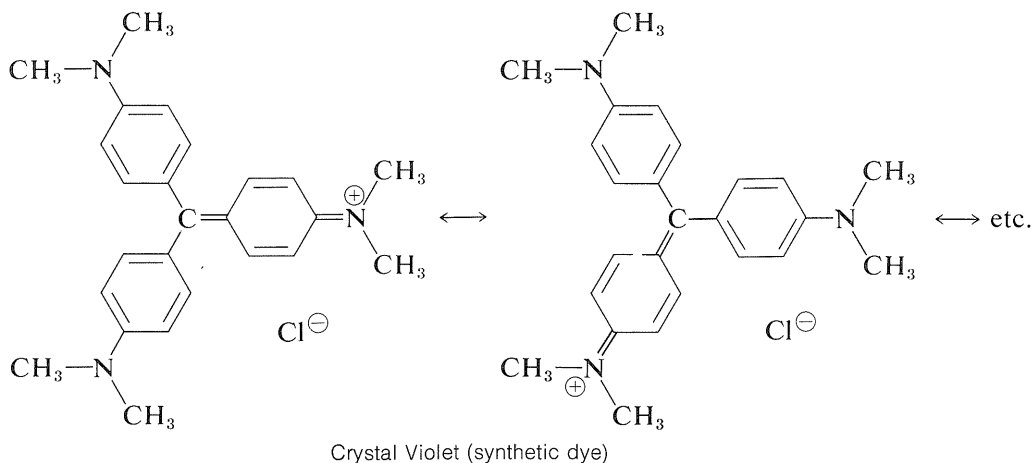
We hope you will understand from the foregoing discussion why it is that many intensely colored substances of natural or synthetic origin have conjugated structures with substituents, often cationic or anionic substituents, that can donate or accept electrons from the conjugated system. Such compounds provide us with many useful dyes, pigments, indicators, and food-coloring agents, as well as conferring color on plants and animals. A few examples follow:



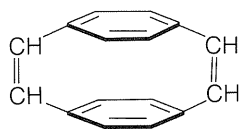
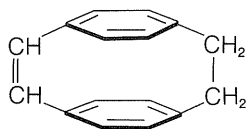
indigo
(a deep-blue dye of natural and synthetic origin)



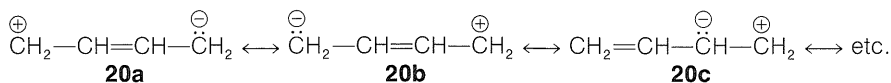
delphinidin
(member of a class of natural compounds, *anthocyanins*, that give color to flowers, leaves, fruits; they occur as glycosides)



Exercise 28-23 How would you expect the spectra of compounds **18** and **19** to compare with each other and with the spectra of *cis*- and *trans*-1,2-diphenylethene (stilbene)? Explain.



Exercise 28-24 Why must the resonance forms **20a**, **b**, **c**, etc. correspond to a singlet state? Formulate the hybrid structure of a triplet state of butadiene in terms of appropriate contributing resonance structures.



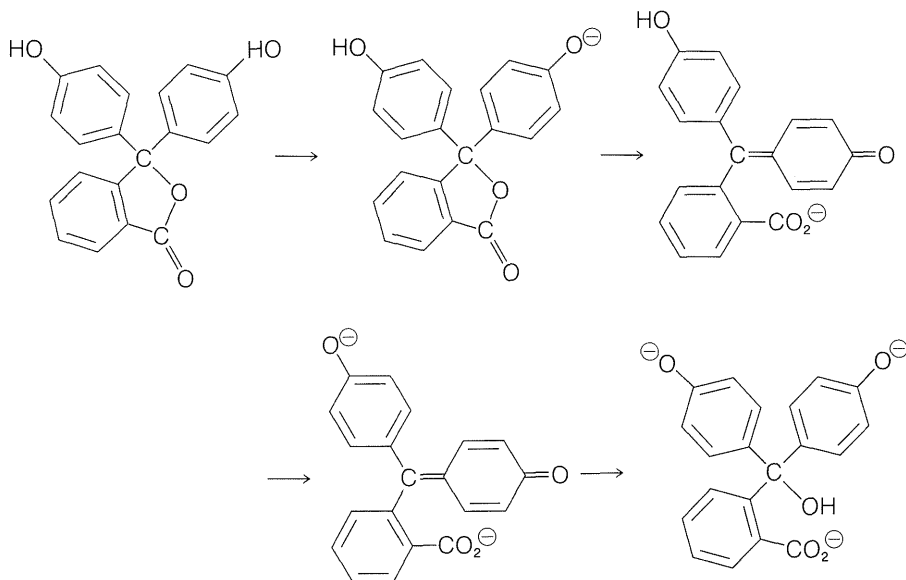
Exercise 28-25 The $\pi \rightarrow \pi^*$ absorption spectra of *trans,trans*-, *trans,cis*-, and *cis,cis*-1,4-diphenylbutadiene show maxima and ϵ values (in parentheses) at about 330 nm (5.5×10^4), 310 nm (3×10^4), and 300 nm (3×10^4), respectively. What is the difference in energy between the transitions of these isomers in kcal per mole? Why should the *trans,trans* isomer have a different λ_{\max} than the other isomers? (It may be helpful to make scale drawings or models.)

