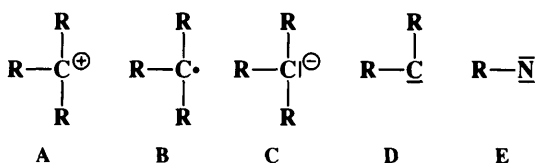


5

CARBOCATIONS, CARBANIONS, FREE RADICALS, CARBENES, AND NITRENES

There are four types of organic species in which a carbon atom has a valence of only 2 or 3.¹ They are usually very short-lived, and most exist only as intermediates that are quickly converted to more stable molecules. However, some are more stable than others and fairly stable examples have been prepared of three of the four types. The four types of species are *carbocations* (**A**), *free radicals* (**B**), *carbanions* (**C**), and *carbenes* (**D**). Of the four, only carbanions have a complete octet around the carbon. There are many other organic ions



and radicals with charges and unpaired electrons on atoms other than carbon, but we will discuss only *nitrenes* (**E**), the nitrogen analogs of carbenes. Each of the five types is discussed in a separate section, which in each case includes brief summaries of the ways in which the species form and react. These summaries are short and schematic. The generation and fate of the five types are more fully treated in appropriate places in Part 2 of this book.

CARBOCATIONS²

Nomenclature

First we must say a word about the naming of **A**. For many years these species were called "carbonium ions," though it was suggested³ as long ago as 1902 that this was inappropriate

¹For general references, see Isaacs *Reactive Intermediates in Organic Chemistry*; Wiley: New York, 1974; McManus *Organic Reactive Intermediates*; Academic Press: New York, 1973. Two serial publications devoted to review articles on this subject are *Reactive Intermediates* (Wiley) and *Reactive Intermediates* (Plenum).

²For a treatise, see Olah; Schleyer *Carbonium Ions*, 5 vols.; Wiley: New York, 1968-1976. For monographs, see Vogel *Carbocation Chemistry*; Elsevier: New York, 1985; Bethell; Gold *Carbonium Ions*; Academic Press: New York, 1967. For reviews, see Saunders; Jiménez-Vázquez *Chem. Rev.* **1991**, *91*, 375-397; Arnett; Hofelich; Schriver *React. Intermed. (Wiley)* **1987**, *3*, 189-226; Bethell; Whittaker *React. Intermed. (Wiley)* **1981**, *2*, 211-250; Bethell *React. Intermed. (Wiley)* **1978**, *1*, 117-161; Olah *Chem. Scr.* **1981**, *18*, 97-125, *Top. Curr. Chem.* **1979**, *80*, 19-88, *Angew. Chem. Int. Ed. Engl.* **1973**, *12*, 173-212 [*Angew. Chem.* *85*, 183-225] (this review has been reprinted as Olah *Carbocations and Electrophilic Reactions*; Wiley: New York, 1974); Isaacs, Ref. 1, pp. 92-199; McManus; Pittman, in McManus, Ref. 1, pp. 193-335; Buss; Schleyer; Allen *Top. Stereochem.* **1973**, *7*, 253-293; Olah; Pittman *Adv. Phys. Org. Chem.* **1966**, *4*, 305-347. For reviews of dicarbocations, see Lammertsma; Schleyer; Schwarz *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1321-1341 [*Angew. Chem.* *101*, 1313-1335]; Lammertsma *Rev. Chem. Int.* **1988**, *9*, 141-169; Pagni *Tetrahedron* **1984**, *40*, 4161-4215; Prakash; Rawdah; Olah *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 390-401 [*Angew. Chem.* *95*, 356-367]. See also the series *Advances in Carbocation Chemistry*.

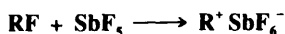
³Gomberg *Ber.* **1902**, *35*, 2397.

because “-onium” usually refers to a covalency higher than that of the neutral atom. Nevertheless, the name “carbonium ion” was well established and created few problems⁴ until some years ago, when George Olah and his co-workers found evidence for another type of intermediate in which there is a positive charge at a carbon atom, but in which the formal covalency of the carbon atom is five rather than three. The simplest example is the methanonium ion CH_5^+ (see p. 580). Olah proposed⁵ that the name “carbonium ion” be henceforth reserved for pentacoordinated positive ions, and that **A** be called “carbenium ions.” He also proposed the term “carbocation” to encompass both types. IUPAC has accepted these definitions.⁶ Although some authors still refer to **A** as carbonium ions and others call them carbenium ions, the general tendency is to refer to them simply as *carbocations*, and we will follow this practice. The pentavalent species are much rarer than **A**, and the use of the term “carbocation” for **A** causes little or no confusion.

Stability and Structure

Carbocations are intermediates in several kinds of reactions. The more stable ones have been prepared in solution and in some cases even as solid salts. In solution the carbocation may be free (this is more likely in polar solvents, in which it is solvated) or it may exist as an ion pair,⁷ which means that it is closely associated with a negative ion, called a *counterion* or *gegenion*. Ion pairs are more likely in nonpolar solvents.

Among simple alkyl carbocations⁸ the order of stability is tertiary > secondary > primary. Many examples are known of rearrangements of primary or secondary carbocations to tertiary, both in solution and in the gas phase. Since simple alkyl cations are not stable in ordinary strong-acid solutions, e.g., H_2SO_4 , the study of these species was greatly facilitated by the discovery that many of them could be kept indefinitely in stable solutions in mixtures of fluorosulfuric acid and antimony pentafluoride. Such mixtures, usually dissolved in SO_2 or SO_2ClF , are among the strongest acidic solutions known and are often called *super acids*.⁹ The original experiments involved the addition of alkyl fluorides to SbF_5 .¹⁰



Subsequently it was found that the same cations could also be generated from alcohols in super acid– SO_2 at -60°C ¹¹ and from alkenes by the addition of a proton from super acid or HF-SbF_5 in SO_2 or SO_2ClF at low temperatures.¹² Even alkanes give carbocations in super acid by loss of H^- . For example,¹³ isobutane gives the *t*-butyl cation



⁴For a history of the term “carbonium ion”, see Traynham *J. Chem. Educ.* **1986**, 63, 930.

⁵Olah *CHEMTECH* **1971**, 1, 506. *J. Am. Chem. Soc.* **1972**, 94, 808.

⁶Gold; Loening; McNaught; Sehmi *Compendium of Chemical Terminology: IUPAC Recommendations*; Blackwell Scientific Publications: Oxford, 1987.

⁷For a treatise, see Szwarc *Ions and Ion Pairs in Organic Reactions*, 2 vols.; Wiley: New York, 1972-1974.

⁸For a review, see Olah; Olah, in Olah; Schleyer, Ref. 2, vol. 2, pp. 715-782.

⁹For a review of carbocations in super acid solutions, see Olah; Prakash; Sommer, in *Superacids*; Wiley: New York, 1985, pp. 65-175.

¹⁰Olah; Baker; Evans; Tolgyesi; McIntyre; Bastien *J. Am. Chem. Soc.* **1964**, 86, 1360; Brouwer; Mackor *Proc. Chem. Soc.* **1964**, 147; Kramer *J. Am. Chem. Soc.* **1969**, 91, 4819.

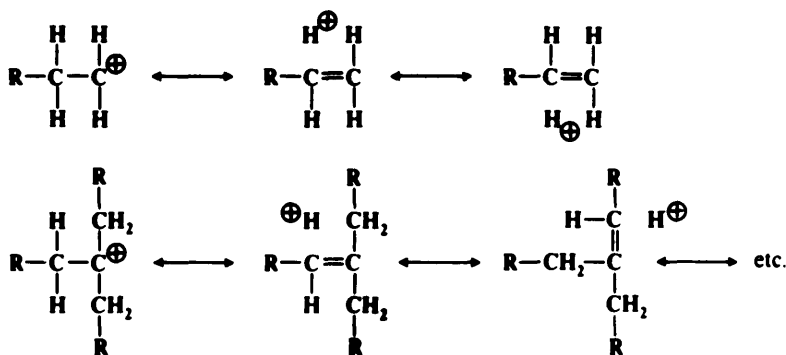
¹¹Olah; Comisarow; Cupas; Pittman *J. Am. Chem. Soc.* **1965**, 87, 2997; Olah; Sommer; Namanworth *J. Am. Chem. Soc.* **1967**, 89, 3576.

¹²Olah; Halpern *J. Org. Chem.* **1971**, 36, 2354. See also Herlem *Pure Appl. Chem.* **1977**, 49, 107.

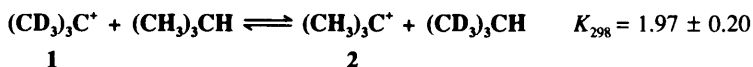
¹³Olah; Lukas *J. Am. Chem. Soc.* **1967**, 89, 4739.

No matter how they are generated, study of the simple alkyl cations has provided dramatic evidence for the stability order. Both propyl fluorides gave the isopropyl cation; all four butyl fluorides¹⁴ gave the *t*-butyl cation, and all seven of the pentyl fluorides tried gave the *t*-pentyl cation. *n*-Butane, in super acid, gave only the *t*-butyl cation. To date no primary cation has survived long enough for detection. Neither methyl nor ethyl fluoride gave the corresponding cations when treated with SbF_5 . At low temperatures, methyl fluoride gave chiefly the methylated sulfur dioxide salt $(\text{CH}_3\text{OSO})^+ \text{SbF}_6^-$ ¹⁵ while ethyl fluoride rapidly formed the *t*-butyl and *t*-hexyl cations by addition of the initially formed ethyl cation to ethylene molecules also formed.¹⁶ At room temperature, methyl fluoride also gave the *t*-butyl cation.¹⁷ In accord with the stability order, hydride ion is abstracted from alkanes by super acid most readily from tertiary and least readily from primary positions.