Exercise 28-26 Aqueous solutions of crystal violet turn from violet to blue to green to yellow on addition of successive amounts of acid. The color changes are reversed by adding alkali. What kind of chemical changes could be taking place to give these color changes?

Exercise 28-27 a. 4-Nitro-*N,N*-dimethylbenzenamine gives a yellow solution in water which fades to colorless when made acidic. Explain.

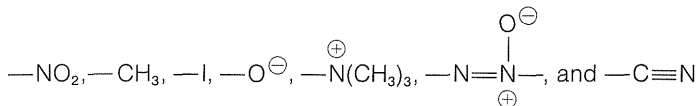
b. 4-(*N,N*-Dimethylamino)azobenzene (Section 23-10C) is bright yellow in aqueous solution (λ_{max} 420 nm) but turns intense red (λ_{max} 530 nm) if dilute acid is added. If the solution is then made very strongly acid, the red color changes to a different yellow (λ_{max} 430 nm) than the starting solution. Show how one proton could be added to 4-(*N,N*-dimethylamino)azobenzene to cause the absorption to shift to longer wavelengths and how addition of a second proton could shift the absorption back to shorter wavelengths.

Exercise 28-28 The well-known indicator and laxative, phenolphthalein, undergoes the following changes as a neutral solution is made more and more basic:



Some of these forms are colorless, some intensely colored. Which would you expect to absorb at sufficiently long wavelengths to absorb visible light. Give your reasoning.

Exercise 28-29 Classify the following groups as strong or weak, chromophores or auxochromes:

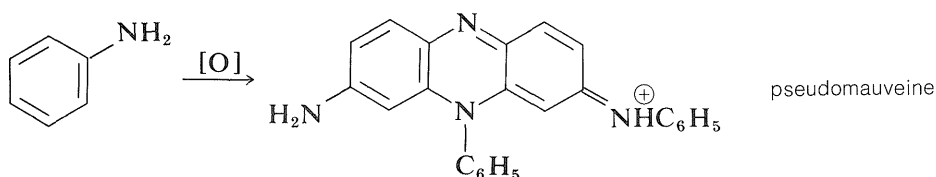


Give your reasoning.

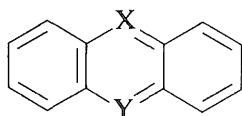
28-4A Dyes

Historically, the dye industry has been closely linked with the development of synthetic organic chemistry. Although dyes have been extracted from natural sources for centuries, it was not until 1856 that a synthetic dye was produced commercially. The previous year, William Henry Perkin—at age 17—oxidized

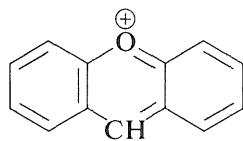
benzenamine (aniline) with potassium dichromate and isolated from the product (which was mostly aniline black; Section 23-11D) a purple compound that was excellent for dyeing silk. Perkin started commercial production of the dye under enormous difficulties. Because there was no organic chemical industry at the time, he had to design and build his own equipment as well as devise efficient syntheses for starting materials. His route to benzenamine started with crude benzene from coal, which he nitrated and then reduced with iron and acid. He had to make the nitric acid (from nitrate salts and sulfuric acid) because concentrated nitric acid was not available. It was not until 1890 that the structure of Perkin's dye, called mauveine, was established by Otto Fischer. The dye was actually a mixture (because the benzene used contained methylbenzene), but the product from the oxidation of benzenamine itself is structurally related to aniline black:



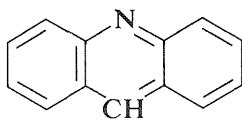
Although the mauveine dyes have been replaced with better dyes, they are representative of a group of useful dyes having the general structure



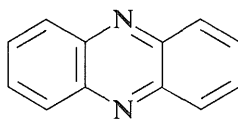
in which X and Y can be oxygen, nitrogen, sulfur, or carbon. The rings invariably carry substituents (hydroxyl or amino) that provide enhanced stabilization of the excited states. Examples of these ring systems follow:



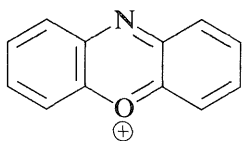
xanthene dyes



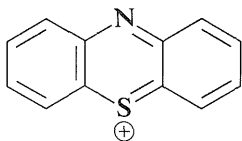
acridine dyes



azine dyes



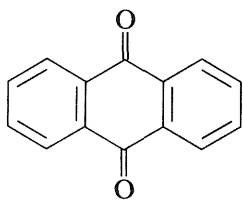
oxazine dyes



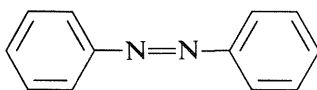
thiazine dyes

A large number of useful dyes are substituted triphenylmethane derivatives. Crystal Violet (Section 28-4) and phenolphthalein (Exercise 28-28) are excellent examples of this kind of dye.