The stability order can be explained by hyperconjugation and by the field effect. In the hyperconjugation explanation,¹⁸ we compare a primary carbocation with a tertiary. It is seen that many more canonical forms are possible for the latter:



In the examples shown the primary ion has only two hyperconjugative forms while the tertiary has six. According to rule 6 (p. 35), the greater the number of equivalent forms, the greater the resonance stability. Evidence for the hyperconjugation explanation is that the equilibrium constant for this reaction:



is 1.97, showing that **2** is more stable than **1**.¹⁹ This is a β secondary isotope effect; there is less hyperconjugation in **1** than in **2** (see p. 228).²⁰

¹⁴The *sec*-butyl cation has been prepared by slow addition of *sec*-butyl chloride to $\text{SbF}_5\text{-SO}_2\text{ClF}$ solution at -110°C [Saunders; Hagen; Rosenfeld *J. Am. Chem. Soc.* **1968**, *90*, 6882] and by allowing molecular beams of the reagents to impinge on a very cold surface [Saunders; Cox; Ohlmstead *J. Am. Chem. Soc.* **1973**, *95*, 3018; Saunders; Cox; Lloyd *J. Am. Chem. Soc.* **1979**, *101*, 6656; Myhre; Yannoni *J. Am. Chem. Soc.* **1981**, *103*, 230].

¹⁵Peterson; Brockington; Vidrine *J. Am. Chem. Soc.* **1976**, *98*, 2660; Olah; Donovan; Lin *J. Am. Chem. Soc.* **1976**, *98*, 2661; Calves; Gillespie *J. Chem. Soc., Chem. Commun.* **1976**, 506; Olah; Donovan *J. Am. Chem. Soc.* **1978**, *100*, 5163.

¹⁶Ref. 8, p. 722.

¹⁷Olah; DeMember; Schlosberg *J. Am. Chem. Soc.* **1969**, *91*, 2112; Bacon; Gillespie *J. Am. Chem. Soc.* **1971**, *91*, 6914.

¹⁸For a review of molecular-orbital theory as applied to carbocations, see Radom; Poppinger; Haddon, in Olah; Schleyer, Ref. 2, vol. 5, pp. 2303-2426.

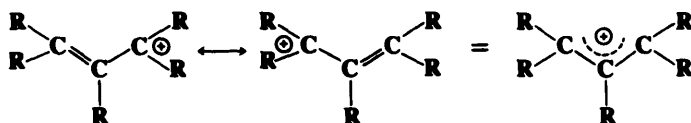
¹⁹Meot-Ner *J. Am. Chem. Soc.* **1967**, *109*, 7947.

²⁰If only the field effect were operating, **1** would be more stable than **2**, since deuterium is electron-donating with respect to hydrogen (p. 19), assuming that the field effect of deuterium could be felt two bonds away.

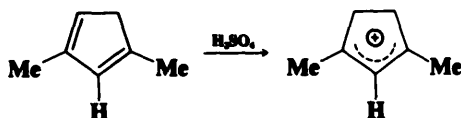
The field effect explanation is that the electron-donating effect of alkyl groups increases the electron density at the charge-bearing carbon, reducing the net charge on the carbon, and in effect spreading the charge over the α carbons. It is a general rule that the more concentrated any charge is, the less stable the species bearing it will be.

The most stable of all alkyl cations is the *t*-butyl cation. Even the relatively stable *t*-pentyl and *t*-hexyl cations fragment at higher temperatures to produce the *t*-butyl cation, as do all other alkyl cations with four or more carbons so far studied.²¹ Methane,²² ethane, and propane, treated with super acid, also yield *t*-butyl cations as the main product (see 2-18). Even paraffin wax and polyethylene give *t*-butyl cation. Solid salts of *t*-butyl and *t*-pentyl cations, e.g., $\text{Me}_3\text{C}^+ \text{SbF}_6^-$, have been prepared from super-acid solutions and are stable below -20°C .²³

Where the positive carbon is in conjugation with a double bond the stability is greater because of increased delocalization due to resonance and because the positive charge is



spread over two atoms instead of being concentrated on one (see the molecular-orbital picture of this species on p. 33). Each of the two atoms has a charge of about $\frac{1}{2}$ (the charge is exactly $\frac{1}{2}$ if all of the R groups are the same). Stable allylic-type cations²⁴ have been prepared by the solution of conjugated dienes in concentrated sulfuric acid, e.g.,²⁵



Both cyclic and acyclic allylic cations have been produced in this way. Stable allylic cations have also been obtained by the reaction between alkyl halides, alcohols, or olefins (by hydride extraction) and SbF_5 in SO_2 or SO_2ClF .²⁶ Divinylmethyl cations²⁷ are more stable than the simple allylic type, and some of these have been prepared in concentrated sulfuric acid.²⁸ Arenium ions (p. 502) are important examples of this type. Propargyl cations ($\text{RC}\equiv\text{CCR}_2^+$) have also been prepared.²⁹

²¹Ref. 13; Ref. 8, pp. 750-764.

²²Olah; Klopman; Schlosberg *J. Am. Chem. Soc.* **1969**, *91*, 3261. See also Hogeveen; Gaasbeek *Recl. Trav. Chim. Pays-Bas* **1968**, *87*, 319.

²³Olah; Svoboda; Ku *Synthesis* **1973**, 492; Ref. 13.

²⁴For reviews, see Deno, in Olah; Schleyer, Ref. 2, vol. 2, pp. 783-806; Richey, in Zabicky *The Chemistry of Alkenes*, vol. 2, Wiley: New York, 1970, pp. 39-114.

²⁵Deno; Richey; Hodge; Wisotsky *J. Am. Chem. Soc.* **1962**, *84*, 1498; Deno; Richey; Friedman; Hodge; Houser; Pittman *J. Am. Chem. Soc.* **1963**, *85*, 2991.

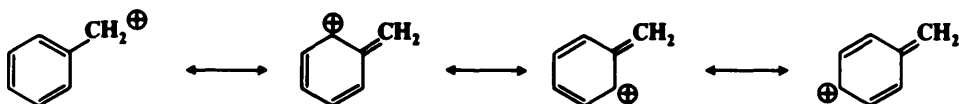
²⁶Olah; Comisarow *J. Am. Chem. Soc.* **1964**, *86*, 5682; Olah; Clifford; Halpern; Johanson *J. Am. Chem. Soc.* **1971**, *93*, 4219; Olah; Liang *J. Am. Chem. Soc.* **1972**, *94*, 6434; Olah; Spear *J. Am. Chem. Soc.* **1975**, *97*, 1539.

²⁷For a review of divinylmethyl and trivinylmethyl cations, see Sorensen, in Olah; Schleyer, Ref. 2, vol. 2, pp. 807-835.

²⁸Deno; Pittman *J. Am. Chem. Soc.* **1964**, *86*, 1871.

²⁹Pittman; Olah *J. Am. Chem. Soc.* **1965**, *87*, 5632; Olah, Spear; Westerman; Denis *J. Am. Chem. Soc.* **1974**, *96*, 5855.

Canonical forms can be drawn for benzylic cations,³⁰ similar to those shown above for allylic cations, e.g.,

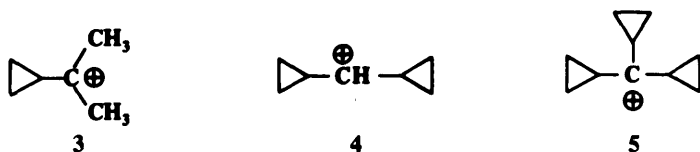


A number of benzylic cations have been obtained in solution as SbF_6^- salts.³¹ Diarylmethyl and triarylmethyl cations are still more stable. Triphenylchloromethane ionizes in polar solvents that do not, like water, react with the ion. In SO_2 , the equilibrium

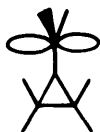


has been known for many years. Both triphenylmethyl and diphenylmethyl cations have been isolated as solid salts³² and, in fact, $\text{Ph}_3\text{C}^+ \text{BF}_4^-$ and related salts are available commercially. Arylmethyl cations are further stabilized if they have electron-donating substituents in ortho or para positions.³³

Cyclopropylmethyl cations³⁴ are even more stable than the benzyl type. **5** has been prepared by solution of the corresponding alcohol in 96% sulfuric acid,³⁵ and **3**, **4**, and similar ions by solution of the alcohols in $\text{FSO}_3\text{H}-\text{SO}_2-\text{SbF}_5$.³⁶ This special stability, which



increases with each additional cyclopropyl group, is a result of conjugation between the bent orbitals of the cyclopropyl rings (p. 152) and the vacant p orbital of the cationic carbon. Nmr and other studies have shown that the vacant p orbital lies parallel to the C-2,C-3 bond of the cyclopropane ring and not perpendicular to it.³⁷ In this respect the geometry is similar



³⁰For a review of benzylic, diarylmethyl, and triarylmethyl cations, see Freedman, in Olah; Schleyer, Ref. 2, vol. 4, pp. 1501-1578.

³¹Bollinger; Comisarow; Cupas; Olah *J. Am. Chem. Soc.* **1967**, *89*, 5687; Olah; Porter; Jeuell; White *J. Am. Chem. Soc.* **1972**, *94*, 2044.

³²Volz *Angew. Chem. Int. Ed. Engl.* **1963**, *2*, 622 [*Angew. Chem.* *75*, 921]; Volz; Schnell *Angew. Chem. Int. Ed. Engl.* **1965**, *4*, 873 [*Angew. Chem.* *77*, 864].

³³Goldacre; Phillips *J. Chem. Soc.* **1949**, 1724; Deno; Schriesheim *J. Am. Chem. Soc.* **1955**, *77*, 3051.

³⁴For reviews, see in Olah; Schleyer, Ref. 2, vol. 3: Richey, pp. 1201-1294; Wiberg; Hess; Ashe, pp. 1295-1345.

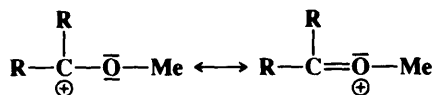
³⁵Deno; Richey; Liu; Hodge; Houser; Wisotsky *J. Am. Chem. Soc.* **1962**, *84*, 2016.

³⁶Pittman; Olah *J. Am. Chem. Soc.* **1965**, *87*, 2998; Deno; Liu; Turner; Fruit *J. Am. Chem. Soc.* **1965**, *87*, 3000.