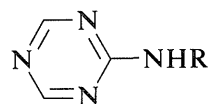
Other important dyes are derivatives of the following types of substances:



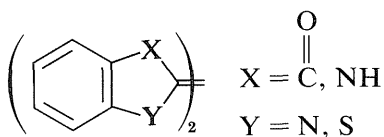
anthraquinone



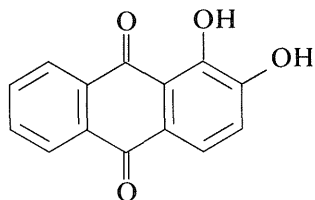
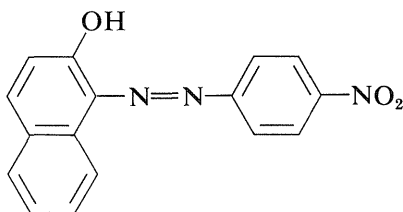
azobenzene



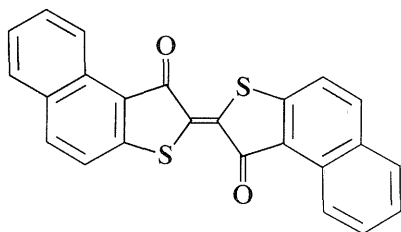
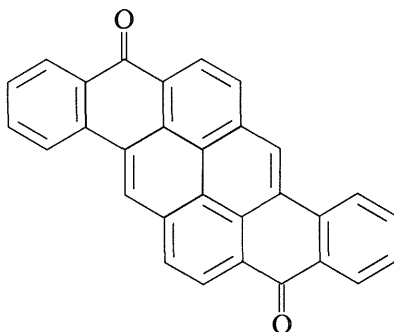
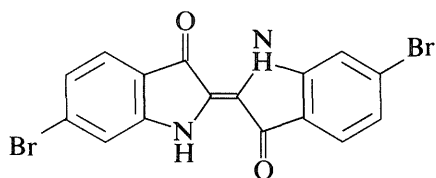
triazine



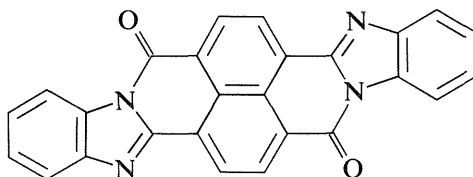
Examples are

1,2-dihydroxyanthraquinone
(alizarin)

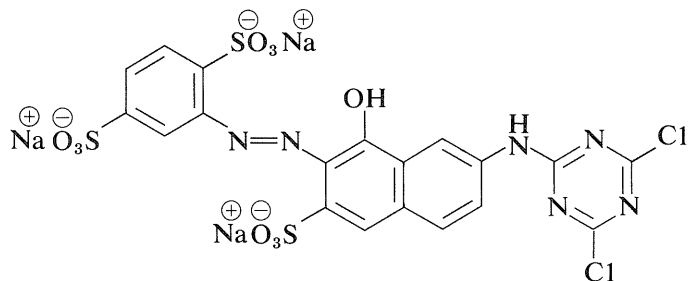
Para Red

4,5,4',5'-dibenzothioindigo
(brown)pyranthrone
(orange)

Tyrian purple



Indanthrene Brilliant Orange



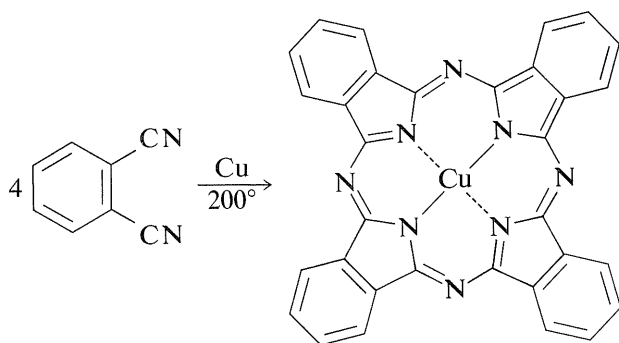
bright scarlet dye

There is more to a successful dye than just an attractive color.⁵ If it is to be useful, say for coloring fabrics, some simple means must be available for introducing the color into the fiber and then, usually of greater difficulty and importance, the color must be reasonably permanent—that is, resistant to normal laundry or cleaning procedures (wash-fast) and stable to light (light-fast). Here again, fundamentally important problems are involved. The scientific approach to improving wash-fastness of fabric dyes has to be based on a knowledge of the structural factors bearing on the intermolecular forces that determine solubilities. Light-fastness is connected with the photochemistry of organic compounds.

28-4B Pigments

The distinction between a dye and a pigment is that a dye actually is absorbed by the material to be colored, whereas a pigment is applied with a binding material to the surface. Pigments usually are highly insoluble substances. Many insoluble inorganic substances that would be wholly unsatisfactory as dyes are useful pigments.

Copper phthalocyanine is an example of a very important class of organic pigments. These are tetraazatetrabenzo derivatives of the porphyrin compounds discussed in Sections 20-9 and 25-8B. Copper phthalocyanine arises from condensation of four molecules of 1,2-benzenedicarbonitrile in the presence of copper metal at 200°:



copper phthalocyanine

⁵For a good account of dyes, see L. F. Fieser and M. Fieser, *Organic Chemistry*, D. C. Heath & Co., Lexington, Mass., 1956, Chapter 36.