³⁷For example, see Ree; Martin *J. Am. Chem. Soc.* **1970**, *92*, 1660; Kabakoff; Namanworth *J. Am. Chem. Soc.* **1970**, *92*, 3234; Buss; Gleiter; Schleyer *J. Am. Chem. Soc.* **1971**, *93*, 3927; Poulter; Spillner *J. Am. Chem. Soc.* **1974**, *96*, 7591; Childs; Kostyk; Lock; Mahendran *J. Am. Chem. Soc.* **1990**, *112*, 8912; Ref. 35.

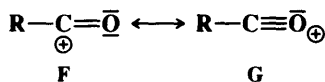
to that of a cyclopropane ring conjugated with a double bond (p. 152). Cyclopropylmethyl cations are further discussed on pp. 323–324. The stabilizing effect just discussed is unique to cyclopropyl groups. Cyclobutyl and larger cyclic groups are about as effective at stabilizing a carbocation as ordinary alkyl groups.³⁸

Another structural feature that increases carbocation stability is the presence, adjacent to the cationic center, of a hetero atom bearing an unshared pair,³⁹ e.g., oxygen,⁴⁰ nitrogen,⁴¹ or halogen.⁴² Such ions are stabilized by resonance:



The methoxymethyl cation can be obtained as a stable solid, $\text{MeOCH}_2^+ \text{SbF}_6^-$.⁴³ Carbocations containing either a β or γ silicon atom are also stabilized,⁴⁴ relative to similar ions without the silicon atom.

Simple acyl cations RCO^+ have been prepared⁴⁵ in solution and the solid state.⁴⁶ The acetyl cation CH_3CO^+ is about as stable as the *t*-butyl cation (see, for example, Table 5.1). The 2,4,6-trimethylbenzoyl and 2,3,4,5,6-pentamethylbenzoyl cations are especially stable (for steric reasons) and are easily formed in 96% H_2SO_4 .⁴⁷ These ions are stabilized by a canonical form containing a triple bond (**G**), though the positive charge is principally located on the carbon,⁴⁸ so that **F** contributes more than **G**.



The stabilities of most other stable carbocations can also be attributed to resonance. Among these are the tropylium, cyclopropenium, and other aromatic cations discussed in Chapter 2. Where resonance stability is completely lacking, as in the phenyl (C_6H_5^+) or

³⁸Sorensen; Miller; Ranganayakulu *Aust. J. Chem.* **1973**, 26, 311.

³⁹For a review, see Hevesi *Bull. Soc. Chim. Fr.* **1990**, 697-703. For examples of stable solutions of such ions, see Kabuss *Angew. Chem. Int. Ed. Engl.* **1966**, 5, 675 [*Angew. Chem.* 78, 714]; Dimroth; Heinrich *Angew. Chem. Int. Ed. Engl.* **1966**, 5, 676 [*Angew. Chem.* 78, 715]; Tomalia; Hart *Tetrahedron Lett.* **1966**, 3389; Ramsey; Taft *J. Am. Chem. Soc.* **1966**, 88, 3058; Olah; Liang; Mo *J. Org. Chem.* **1974**, 39, 2394; Borch *J. Am. Chem. Soc.* **1968**, 90, 5303; Rabinovitz; Bruck *Tetrahedron Lett.* **1971**, 245.

⁴⁰For a review of ions of the form $\text{R}_2\text{C}^+-\text{OR}'$, see Rakhmankulov; Akhmatdinov; Kantor *Russ. Chem. Rev.* **1984**, 53, 888-899. For a review of ions of the form $\text{R}'\text{C}^+(\text{OR})_2$ and $\text{C}^+(\text{OR})_3$, see Pindur; Müller; Flo; Witzel *Chem. Soc. Rev.* **1987**, 16, 75-87.

⁴¹For a review of such ions where nitrogen is the hetero atom, see Scott; Butler, in Olah; Schleyer, Ref. 2, vol. 4, pp. 1643-1696.

⁴²For reviews of such ions where the hetero atom is halogen, see Allen; Tidwell *Adv. Carbocation Chem.* **1989**, 1, 1-44; Olah; Mo, in Olah; Schleyer, Ref. 2, vol. 5, pp. 2135-2262, *Adv. Fluorine Chem.* **1973**, 7, 69-112. For the preparation, in superacid solution, of the ions CX_3^+ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), see Olah; Heiliger; Prakash *J. Am. Chem. Soc.* **1989**, 111, 8020.

⁴³Olah; Svoboda *Synthesis* **1973**, 52.

⁴⁴For a review and discussion of the causes, see Lambert *Tetrahedron* **1990**, 46, 2677-2689. See also Lambert; Chelius *J. Am. Chem. Soc.* **1990**, 112, 8120.

⁴⁵For reviews of acyl cations, see Al-Talib; Tashtoush *Org. Prep. Proced. Int.* **1990**, 22, 1-36; Olah; Germain; White; in Olah; Schleyer, Ref. 2, vol. 5, pp. 2049-2133. For a review of the preparation of acyl cations from acyl halides and Lewis acids, see Lindner *Angew. Chem. Int. Ed. Engl.* **1970**, 9, 114-123 [*Angew. Chem.* 82, 143-153].

⁴⁶See, for example, Olah; Kuhn; Tolgyesi; Baker *J. Am. Chem. Soc.* **1962**, 84, 2733; Deno; Pittman; Wisotsky *J. Am. Chem. Soc.* **1964**, 86, 4370; Olah; Dunne; Mo; Szilagy *J. Am. Chem. Soc.* **1972**, 94, 4200; Olah; Svoboda *Synthesis* **1972**, 306.

⁴⁷Hammett; Deyrup *J. Am. Chem. Soc.* **1933**, 55, 1900; Newman; Deno *J. Am. Chem. Soc.* **1951**, 73, 3651.

⁴⁸Boer *J. Am. Chem. Soc.* **1968**, 90, 6706; Le Carpentier; Weiss *Acta Crystallogr. Sect. B* **1972**, 1430. See also Olah; Westerman *J. Am. Chem. Soc.* **1973**, 95, 3706.

vinyl cations, the ion, if formed at all, is usually very short-lived.⁴⁹ Neither vinyl⁵⁰ nor phenyl cation has as yet been prepared as a stable species in solution.⁵¹

Various quantitative methods have been developed to express the relative stabilities of carbocations.⁵² One of the most common of these, though useful only for relatively stable cations that are formed by ionization of alcohols in acidic solutions, is based on the equation⁵³

$$H_R = pK_{R^+} - \log \frac{C_{R^+}}{C_{ROH}}$$

pK_{R^+} is the pK value for the reaction $R^+ + 2H_2O \rightleftharpoons ROH + H_3O^+$ and is a measure of the stability of the carbocation. H_R is an easily obtainable measurement of the acidity of a solvent (see p. 256) and approaches pH at low concentrations of acid. In order to obtain pK_{R^+} for a cation R^+ , one dissolves the alcohol ROH in an acidic solution of known H_R . Then the concentrations of R^+ and ROH are obtained, generally from spectra, and pK_{R^+} is easily calculated.⁵⁴ A measure of carbocation stability that applies to less-stable ions is the dissociation energy $D(R^+—H^-)$ for the cleavage reaction $R—H \rightarrow R^+ + H^-$, which can be obtained from photoelectron spectroscopy and other measurements. Some values of $D(R^+—H^-)$ are shown in Table 5.1.⁵⁷ Within a given class of ion, e.g. primary, secondary, allylic, aryl, etc., $D(R^+—H^-)$ has been shown to be a linear function of the logarithm of the number of atoms in R^+ , with larger ions being more stable.⁵⁶

TABLE 5.1 Heterolytic $R—H \rightarrow R^+ + H^-$ dissociation energies in the gas phase

Ion	$D(R^+—H^-)$		Ref.
	kcal/mol	kJ/mol	
CH_3^+	314.6	1316	55
$C_2H_5^+$	276.7	1158	55
$(CH_3)_2CH^+$	249.2	1043	55
$(CH_3)_3C^+$	231.9	970.3	55
$C_6H_5^+$	294	1230	56
$H_2C=CH^+$	287	1200	56
$H_2C=CH—CH_2^+$	256	1070	56
cyclopentyl	246	1030	56
$C_6H_5CH_2^+$	238	996	56
CH_3CO^+	230	962	56

⁴⁹For a review of destabilized carbocations, see Tidwell *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 20-32 [*Angew. Chem.* **96**, 16-28].

⁵⁰Solutions of aryl-substituted vinyl cations have been reported to be stable for at least a short time at low temperatures. Nmr spectra have been obtained: Abram; Watts *J. Chem. Soc., Chem. Commun.* **1974**, 857; Siehl; Carnahan; Eckes; Hanack *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 675 [*Angew. Chem.* **86**, 677]. The 1-cyclobutenyl cation has been reported to be stable in the gas phase: Franke; Schwarz; Stahl *J. Org. Chem.* **1980**, *45*, 3493. See also Siehl; Koch *J. Org. Chem.* **1984**, *49*, 575.

⁵¹For a monograph, see Stang; Rappoport; Hanack; Subramanian *Vinyl Cations*, Academic Press: New York, 1979. For reviews of aryl and/or vinyl cations, see Hanack *Pure Appl. Chem.* **1984**, *56*, 1819-1830, *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 333-341 [*Angew. Chem.* **90**, 346-359], *Acc. Chem. Res.* **1976**, *9*, 364-371; Rappoport *Reactiv. Intermed. (Plenum)* **1983**, *3*, 427-615; Ambroz; Kemp *Chem. Soc. Rev.* **1979**, *8*, 353-365; Richey; Richey, in Olah; Schleyer, Ref. 2, vol. 2, pp. 899-957; Richey, Ref. 24, pp. 42-49; Modena; Tonellato *Adv. Phys. Org. Chem.* **1971**, *9*, 185-280; Stang *Prog. Phys. Org. Chem.* **1973**, *10*, 205-325. See also Charton *Mol. Struct. Energ.* **1987**, *4*, 271-316.

⁵²For reviews, see Bagno; Scorrano; More O'Ferrall *Rev. Chem. Intermed.* **1987**, *7*, 313-352; Bethell; Gold, Ref. 2, pp. 59-87.