28-5 THE SENSATION OF COLOR

The sensation of color can be achieved in different ways. According to Table 28-1, which relates wavelength to color, we could recognize a given color, say yellow, by direct perception of light encompassing a narrow band of wavelengths around 580 nm, or by subtraction of blue light (435–480 nm) from white light.

A third way of producing color is by an additive process. In fact, a wide range of colors can be achieved by the addition of three colors—red, green, and blue—as indicated in Figure 28-10. Mixing all three so-called *primary additive colors*, in the right intensities, gives white light; mixing only red and green gives yellow. It is important to recognize that addition of any two primary colors is equivalent to subtracting the third. This point is amplified in Figure 28-10. Subtraction of the three primary additive colors, red, green, and blue, from white light gives, respectively, the three *primary subtraction colors*, cyan, magenta, and yellow. Application of additive and subtractive processes in color perception is illustrated in the following sections.

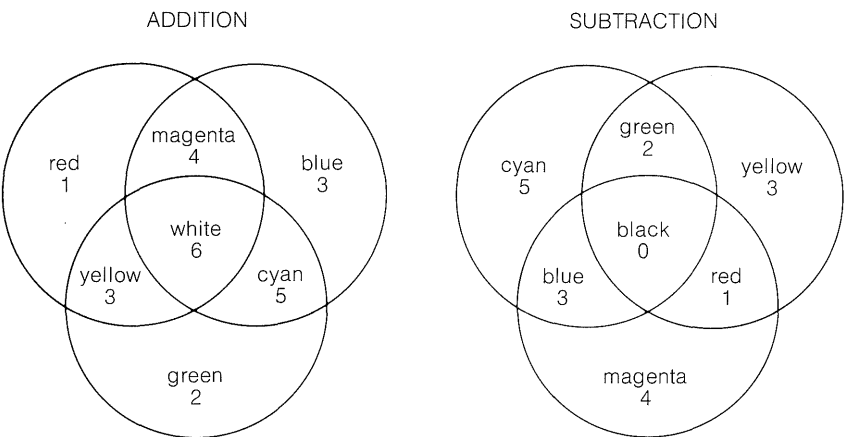


Figure 28-10 The primary addition colors can be combined additively to produce white, yellow, cyan, or magenta, as shown on the left. Numbers are assigned so that red = 1, green = 2, blue = 3, and so on, to permit ready recall that red + blue = magenta, or $1 + 3 = 4$. Likewise, white light (6) can be achieved in various ways, red + green + blue = white ($1 + 2 + 3 = 6$); red + cyan = white ($1 + 5 = 6$); blue + yellow ($3 + 3 = 6$); and so on. The primary subtraction colors are shown as the large overlapping circles in the diagram to the right. Subtraction of any of these colors from white light (6) gives the additive color. That is, white – cyan = red, or $6 - 5 = 1$. Black can be the result of $6 - 3 - 2 - 1 = 0$ (white – blue – green – red = black) or of $3 - 3 = 0$ (yellow – blue).

28-6 COLOR PHOTOGRAPHY

28-6A Subtractive Color Process

Photography is a popular activity for many, but relatively few have an understanding of the chemistry involved, particularly in color photography. This is unfortunate because color photography represents an interesting combination of photochemistry (energy transfer), organic chemistry (dye formation), optics, psychology and physiology (color perception), and engineering (production and development of film).

The sensation of full color in color transparencies produced by photographic means is achieved by *subtraction*. As a simple example, let us suppose that the subject to be photographed is blue. To obtain a blue image by shining white light through a transparency, the transparency is made to subtract (absorb) yellow light—that is, to absorb strongly in the 580-nm region. How a color image of the subject is recorded chemically on the film and how the film is developed into a transparency will become clearer from the following discussion.

28-6B Color Film

The emulsion of a typical color film has three silver-bromide layers separately sensitized by suitable dyes to blue, green, and red light (Figure 28-11). When processed (Section 28-6C), the color formed in each layer is *complementary* to the color to which the layer is sensitive. Thus, if *unexposed* film is processed, intense yellow, magenta, and cyan colors are respectively formed in the blue-, green-, and red-sensitive layers. Then, when white light strikes this processed

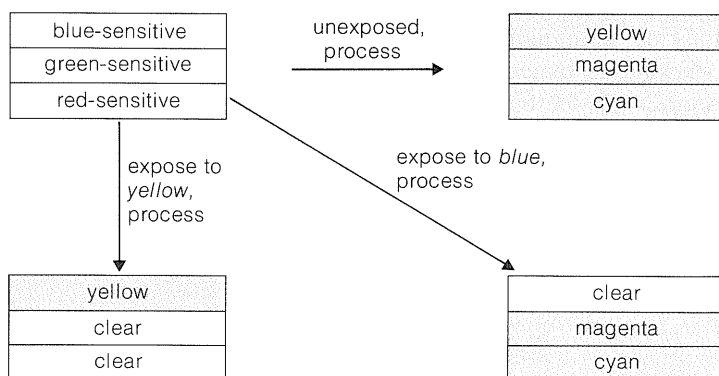


Figure 28-11 Schematic representation of the layer structure of color film and the color changes that occur on development. The actual film also contains a filter below the blue-sensitive layer to remove the blue light passing through this layer (because all emulsions are sensitive to blue), an antihalation layer below the red to prevent scattering of the light back through the emulsion, and a film base, such as cellulose acetate or poly-1,2-ethanediyl 1,4-benzenedioate, to support the emulsion.

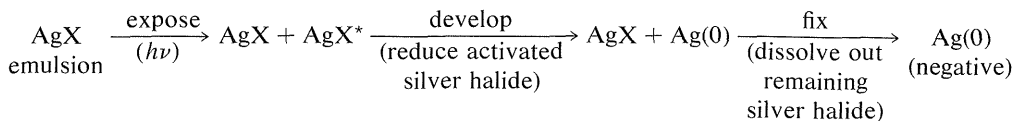
film, the yellow layer subtracts the blue, the magenta subtracts the green, and the cyan subtracts the red, with the result that the film appears black (or nearly so), as corresponds to *no* exposure to light. However, if the film is exposed to strong blue light *before* processing, the blue-sensitive layer responds, and when the film is processed, no yellow dye is formed in the blue-sensitive layer (see Figure 28-11). The transparency then contains only the subtraction colors, magenta and cyan. When white light enters a transparency of superimposed magenta and cyan dyes, only blue light is transmitted, as befits the color of the original sensitizing light. (From the right side of Figure 28-10, we see the overlap of 5 and 4 leads to blue.) Similarly, exposure of the film to strong yellow light (containing no blue), followed by processing, results in formation of yellow dye and no magenta nor cyan. This is because the green- and red-sensitive emulsions both are sensitive to yellow light, while the blue-sensitive emulsion does not respond to yellow light.

In summary, the overall process from color film to the projection of a color image involves two separate conversions of each color into its complement, the net result being an image that has the same colors as the original subject.

Exercise 28-30 Use Figure 28-10 to determine what colors you would expect in the layers of a processed color film of the type shown in Figure 28-11 if the incident light were (a) white, (b) green, (c) magenta, (d) orange? Explain.

28-6C Chemistry of Color Developers

We have seen that full color perception can be achieved by subtraction methods using dyes in suitable combinations. We now have to consider how such dyes are formed on exposure and development of color film. First though, you should recognize that a photographic emulsion, whether for color or black-and-white film, is light-sensitive primarily because of the presence of silver halide. You will recall from previous discussions (Section 26-2C) that the sequence from exposure to development involves the following:



In color film, a silver halide is a component of all three color-sensitive layers (see Figure 28-12), but it is *directly* activated by light only in the first layer. In the other layers, activation is achieved *indirectly* by a sensitizing dye which, on absorbing light, can transfer energy to the silver halide. The sensitizing dyes are *not* the same as the color-forming dyes, as we shall see. Among the most

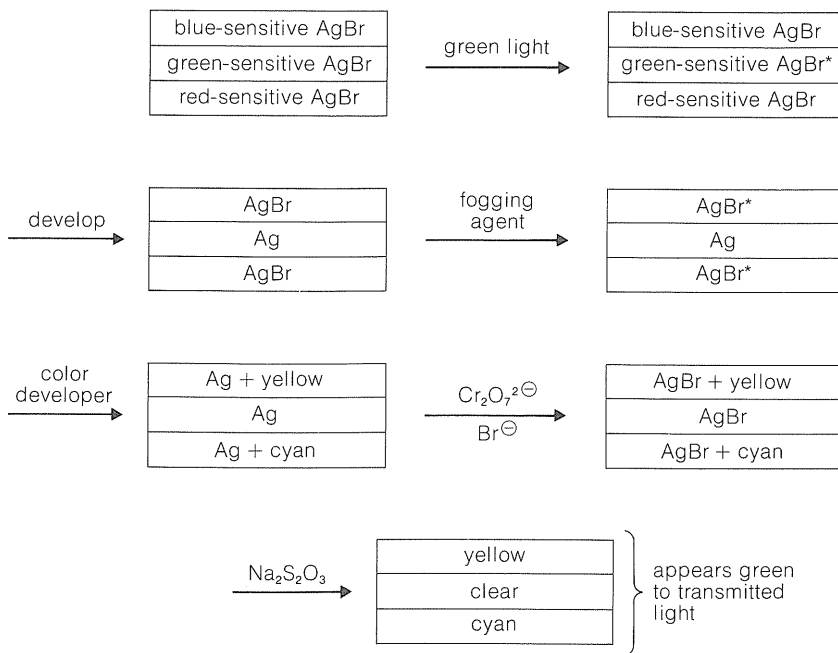
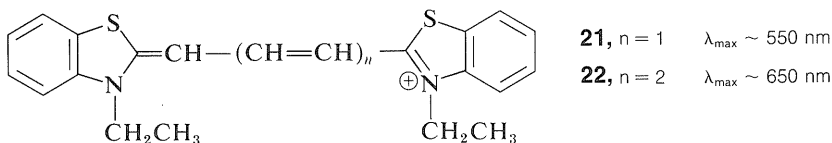


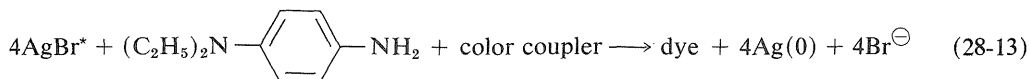
Figure 28-12 Schematic changes in the development of a color film exposed to green light. The color couplers are present in the original sensitized layers.