⁵³Deno; Jaruzelski; Schriesheim *J. Am. Chem. Soc.* **1955**, *77*, 3044; Deno; Schriesheim *J. Am. Chem. Soc.* **1955**, *77*, 3051; Deno; Berkheimer; Evans; Peterson *J. Am. Chem. Soc.* **1959**, *81*, 2344.

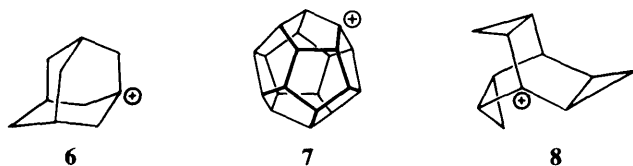
⁵⁴For a list of stabilities of 39 typical carbocations, see Arnett; Hofelich *J. Am. Chem. Soc.* **1983**, *105*, 2889. See also Schade; Mayr; Arnett *J. Am. Chem. Soc.* **1988**, *110*, 567; Schade; Mayr *Tetrahedron* **1988**, *44*, 5761.

⁵⁵Schultz; Houle; Beauchamp *J. Am. Chem. Soc.* **1984**, *106*, 3917.

⁵⁶Lossing; Holmes *J. Am. Chem. Soc.* **1984**, *106*, 6917.

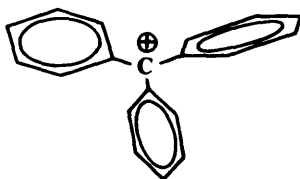
⁵⁷Refs. 55, 56. See also Staley; Wieting; Beauchamp *J. Am. Chem. Soc.* **1977**, *99*, 5964; Arnett; Petro *J. Am. Chem. Soc.* **1978**, *100*, 5408; Arnett; Pienta *J. Am. Chem. Soc.* **1980**, *102*, 3329.

Since the central carbon of tricoordinated carbocations has only three bonds and no other valence electrons, the bonds are sp^2 and should be planar.⁵⁸ Raman, ir, and nmr spectroscopic data on simple alkyl cations show this to be so.⁵⁹ Other evidence is that carbocations are difficult or impossible to form at bridgehead atoms in [2.2.1] systems,⁶⁰ where they cannot be planar (see p. 301). However, larger bridgehead ions can exist. For example, the adamantyl cation (**6**) has been synthesized, as the SF_6^- salt.⁶¹ Among other bridgehead cations that have been prepared in super-acid solution at $-78^\circ C$ are the dodecahydrol cation (**7**)⁶²



and the 1-trishomobarrellyl cation (**8**).⁶³ In the latter case the instability of the bridgehead position is balanced by the extra stability gained from the conjugation with the three cyclopropyl groups.

Triarylmethyl cations⁶⁴ are propeller-shaped, though the central carbon and the three ring carbons connected to it are in a plane:⁶⁵



The three benzene rings cannot be all in the same plane because of steric hindrance, though increased resonance energy would be gained if they could.

An important tool for the investigation of carbocation structure is measurement of the ^{13}C nmr chemical shift of the carbon atom bearing the positive charge.⁶⁶ This shift approximately correlates with electron density on the carbon. ^{13}C chemical shifts for a number of ions are given in Table 5.2.⁶⁷ As shown in the table, the substitution of an ethyl for a methyl or a methyl for a hydrogen causes a downfield shift, indicating that the central carbon

⁵⁸For discussions of the stereochemistry of carbocations, see Henderson *Chem. Soc. Rev.* **1973**, 2, 397-413; Buss; Schleyer; Allen, Ref. 2; Schleyer in Chiurdoglu *Conformational Analysis*; Academic Press: New York, 1971, pp. 241-249; Hehre *Acc. Chem. Res.* **1975**, 8, 369-376; Ref. 30, pp. 1561-1574.

⁵⁹Olah; DeMember; Commeyras; Bribes *J. Am. Chem. Soc.* **1971**, 93, 459; Olah et al., Ref. 10; Yannoni; Kendrick; Myhre; Bebout; Petersen *J. Am. Chem. Soc.* **1989**, 111, 6440.

⁶⁰For a review of bridgehead carbocations, see Fort, in Olah; Schleyer, Ref. 2, vol. 4, pp. 1783-1835.

⁶¹Schleyer; Fort; Watts; Comisarow; Olah *J. Am. Chem. Soc.* **1964**, 86, 4195; Olah; Prakash; Shih; Krishnamurthy; Mateescu; Liang; Sipos; Buss; Gund; Schleyer *J. Am. Chem. Soc.* **1985**, 107, 2764. See also Kruppa; Beauchamp *J. Am. Chem. Soc.* **1986**, 108, 2162; Laube *Angew. Chem. Int. Ed. Engl.* **1986**, 25, 349 [*Angew. Chem.* 98, 368].

⁶²Olah; Prakash; Fessner; Kobayashi; Paquette *J. Am. Chem. Soc.* **1988**, 110, 8599.

⁶³de Meijere; Schallner *Angew. Chem. Int. Ed. Engl.* **1973**, 12, 399 [*Angew. Chem.* 85, 400].

⁶⁴For a review of crystal-structure determinations of triarylmethyl cations and other carbocations that can be isolated in stable solids, see Sundaralingam; Chwang, in Olah; Schleyer, Ref. 2, vol. 5, pp. 2427-2476.

⁶⁵Sharp; Sheppard *J. Chem. Soc.* **1957**, 674; Gomes de Mesquita; MacGillavry; Eriks *Acta Crystallogr.* **1965**, 18, 437; Schuster; Colter; Kurland *J. Am. Chem. Soc.* **1968**, 90, 4679.

⁶⁶For reviews of the nmr spectra of carbocations, see Young *Prog. Nucl. Magn. Reson. Spectrosc.* **1979**, 12, 261-286; Farnum *Adv. Phys. Org. Chem.* **1975**, 11, 123-175.

⁶⁷Olah; White *J. Am. Chem. Soc.* **1968**, 90, 1884, **1969**, 91, 5801. For ^{13}C nmr data for additional ions, see Olah; Donovan *J. Am. Chem. Soc.* **1977**, 99, 5026; Olah; Prakash; Liang *J. Org. Chem.* **1977**, 42, 2666.

TABLE 5.2 ^{13}C chemical-shift values, in parts per million from $^{13}\text{CS}_2$, for the charged carbon atom of some carbocations in $\text{SO}_2\text{ClF-SbF}_5$, $\text{SO}_2\text{-FSO}_3\text{H-SbF}_5$, or $\text{SO}_2\text{-SbF}_5$ ⁶⁷

Ion	Chemical shift	Temp., °C	Ion	Chemical shift	Temp., °C
Et_2MeC^+	-139.4	-20	C(OH)_3^+	+28.0	-50
Me_2EtC^+	-139.2	-60	PhMe_2C^+	-61.1	-60
Me_3C^+	-135.4	-20	PhMeCH^+	-40 ⁶⁸	
Me_2CH^+	-125.0	-20	Ph_2CH^+	-5.6	-60
Me_2COH^+	-55.7	-50	Ph_3C^+	-18.1	-60
MeC(OH)_2^+	-1.6	-30	$\text{Me}_2(\text{cyclopropyl})\text{C}^+$	-86.8	-60
HC(OH)_2^+	+17.0	-30			

becomes somewhat more positive. On the other hand, the presence of hydroxy or phenyl groups decreases the positive character of the central carbon. The ^{13}C chemical shifts are not always in exact order of carbocation stabilities as determined in other ways. Thus the chemical shift shows that the triphenylmethyl cation has a more positive central carbon than diphenylmethyl cation, though the former is more stable. Also, the 2-cyclopropylpropyl and 2-phenylpropyl cations have shifts of -86.8 and -61.1 , respectively, though we have seen that according to other criteria a cyclopropyl group is better than a phenyl group at stabilizing a carbocation.⁶⁸ The reasons for this discrepancy are not fully understood.^{66,69}

Nonclassical Carbocations

These are discussed at pp. 312–326.

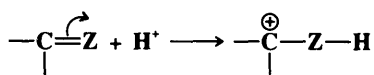
The Generation and Fate of Carbocations

Carbocations, stable or unstable, are usually generated in one of two general ways:

1. A direct ionization, in which a group attached to a carbon atom leaves with its pair of electrons (see Chapters 10, 13, 17, 18):



2. A proton or other positive species adds to one atom of an unsaturated system, leaving the adjacent carbon atom with a positive charge (see Chapters 11, 15, 16).



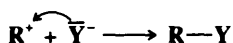
Formed by either process, carbocations are most often short-lived transient species and react further without being isolated.

⁶⁶Olah; Porter; Kelly *J. Am. Chem. Soc.* **1971**, *93*, 464.

⁶⁹For discussions, see Brown; Peters *J. Am. Chem. Soc.* **1973**, *95*, 2400. **1977**, *99*, 1712; Olah; Westerman; Nishimura *J. Am. Chem. Soc.* **1974**, *96*, 3548; Wolf; Harch; Taft; Hehre *J. Am. Chem. Soc.* **1975**, *97*, 2902; Fliszár *Can. J. Chem.* **1976**, *54*, 2839; Kitching; Adcock; Aldous *J. Org. Chem.* **1979**, *44*, 2652. See also Larsen; Bouis *J. Am. Chem. Soc.* **1975**, *97*, 4418; Volz; Shin; Streicher *Tetrahedron Lett.* **1975**, 1297; Larsen *J. Am. Chem. Soc.* **1978**, *100*, 330.

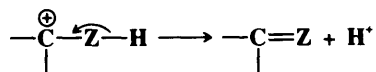
The two chief pathways by which carbocations react to give stable products are the reverse of the two pathways just described.