important sensitizing dyes are the cyanine dyes, such as the thiacyanines, **21** and **22**. Compound **21** is magenta-colored (absorbs green light), and compound **22** is cyan-colored (absorbs red light). Structurally they differ only by one $\text{CH}=\text{CH}$ unit:



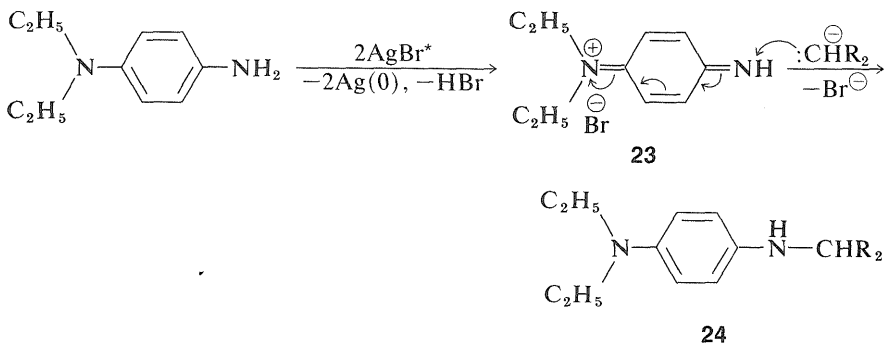
The chemistry involved in the formation of the dyes in the usual color films is highly ingenious and is achieved through steps shown in Figure 28-12 which, for purposes of illustration, are carried through for an initial exposure to green light. The exposure activates only the green-sensitive emulsion, and development with an ordinary developer such as metol-hydroquinone (Section 26-2C) produces silver metal only in the green-sensitive layer. The film now has the visual appearance of a milky negative. The developer then is washed out and the film is fogged, a process that activates the silver bromide remaining unreduced in the first step. The activated silver bromide so formed then is reduced with a **color developer**, usually 4-amino-*N,N*-diethylbenzenamine, in the presence of a **color coupler**. Production of dye occurs in direct proportion to the

amount of activated silver bromide present, in close conformity with the following equation:



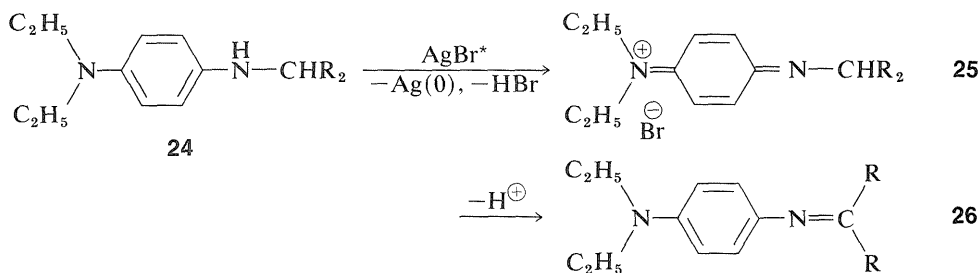
A different color coupler is used for each layer of the emulsion and, although the complete color picture is formed in this step, the film is coal black because of the metallic silver produced at the same time. The silver then is oxidized to silver bromide with dichromate solution containing bromide ion and removed with thiosulfate solution. The final image thus contains no silver.

The color-forming reactions obviously are critical to the success of the overall process and, of necessity, involve some degree of compromise between requirements for yield, reproducibility, suitability of color, and light-fastness. In reactions of the type shown in Equation 28-13, the color coupler is a methylene compound, R_2CH_2 , in which the R groups have sufficient electron-attracting character to undergo some degree of formation of $\text{R}_2\text{CH}^\ominus$ in the alkaline medium used for color development. The first two steps in the overall sequence follow:

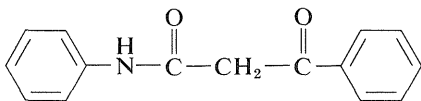


The color developer is oxidized by the activated silver bromide produced in the third step of Figure 28-12 to a quinonimmonium salt, **23**. This substance readily undergoes a Michael-type conjugate addition (Section 18-9D) with the anion, $\text{R}_2\text{CH}^\ominus$, of the active methylene compound to give an *N'*-substituted 4-amino-*N,N*-diethylbenzenamine, **24**.

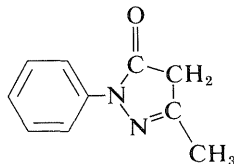
The product **24** is a photographic developer and is oxidized either by activated silver bromide or by **23** to a new quinonimmonium salt, **25**:



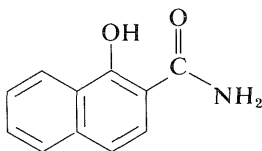
This substance has an acidic hydrogen at the $-\text{CHR}_2$ and, on loss of this proton, a neutral conjugated imine results, **26**, which is the actual dye. Color is expected for these molecules because the R groups are electron-attracting and the diethylamino group at the other end of the conjugated system is electron-donating. The remaining important question is how to adjust the R groups to obtain the proper colors in each layer of the film. Compounds that give yellow, magenta, and cyan dyes with 4-amino-*N,N*-diethylbenzenamine and activated silver bromide are shown below.