1. The carbocation may combine with a species possessing an electron pair (a Lewis acid–base reactions, see Chapter 8):



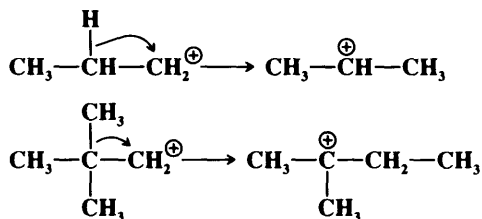
This species may be OH^{-} , halide ion, or any other negative ion, or it may be a neutral species with a pair to donate, in which case, of course, the immediate product must bear a positive charge (see Chapters 10, 13, 15, 16).

2. The carbocation may lose a proton (or much less often, another positive ion) from the adjacent atom (see Chapters 11, 17):

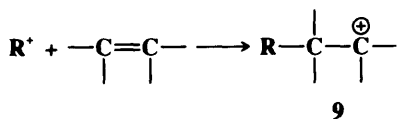


Carbocations can also adopt two other pathways that lead not to stable products, but to other carbocations:

3. *Rearrangement.* An alkyl or aryl group or a hydrogen (sometimes another group) migrates with its electron pair to the positive center, leaving another positive charge behind (see Chapter 18):



4. *Addition.* A carbocation may add to a double bond, generating a positive charge at a new position (see Chapters 11, 15):



Whether formed by pathway 3 or 4, the new carbocation normally reacts further in an effort to stabilize itself, usually by pathway 1 or 2. However, **9** can add to another alkene molecule, and this product can add to still another, etc. This is one of the mechanisms for vinyl polymerization.

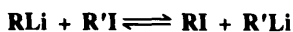
CARBANIONS

Stability and Structure⁷⁰

An *organometallic compound* is a compound that contains a bond between a carbon atom and a metal atom. Many such compounds are known, and organometallic chemistry is a very large area, occupying a borderline region between organic and inorganic chemistry. Many carbon–metal bonds, e.g., carbon–mercury bonds, are undoubtedly covalent, but in bonds between carbon and the more active metals the electrons are closer to the carbon. Whether the position of the electrons in a given bond is close enough to the carbon to justify calling the bond ionic and the carbon moiety a carbanion depends on the metal, on the structure of the carbon moiety, and on the solvent and in some cases is a matter of speculation. In this section we discuss carbanions with little reference to the metal. In the next section we shall deal with the structures of organometallic compounds.

By definition, every carbanion possesses an unshared pair of electrons and is therefore a base. When a carbanion accepts a proton, it is converted to its conjugate acid (see Chapter 8). The stability of the carbanion is directly related to the strength of the conjugate acid. The weaker the acid, the greater the base strength and the lower the stability of the carbanion.⁷¹ By stability here we mean stability toward a proton donor; the lower the stability, the more willing the carbanion is to accept a proton from any available source and hence to end its existence as a carbanion. Thus the determination of the order of stability of a series of carbanions is equivalent to a determination of the order of strengths of the conjugate acids, and one can obtain information about relative carbanion stability from a table of acid strengths like Table 8.1.

Unfortunately, it is not easy to measure acid strengths of very weak acids like the conjugate acids of simple unsubstituted carbanions. There is little doubt that these carbanions are very unstable in solution, and in contrast to the situation with carbocations, efforts to prepare solutions in which carbanions such as ethyl or isopropyl exist in a relatively free state have not yet been successful. Nor has it been possible to form these carbanions in the gas phase. Indeed, there is evidence that simple carbanions such as ethyl and isopropyl are unstable towards loss of an electron, which converts them to radicals.⁷² Nevertheless, there have been several approaches to the problem. Applequist and O'Brien⁷³ studied the position of equilibrium for the reaction



in ether and ether–pentane. The reasoning in these experiments was that the R group that forms the more stable carbanion would be more likely to be bonded to lithium than to

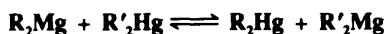
⁷⁰For monographs, see Buncel; Durst *Comprehensive Carbanion Chemistry*, pts. A, B, and C; Elsevier: New York, 1980, 1984, 1987; Bates; Ogle *Carbanion Chemistry*; Springer: New York, 1983; Stowell *Carbanions in Organic Synthesis*; Wiley: New York, 1979; Cram *Fundamentals of Carbanion Chemistry*; Academic Press: New York, 1965. For reviews, see Staley *React. Intermed. (Wiley)* **1985**, *3*, 19–43; Staley; Dustman *React. Intermed. (Wiley)* **1981**, *2*, 15–57; le Noble *React. Intermed. (Wiley)* **1978**, *1*, 27–67; Solov'yanov; Beletskaya *Russ. Chem. Rev.* **1978**, *47*, 425–439; Isaacs, Ref. 1, pp. 234–293; Kaiser; Slocum, in McManus, Ref. 1, pp. 337–422; Ebel *Fortchr. Chem. Forsch.* **1969**, *12*, 387–439; Cram *Surv. Prog. Chem.* **1968**, *4*, 45–68; Reutov; Beletskaya *Reaction Mechanisms of Organometallic Compounds*; North Holland Publishing Co.: Amsterdam, 1968, pp. 1–64; Streitwieser; Hammons *Prog. Phys. Org. Chem.* **1965**, *3*, 41–80. For reviews of nmr spectra of carbanions, see Young, Ref. 66; O'Brien, in *Comprehensive Carbanion Chemistry*, pt. A, cited above, pp. 271–322. For a review of dicarbanions, see Thompson; Green *Tetrahedron* **1991**, *47*, 4223–4285.

⁷¹For a monograph on hydrocarbon acidity, see Reutov; Beletskaya; Butin *CH-Acids*; Pergamon: Elmsford, NY, 1978. For a review, see Fischer; Rewicki *Prog. Org. Chem.* **1968**, *7*, 116–161.

⁷²See Graul; Squires *J. Am. Chem. Soc.* **1988**, *110*, 607; Schleyer; Spitznagel; Chandrasekhar *Tetrahedron Lett.* **1986**, *27*, 4411.

⁷³Applequist; O'Brien *J. Am. Chem. Soc.* **1963**, *85*, 743.

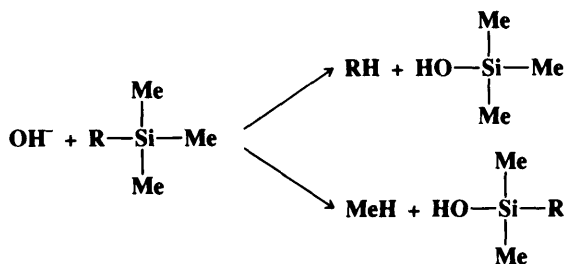
iodine. Carbanion stability was found to be in this order: vinyl > phenyl > cyclopropyl > ethyl > *n*-propyl > isobutyl > neopentyl > cyclobutyl > cyclopentyl. In a somewhat similar approach, Dessy and co-workers⁷⁴ treated a number of alkyllmagnesium compounds with a number of alkylmercury compounds in THF, setting up the equilibrium



where the group of greater carbanion stability is linked to magnesium. The carbanion stability determined this way was in the order phenyl > vinyl > cyclopropyl > methyl > ethyl > isopropyl. The two stability orders are in fairly good agreement, and they show that stability of simple carbanions decreases in the order methyl > primary > secondary. It was not possible by the experiments of Dessy and co-workers to determine the position of *t*-butyl, but there seems little doubt that it is still less stable. We can interpret this stability order solely as a consequence of the field effect since resonance is absent. The electron-donating alkyl groups of isopropyl result in a greater negative charge density at the central carbon atom (compared with methyl), thus decreasing its stability. The results of Applequist and O'Brien show that β branching also decreases carbanion stability. Cyclopropyl occupies an apparently anomalous position, but this is probably due to the large amount of *s* character in the carbanionic carbon (see p. 178).

A different approach to the problem of hydrocarbon acidity and hence carbanion stability is that of Shatenshtein and co-workers, who treated hydrocarbons with deuterated potassium amide and measured the rates of hydrogen exchange.⁷⁵ The experiments did not measure *thermodynamic* acidity, since rates were measured, not positions of equilibria. They measured *kinetic* acidity, i.e., which compounds gave up protons most rapidly (see p. 214 for the distinction between thermodynamic and kinetic control of product). Measurements of rates of hydrogen exchange enable one to compare acidities of a series of acids against a given base even where the positions of the equilibria cannot be measured because they lie too far to the side of the starting materials, i.e., where the acids are too weak to be converted to their conjugate bases in measurable amounts. Although the correlation between thermodynamic and kinetic acidity is far from perfect,⁷⁶ the results of the rate measurements, too, indicated that the order of carbanion stability is methyl > primary > secondary > tertiary.⁷⁵

However, experiments in the gas phase gave different results. In reactions of OH⁻ with alkyltrimethylsilanes it is possible for either R or Me to cleave. Since the R or Me comes



off as a carbanion or incipient carbanion, the product ratio RH:MeH can be used to establish the relative stabilities of various R groups. From these experiments a stability order of

⁷⁴Dessy; Kitching; Psarras; Salinger; Chen; Chivers *J. Am. Chem. Soc.* **1966**, *88*, 460.

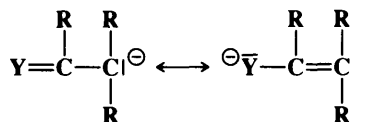
⁷⁵For reviews, see Jones *Surv. Prog. Chem.* **1973**, *6*, 83-112; Shatenshtein; Shapiro *Russ. Chem. Rev.* **1968**, *37*, 845-854.

⁷⁶For example, see Bordwell; Matthews; Vanier *J. Am. Chem. Soc.* **1975**, *97*, 442.