N-phenyl-3-phenyl-3-oxopropanamide
(yellow)

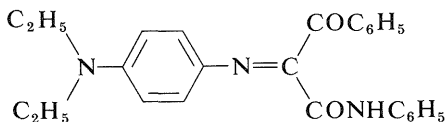


1-phenyl-3-methyl-1,2-diazacyclopent-2-en-5-one
(magenta)



1-hydroxy-2-naphthalenecarboxamide
(cyan)

In the case of *N*-phenyl-3-phenyl-3-oxopropanamide, the yellow dye formed has the following structure:

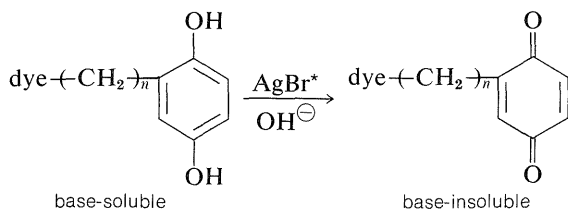


Such dyes often are called **azomethines**. The nature of the exact color couplers used in color film is not well publicized. It is important that the couplers not diffuse out of the layers where they belong and, for this reason, insolubilizing substituent groups are attached to strategic positions on the color couplers.

The "instant" color process pioneered by Polaroid operates by a wonderfully ingenious, subtractive-color, three-layer scheme basically similar to the one shown in Figures 28-11 and 28-12. A very important difference is that the colors are transferred from the emulsion to a layer of white pigment (TiO_2), so the process actually is a printing process. The subtractive dyes (yellow, magenta, and cyan) are present in the emulsion as substituent groups on base-soluble photographic developers, schematically $[\text{dye}-(\text{CH}_2)_n\text{developer}]$. A copper phthalocyanine derivative (Section 28-4B) is used to provide the cyan color.

What occurs in a given layer of the film is roughly as follows: Activation of the silver bromide in the layer by the light to which it is sensitized, and then

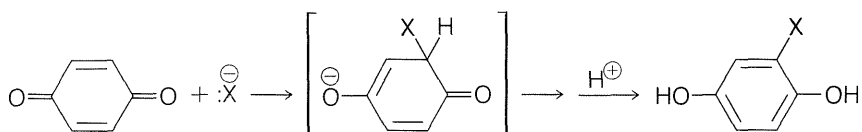
development with an alkaline developer solution converts the “dye developer” to a base-insoluble form (Section 26-2C) in proportion to the light absorbed:



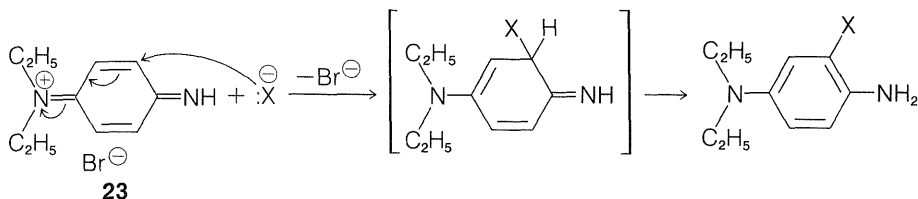
The unused soluble “dye developer” diffuses to the printing surface, where it is rendered insoluble. The subtractive color therefore is produced in inverse proportion to the intensity of the sensitizing light (as in Figure 28-11). The process has the considerable advantage of having no color-forming reactions during development. The emulsion is protected from light when the undeveloped picture first leaves the camera by spreading an opaque dye over the surface of the picture. This dye later fades as development becomes complete.

Exercise 28-31* Write a reasonable stepwise mechanism for the formation of a cyan dye from 1-hydroxy-2-naphthalenecarboxamide in the overall reaction expressed by Equation 28-13 (review Section 26-1E).

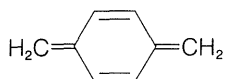
Exercise 28-32* Quinones react with nucleophilic agents at carbon (Section 26-2D):



However, the quinonimmonium salt, **23**, adds preferentially at nitrogen to give **24** rather than by the following path:



Explain why nucleophilic addition to **23** to give **24** by attack at nitrogen is more likely than the corresponding addition to a quinone by attack at oxygen. At what position would you expect nucleophilic addition to occur most readily to *para*-xylylene? Explain.



3,6-dimethylenidene-1,4-cyclohexadiene
(*para*-xylylene)

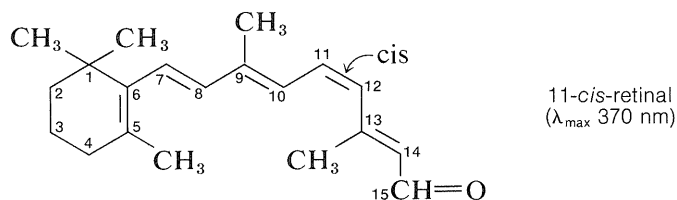
28-7 CHEMISTRY OF VISION

Vision is a process in which light is absorbed by a pigment in a photoreceptor cell (by a dye in the eye) and the photochemistry that ensues ultimately produces a transient electrical signal that is transmitted to the brain and interpreted as a visual image. There is much that is not fully understood about this process, but we shall discuss briefly the chemistry involved.