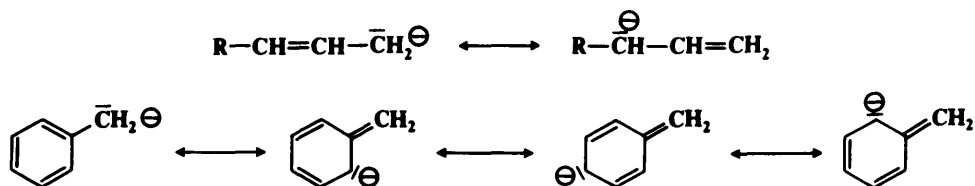
neopentyl > cyclopropyl > *t*-butyl > *n*-propyl > methyl > isopropyl > ethyl was found.⁷⁷ On the other hand, in a different kind of gas-phase experiment, Graul and Squires were able to observe CH_3^- ions, but not the ethyl, isopropyl, or *t*-butyl ions.⁷⁸

Many carbanions are far more stable than the simple kind mentioned above. The increased stability is due to certain structural features:

1. *Conjugation of the unshared pair with an unsaturated bond:*

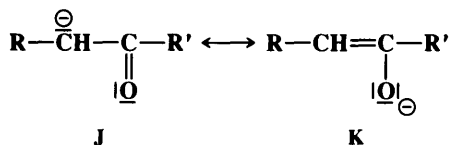


In cases where a double or triple bond is located α to the carbanionic carbon, the ion is stabilized by resonance in which the unshared pair overlaps with the π electrons of the double bond. This factor is responsible for the stability of the allylic⁷⁹ and benzylic⁸⁰ types of carbanions:



Diphenylmethyl and triphenylmethyl anions are still more stable and can be kept in solution indefinitely if water is rigidly excluded.⁸¹ X-ray crystallographic structures have been obtained for Ph_2CH^- and Ph_3C^- enclosed in crown ethers.⁸²

Where the carbanionic carbon is conjugated with a carbon–oxygen or carbon–nitrogen multiple bond ($\text{Y} = \text{O}$ or N), the stability of the ion is greater than that of the triarylmethyl anions, since these electronegative atoms are better capable of bearing a negative charge than carbon. However, it is questionable whether ions of this type should be called carbanions at all, since in the case of enolate ions, for example, **K** contributes more to the hybrid than **J** though such ions react more often at the carbon than at the oxygen. Enolate ions can also be kept in stable solutions. A nitro group is particularly effective in stabilizing a negative



⁷⁷DePuy; Gronert; Barlow; Bierbaum; Damrauer *J. Am. Chem. Soc.* **1989**, *111*, 1968. The same order (for *t*-Bu, Me, *i*-Pr, and Et) was found in gas-phase cleavages of alkoxides (2-41): Tumas; Foster; Brauman *J. Am. Chem. Soc.* **1984**, *106*, 4053.

⁷⁸Graul; Squires, Ref. 72.

⁷⁹For a review of allylic anions, see Richey, Ref. 24, pp. 67-77.

⁸⁰Although benzylic carbanions are more stable than the simple alkyl type, they have not proved stable enough for isolation so far. The benzylic carbanion has been formed and studied in submicrosecond times; Bockrath; Dorfman *J. Am. Chem. Soc.* **1974**, *96*, 5708.

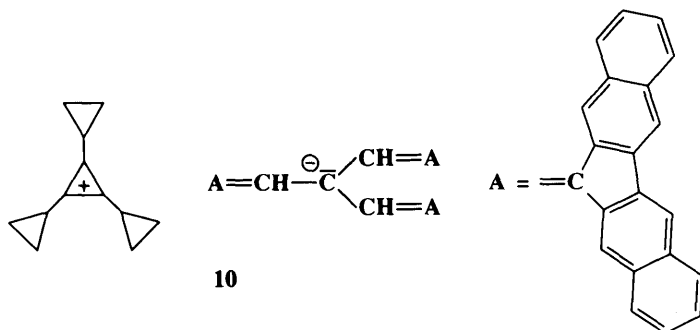
⁸¹For a review of spectrophotometric investigations of this type of carbanion, see Buncel; Menon, in Buncel; Durst, Ref. 70, pp. 97-124.

⁸²Olmstead; Power *J. Am. Chem. Soc.* **1985**, *107*, 2174.

charge on an adjacent carbon, and the anions of simple nitro alkanes can exist in water. Thus pK_a for nitromethane is 10.2. Dinitromethane is even more acidic ($pK_a = 3.6$).

In contrast to the stability of cyclopropylmethyl cations (p. 169), the cyclopropyl group exerts only a weak stabilizing effect on an adjacent carbanionic carbon.⁸³

By combining a very stable carbanion with a very stable carbocation, Okamoto and



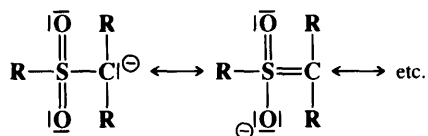
co-workers were able to isolate the salt **10**, as well as several similar salts, as stable solids. These are salts that consist entirely of carbon and hydrogen.⁸⁴

2. Carbanions increase in stability with an increase in the amount of s character at the carbanionic carbon. Thus the order of stability is



Acetylene, where the carbon is sp -hybridized with 50% s character, is much more acidic than ethylene⁸⁵ (sp^2 , 33% s), which in turn is more acidic than ethane, with 25% s character. Increased s character means that the electrons are closer to the nucleus and hence of lower energy. As previously mentioned, cyclopropyl carbanions are more stable than methyl, owing to the larger amount of s character as a result of strain (see p. 152).

3. Stabilization by sulfur⁸⁶ or phosphorus. Attachment to the carbanionic carbon of a sulfur or phosphorus atom causes an increase in carbanion stability, though the reasons for this are in dispute. One theory is that there is overlap of the unshared pair with an empty d orbital⁸⁷ ($p\pi-d\pi$ bonding, see p. 38). For example, a carbanion containing the SO_2R group would be written



⁸³Perkins; Ward *J. Chem. Soc., Perkin Trans. I* **1974**, 667; Perkins; Peynircioglu *Tetrahedron* **1985**, 41, 225.

⁸⁴Okamoto; Kitagawa; Takeuchi; Komatsu; Kinoshita; Aonuma; Nagai; Miyabo *J. Org. Chem.* **1990**, 55, 996. See also Okamoto; Kitagawa; Takeuchi; Komatsu; Miyabo *J. Chem. Soc., Chem. Commun.* **1988**, 923.

⁸⁵For a review of vinylic anions, see Richey, Ref. 24, pp. 49-56.

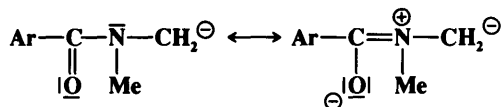
⁸⁶For reviews of sulfur-containing carbanions, see Oae; Uchida in Patai; Rappoport; Stirling *The Chemistry of Sulphones and Sulphoxides*; Wiley: New York, 1988, pp. 583-664; Wolfe, in Bernardi; Csizmadia; Mangini *Organic Sulfur Chemistry*; Elsevier, New York, 1985, pp. 133-190; Block *Reactions of Organosulfur Compounds*; Academic Press: New York, 1978, pp. 42-56; Durst; Viau *Intra-Sci. Chem. Rep.* **1973**, 7 (3), 63-74. For a review of selenium-stabilized carbanions, see Reich, in Liotta *Organoselenium Chemistry*; Wiley: New York, 1987, pp. 243-276.

⁸⁷For support for this theory, see Wolfe; LaJohn; Bernardi; Mangini; Tonachini *Tetrahedron Lett.* **1983**, 24, 3789; Wolfe; Stolow; LaJohn *Tetrahedron Lett.* **1983**, 24, 4071.

However, there is evidence against *d*-orbital overlap; and the stabilizing effects have been attributed to other causes.⁸⁸ An α silicon atom also stabilizes carbanions.⁸⁹

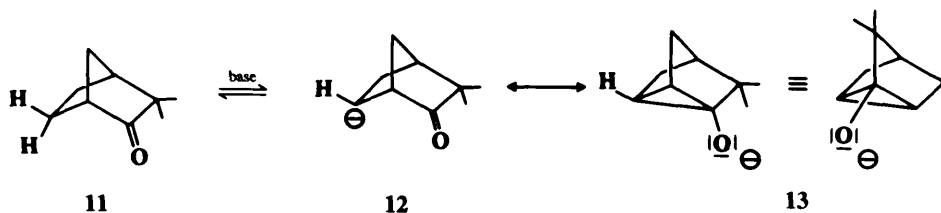
4. *Field effects.* Most of the groups that stabilize carbanions by resonance effects (either the kind discussed in paragraph 1 above or the kind discussed in paragraph 3) have electron-withdrawing field effects and thereby stabilize the carbanion further by spreading the negative charge, though it is difficult to separate the field effect from the resonance effect.

However, in a nitrogen ylide $R_3\overset{\oplus}{N}-\overset{\ominus}{C}R_2$ (see p. 39), where a positive nitrogen is adjacent to the negatively charged carbon, only the field effect operates. Ylides are more stable than the corresponding simple carbanions. Carbanions are stabilized by a field effect if there is any hetero atom (O, N, or S) connected to the carbanionic carbon, provided that the hetero atom bears a positive charge in at least one important canonical form,⁹⁰ e.g.,



5. Certain carbanions are stable because they are aromatic (see the cyclopentadienyl anion p. 46, and other aromatic anions in Chapter 2).

6. *Stabilization by a nonadjacent π bond.*⁹¹ In contrast to the situation with carbocations (see pp. 314-316), there have been fewer reports of carbanions stabilized by interaction with a nonadjacent π bond. One that may be mentioned is **13**, formed when optically active camphenilone (**11**) was treated with a strong base (potassium *t*-butoxide).⁹² That **13** was



truly formed was shown by the following facts: (1) A proton was abstracted: ordinary CH_2 groups are not acidic enough for this base; (2) recovered **11** was racemized: **13** is symmetrical and can be attacked equally well from either side; (3) when the experiment was performed in deuterated solvent, the rate of deuterium uptake was equal to the rate of racemization; and (4) recovered **11** contained up to three atoms of deuterium per molecule, though if **12** were the only ion, no more than two could be taken up. Ions of this type, in which a

⁸⁸Bernardi; Csizmadia; Mangini; Schlegel; Whangbo; Wolfe *J. Am. Chem. Soc.* **1975**, *97*, 2209; Epiotis; Yates; Bernardi; Wolfe *J. Am. Chem. Soc.* **1976**, *98*, 5435; Lehn; Wipff *J. Am. Chem. Soc.* **1976**, *98*, 7498; Borden; Davidson; Andersen; Denniston; Epiotis *J. Am. Chem. Soc.* **1978**, *100*, 1604; Bernardi; Bottoni; Venturini; Mangini *J. Am. Chem. Soc.* **1986**, *108*, 8171.

⁸⁹Wetzel; Brauman *J. Am. Chem. Soc.* **1968**, *110*, 8333.

⁹⁰For a review of such carbanions, see Beak; Reitz *Chem. Rev.* **1978**, *78*, 275-316. See also Rondan; Houk; Beak; Zajdel; Chandrasekhar; Schleyer *J. Org. Chem.* **1981**, *46*, 4108.

⁹¹For reviews, see Werstiuk *Tetrahedron* **1983**, *39*, 205-268; Hunter; Stothers; Warnhoff, in de Mayo *Rearrangements in Ground and Excited States*, vol. 1; Academic Press: New York, 1980, pp. 410-437.

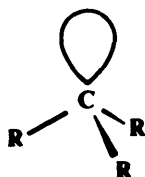
⁹²Nickon; Lambert *J. Am. Chem. Soc.* **1966**, *88*, 1905. Also see Brown; Occolowitz *Chem. Commun.* **1965**, 376; Grutzner; Winstein *J. Am. Chem. Soc.* **1968**, *90*, 6562; Staley; Reichard *J. Am. Chem. Soc.* **1969**, *91*, 3998; Hunter; Johnson; Stothers; Nickon; Lambert; Covey *J. Am. Chem. Soc.* **1972**, *94*, 8582; Miller *J. Am. Chem. Soc.* **1969**, *91*, 751; Werstiuk; Yeroushalmi; Timmins *Can. J. Chem.* **1983**, *61*, 1945; Lee; Squires *J. Am. Chem. Soc.* **1986**, *108*, 5078; Peiris; Ragauskas; Stothers *Can. J. Chem.* **1987**, *65*, 789; Shiner; Berks; Fisher *J. Am. Chem. Soc.* **1988**, *110*, 957.

negatively charged carbon is stabilized by a carbonyl group two carbons away, are called *homoenolate ions*.

Overall, functional groups in the α position stabilize carbanions in the following order: $\text{NO}_2 > \text{RCO} > \text{COOR} > \text{SO}_2 > \text{CN} \approx \text{CONH}_2 > \text{Hal} > \text{H} > \text{R}$.

It is unlikely that free carbanions exist in solution. Like carbocations, they are usually in ion pairs or else solvated.⁹³ Among experiments which demonstrated this was the treatment of $\text{PhCO}\bar{\text{C}}\text{HMe}^- \text{M}^+$ with ethyl iodide, where M^+ was Li^+ , Na^+ , or K^+ . The half-lives of the reaction were⁹⁴ for Li, 31×10^{-6} ; Na, 0.39×10^{-6} ; and K, 0.0045×10^{-6} , demonstrating that the species involved were not identical. Similar results⁹⁵ were obtained with Li, Na, and Cs triphenylmethides $\text{Ph}_3\text{C}^- \text{M}^+$.⁹⁶ Where ion pairs are unimportant, carbanions are solvated. Cram⁷⁰ has demonstrated solvation of carbanions in many solvents. There may be a difference in the structure of a carbanion depending on whether it is free (e.g., in the gas phase) or in solution. The negative charge may be more localized in solution in order to maximize the electrostatic attraction to the counterion.⁹⁷

The structure of simple unsubstituted carbanions is not known with certainty since they have not been isolated, but it seems likely that the central carbon is sp^3 -hybridized, with the unshared pair occupying one apex of the tetrahedron. Carbanions would thus have pyramidal structures similar to those of amines.



The methyl anion CH_3^- has been observed in the gas phase and reported to have a pyramidal structure.⁹⁸ If this is a general structure for carbanions, then any carbanion in which the three R groups are different should be chiral and reactions in which it is an intermediate should give retention of configuration. Attempts have been made to demonstrate this but without success.⁹⁹ A possible explanation is that pyramidal inversion takes place here, as in amines, so that the unshared pair and the central carbon rapidly oscillate from one side of the plane to the other. There is, however, other evidence for the sp^3 nature of the central carbon and for its tetrahedral structure. Carbons at bridgeheads, though extremely reluctant to undergo reactions in which they must be converted to carbocations, undergo with ease reactions in which they must be carbanions and stable bridgehead carbanions are known.¹⁰⁰

⁹³For reviews of carbanion pairs, see Hogen-Esch *Adv. Phys. Org. Chem.* **1977**, *15*, 153-266; Jackman; Lange *Tetrahedron* **1977**, *33*, 2737-2769. See also Ref 7.

⁹⁴Zook; Gumby *J. Am. Chem. Soc.* **1960**, *82*, 1386.

⁹⁵Solov'yanov; Karpyuk; Beletskaya; Reutov *J. Org. Chem. USSR* **1981**, *17*, 381. See also Solov'yanov; Beletskaya; Reutov *J. Org. Chem. USSR* **1983**, *19*, 1964.

⁹⁶For other evidence for the existence of carbanionic pairs, see Hogen-Esch; Smid *J. Am. Chem. Soc.* **1966**, *88*, 307, 318; **1969**, *91*, 4580; Abatjoglou; Eliel; Kuyper *J. Am. Chem. Soc.* **1977**, *99*, 8262; Solov'yanov; Karpyuk; Beletskaya; Reutov *Doklad. Chem.* **1977**, *237*, 668; DePalma; Arnett *J. Am. Chem. Soc.* **1978**, *100*, 3514; Buncel; Menon *J. Org. Chem.* **1979**, *44*, 317; O'Brien; Russell; Hart *J. Am. Chem. Soc.* **1979**, *101*, 633; Streitwieser; Shen *Tetrahedron Lett.* **1979**, 327; Streitwieser *Acc. Chem. Res.* **1984**, *17*, 353.

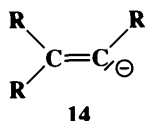
⁹⁷See Schade; Schleyer; Geissler; Weiss *Angew. Chem. Int. Ed. Engl.* **1986**, *21*, 902 [*Angew. Chem.* **98**, 922].

⁹⁸Ellison; Engelking; Lineberger *J. Am. Chem. Soc.* **1978**, *100*, 2556.

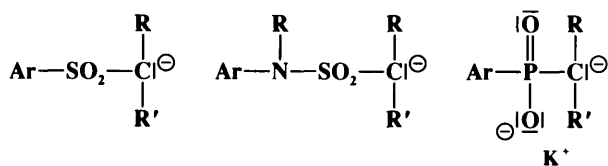
⁹⁹Retention of configuration has never been observed with simple carbanions. Cram has obtained retention with carbanions stabilized by resonance. However, these carbanions are known to be planar or nearly planar, and retention was caused by asymmetric solvation of the planar carbanions (see p. 574).

¹⁰⁰For other evidence that carbanions are pyramidal, see Streitwieser; Young *J. Am. Chem. Soc.* **1969**, *91*, 529; Peoples; Grutzner *J. Am. Chem. Soc.* **1980**, *102*, 4709.

Also, reactions at vinylic carbons proceed with retention,¹⁰¹ indicating that the intermediate **14** has sp^2 hybridization and not the sp hybridization that would be expected in the analogous carbocation. A cyclopropyl anion can also hold its configuration.¹⁰²



Carbanions in which the negative charge is stabilized by resonance involving overlap of the unshared-pair orbital with the π electrons of a multiple bond are essentially planar, as would be expected by the necessity for planarity in resonance, though unsymmetrical solvation or ion-pairing effects may cause the structure to deviate somewhat from true planarity.¹⁰³ Cram and co-workers have shown that where chiral carbanions possessing this type of resonance are generated, retention, inversion, or racemization can result, depending on the solvent (see p. 574). This result is explained by unsymmetrical solvation of planar or near-planar carbanions. However, some carbanions that are stabilized by adjacent sulfur or phosphorus, e.g.,



are inherently chiral, since retention of configuration is observed where they are generated, even in solvents that cause racemization or inversion with other carbanions.¹⁰⁴ The configuration about the carbanionic carbon, at least for some of the α -sulfonyl carbanions, seems to be planar,¹⁰⁵ and the inherent chirality is caused by lack of rotation about the C—S bond.¹⁰⁶

¹⁰¹Curtin; Harris *J. Am. Chem. Soc.* **1951**, *73*, 2716, 4519; Braude; Coles *J. Chem. Soc.* **1951**, 2078; Nesmeyanov; Borisov *Tetrahedron* **1957**, *1*, 158. Also see Miller; Lee *J. Am. Chem. Soc.* **1959**, *81*, 6313; Hunter; Cram *J. Am. Chem. Soc.* **1964**, *86*, 5478; Walborsky; Turner *J. Am. Chem. Soc.* **1972**, *94*, 2273; Arnett; Walborsky *J. Org. Chem.* **1972**, *37*, 3678; Feit; Melamed; Speer; Schmidt *J. Chem. Soc., Perkin Trans. 1* **1984**, 775; Chou; Kass *J. Am. Chem. Soc.* **1991**, *113*, 4357.

¹⁰²Walborsky; Motes *J. Am. Chem. Soc.* **1970**, *92*, 2445; Motes; Walborsky *J. Am. Chem. Soc.* **1970**, *92*, 3697; Boche; Harms; Marsch *J. Am. Chem. Soc.* **1988**, *110*, 6925. For a monograph on cyclopropyl anions, cations, and radicals, see Boche; Walborsky *Cyclopropane Derived Reactive Intermediates*; Wiley: New York, 1990. For a review, see Boche; Walborsky, in Rappoport *The Chemistry of the Cyclopropyl Group*, pt. 1; Wiley: New York, 1987, pp. 701-808 (the monograph includes and updates the review).

¹⁰³See the discussion in Cram *Fundamentals of Carbanion Chemistry*; Academic Press: New York, 1965, pp. 85-105.