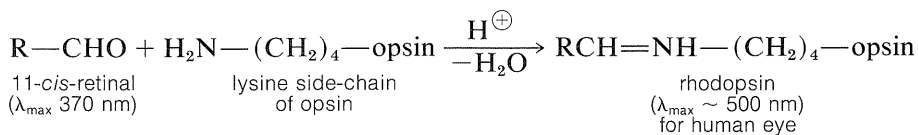
The eye is an extraordinarily sensitive instrument. To be sure, its wavelength response is restricted to 400–800 nm, but its degree of sensitivity is such that a fully dark-adapted eye can clearly detect objects in light so dim as to correspond to a light input over the retina of only about 10,000 quanta per second—one light quantum per three minutes per receptor cell in the retina!

The retina is made up of two kinds of light-sensitive (photoreceptor) cells, known as rods and cones. The rods are the more sensitive and are responsible for vision in dim light. The cones are much fewer in number than the rods and provide detail and color vision in good light. The part of the retina that corresponds to the center of the visual field contains only cones. A red pigment called **rhodopsin** is the photosensitive substance in the rod cells of the retina. It absorbs most strongly in the blue-green region of the visible spectrum (λ_{\max} 500 nm) and is essentially unaffected by the far-red end of the spectrum. Cone vision appears to involve a different pigment called **iodopsin**, which absorbs farther toward the red than does rhodopsin.

Rhodopsin is a combination of a protein called **opsin**, and the highly conjugated aldehyde, 11-*cis*-retinal:



The structure of opsin is unknown, but its prosthetic group (11-*cis*-retinal) is bonded to it through an imine (Schiff base) function formed between the aldehyde group of the retinal and the side-chain amino function of a lysine unit of opsin:



Opsin itself is colorless, whereas 11-*cis*-retinal absorbs strongly at 370 nm. The combination of opsin with 11-*cis*-retinal produces a remarkable shift of λ_{\max} to longer wavelengths (430 nm to 620 nm, depending on the species). Similar shifts in wavelength for 11-*cis*-retinal in combination with simple

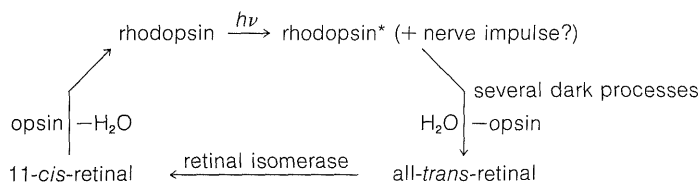
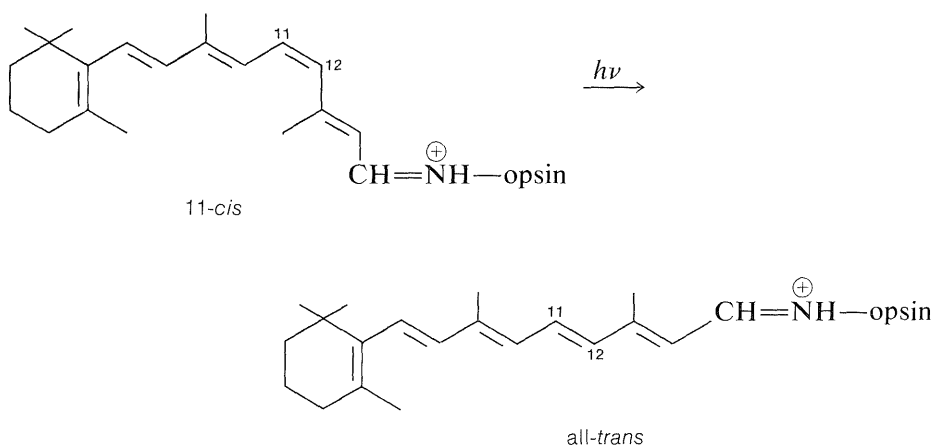


Figure 28-13 Schematic representation of the retinal cycle

amines are observed only up to λ_{max} of 440 nm, and only then for the protonated Schiff base. From this evidence, the chromophore in rhodopsin is believed to be protonated and to be profoundly modified by the structure of the opsin.

Light striking the retina changes the color of rhodopsin from red to yellow. The primary photochemical event in this process was established by G. Wald (Nobel Laureate in Physiology and Medicine, 1967), who showed that light absorption led to a change of configuration about the C11–C12 double bond of the retinal chromophore from *cis* to *trans*:



There ensues a series of dark reactions or conformational changes that have the effect of greatly activating the imine linkage of the all-*trans*-rhodopsin towards hydrolysis. On hydrolysis, all-*trans*-retinal is released and is unable to recombine with opsin until it is reconverted to the 11-*cis* isomer. The *trans*-to-*cis* rearrangement is a thermal rather than a photochemical reaction and is catalyzed by the enzyme *retinal isomerase*. The cycle of reactions is summarized in Figure 28-13.

The exact point at which the nerve impulse is transmitted is not established with certainty, but it has to occur *before* the hydrolysis step because hydrolysis is too slow to account for the nerve impulse. One theory suggests that an electrical signal is generated at the instant of light absorption by electron transfer to a $\pi \longrightarrow \pi^*$ singlet excited state that has substantially charged carbon atoms.

Additional Reading

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