¹⁰⁴Cram; Nielsen; Rickborn *J. Am. Chem. Soc.* **1960**, *82*, 6415; Cram; Wingrove *J. Am. Chem. Soc.* **1962**, *84*, 1496; Corey; Kaiser *J. Am. Chem. Soc.* **1961**, *83*, 490; Goering; Towns; Dittmer *J. Org. Chem.* **1962**, *27*, 736; Corey; Lowry *Tetrahedron Lett.* **1965**, 803; Bordwell; Phillips; Williams *J. Am. Chem. Soc.* **1968**, *90*, 426; Annunziata; Cinquini; Colonna; Cozzi *J. Chem. Soc., Chem. Commun.* **1981**, 1005; Chassaing; Marquet; Corset; Froment *J. Organomet. Chem.* **1982**, *232*, 293. For a discussion, see Ref. 103, pp. 105-113.

¹⁰⁵Boche; Marsch; Harms; Sheldrick *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 573 [*Angew. Chem.* **97**, 577]; Gais; Vollhardt; Hellmann; Paulus; Lindner *Tetrahedron Lett.* **1988**, *29*, 1259; Gais; Müller; Vollhardt; Lindner *J. Am. Chem. Soc.* **1991**, *113*, 4002. For a contrary view, see Trost; Schmuft *J. Am. Chem. Soc.* **1985**, *107*, 396.

¹⁰⁶Grossert; Hoyle; Cameron; Roe; Vincent *Can. J. Chem.* **1987**, *65*, 1407.

The Structure of Organometallic Compounds¹⁰⁷

Whether a carbon-metal bond is ionic or polar-covalent is determined chiefly by the electronegativity of the metal and the structure of the organic part of the molecule. Ionic bonds become more likely as the negative charge on the metal-bearing carbon is decreased by resonance or field effects. Thus the sodium salt of acetoacetic ester has a more ionic carbon-sodium bond than methylsodium.

Most organometallic bonds are polar-covalent. Only the alkali metals have electronegativities low enough to form ionic bonds with carbon, and even here the behavior of lithium alkyls shows considerable covalent character. The simple alkyls and aryls of sodium, potassium, rubidium, and cesium¹⁰⁸ are nonvolatile solids¹⁰⁹ insoluble in benzene or other organic solvents, while alkyllithiums are soluble, although they too are generally nonvolatile solids. Alkyllithiums do not exist as monomeric species in hydrocarbon solvents or ether.¹¹⁰ In benzene and cyclohexane, freezing-point-depression studies have shown that alkyllithiums are normally hexameric unless steric interactions favor tetrameric aggregates.¹¹¹ Nmr studies, especially measurements of ¹³C-⁶Li coupling, have also shown aggregation in hydrocarbon solvents.¹¹² Boiling-point-elevation studies have been performed in ether solutions, where alkyllithiums exist in two- to fivefold aggregates.¹¹³ Even in the gas phase¹¹⁴ and in the solid state,¹¹⁵ alkyllithiums exist as aggregates. X-ray crystallography has shown that methylolithium has the same tetrahedral structure in the solid state as in ether solution.¹¹⁵ However, *t*-butyllithium is monomeric in THF, though dimeric in ether and tetrameric in hydrocarbon solvents.¹¹⁶ Neopentylolithium exists as a mixture of monomers and dimers in THF.¹¹⁷

The C-Mg bond in Grignard reagents is covalent and not ionic. The actual structure of Grignard reagents in solution has been a matter of much controversy over the years.¹¹⁸ In 1929 it was discovered¹¹⁹ that the addition of dioxane to an ethereal Grignard solution precipitates all the magnesium halide and leaves a solution of R₂Mg in ether; i.e., there can

¹⁰⁷For a monograph, see Elschenbroich; Salzer *Organometallics*; VCH: New York, 1989. For reviews, see Oliver, in Hartley; Patai *The Chemistry of the Metal-Carbon Bond*, vol. 2; Wiley: New York, 1985, pp. 789-826; Coates; Green; Wade *Organometallic Compounds*, 3rd ed., vol. 1; Methuen: London, 1967. For a review of the structures of organodialkali compounds, see Grovenstein, in Bunzel; Durst, Ref. 70, pt. C, pp. 175-221.

¹⁰⁸For a review of x-ray crystallographic studies of organic compounds of the alkali metals, see Schade; Schleyer *Adv. Organomet. Chem.* **1987**, *27*, 169-278.

¹⁰⁹X-ray crystallography of potassium, rubidium, and cesium methyls shows completely ionic crystal lattices; Weiss; Sauermann *Chem. Ber.* **1970**, *103*, 265; Weiss; Köster *Chem. Ber.* **1977**, *110*, 717.

¹¹⁰For reviews of the structure of alkyllithium compounds, see Setzer; Schleyer *Adv. Organomet. Chem.* **1985**, *24*, 353-451; Schleyer *Pure Appl. Chem.* **1984**, *56*, 151-162; Brown *Pure Appl. Chem.* **1970**, *23*, 447-462, *Adv. Organomet. Chem.* **1965**, *3*, 365-395; Kovrizhnykh; Shatenshtein *Russ. Chem. Rev.* **1969**, *38*, 840-849. For reviews of the structures of lithium enolates and related compounds, see Boche *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 277-297 [*Angew. Chem.* *101*, 286-306]; Seebach *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1624-1654 [*Angew. Chem.* *100*, 1685-1715]. For a review of the use of nmr to study these structures, see Günther; Moskau; Bast; Schmalz *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1212-1220 [*Angew. Chem.* *99*, 1242-1250]. For monographs on organolithium compounds, see Wakefield *Organolithium Methods*; Academic Press: New York, 1988, *The Chemistry of Organolithium Compounds*; Pergamon: Elmsford, NY, 1974.

¹¹¹Lewis; Brown *J. Am. Chem. Soc.* **1970**, *92*, 4664; Brown; Rogers *J. Am. Chem. Soc.* **1957**, *79*, 1859; Weiner; Vogel; West *Inorg. Chem.* **1962**, *1*, 654.

¹¹²Fraenkel; Henrichs; Hewitt; Su *J. Am. Chem. Soc.* **1984**, *106*, 255; Thomas; Jensen; Young *Organometallics* **1987**, *6*, 565. See also Kaufman; Gronert; Streitwieser *J. Am. Chem. Soc.* **1988**, *110*, 2829.

¹¹³Wittig; Meyer; Lange *Liebigs Ann. Chem.* **1951**, *571*, 167. See also McGarrity; Ogle *J. Am. Chem. Soc.* **1985**, *107*, 1805; Bates; Clarke; Thomas *J. Am. Chem. Soc.* **1988**, *110*, 5109.

¹¹⁴Berkowitz; Bafus; Brown *J. Phys. Chem.* **1961**, *65*, 1380; Brown; Dickerhoof; Bafus *J. Am. Chem. Soc.* **1962**, *84*, 1371; Chinn; Lagow *Organometallics* **1984**, *3*, 75; Plavšić; Srzić; Klasinc *J. Phys. Chem.* **1986**, *90*, 2075.

¹¹⁵Dietrich *Acta Crystallogr.* **1963**, *16*, 681; Weiss; Lucken *J. Organomet. Chem.* **1964**, *2*, 197; Weiss; Sauermann; Thirase *Chem. Ber.* **1983**, *116*, 74.

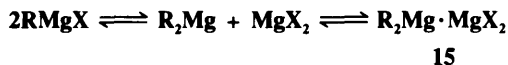
¹¹⁶Bauer; Winchester; Schleyer *Organometallics* **1987**, *6*, 2371.

¹¹⁷Fraenkel; Chow; Winchester *J. Am. Chem. Soc.* **1990**, *112*, 6190.

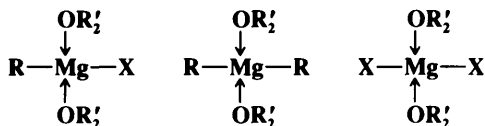
¹¹⁸For reviews, see Ashby *Bull. Soc. Chim. Fr.* **1972**, 2133-2142, *Q. Rev., Chem. Soc.* **1967**, *21*, 259-285; Wakefield *Organomet. Chem. Rev.* **1966**, *1*, 131-156; Bell *Educ. Chem.* **1973**, 143-145.

¹¹⁹Schlenk; Schlenk *Ber.* **1929**, *62B*, 920.

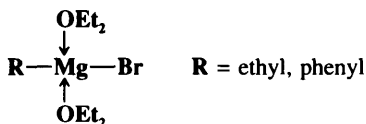
be no RMgX in the solution since there is no halide. The following equilibrium, now called the *Schlenk equilibrium*, was proposed as the composition of the Grignard solution:



in which 15 is a complex of some type. Much work has demonstrated that the Schlenk equilibrium actually exists and that the position of the equilibrium is dependent on the identity of R, X, the solvent, the concentration, and the temperature.¹²⁰ It has been known for many years that the magnesium in a Grignard solution, no matter whether it is RMgX , R_2Mg , or MgX_2 , can coordinate with two molecules of ether in addition to the two covalent bonds:



Rundle and co-workers performed x-ray-diffraction studies on solid phenylmagnesium bromide dietherate and on ethylmagnesium bromide dietherate, which they obtained by cooling ordinary ethereal Grignard solutions until the solids crystallized.¹²¹ They found that the structures were monomeric:



These solids still contained ether. When ordinary ethereal Grignard solutions prepared from bromomethane, chloromethane, bromoethane, and chloroethane were evaporated at about 100°C under vacuum so that the solid remaining contained no ether, x-ray diffraction showed *no* RMgX but a mixture of R_2Mg and MgX_2 .¹²² These results indicate that in the presence of ether $\text{RMgX} \cdot 2\text{Et}_2\text{O}$ is the preferred structure, while the loss of ether drives the Schlenk equilibrium to $\text{R}_2\text{Mg} + \text{MgX}_2$. However, conclusions drawn from a study of the solid materials do not necessarily apply to the structures in solution.

Boiling-point-elevation and freezing-point-depression measurements have demonstrated that in tetrahydrofuran at all concentrations and in ether at low concentrations (up to about 0.1 M) Grignard reagents prepared from alkyl bromides and iodides are monomeric, i.e., there are few or no molecules with two magnesium atoms.¹²³ Thus, part of the Schlenk equilibrium is operating



¹²⁰See Parris; Ashby *J. Am. Chem. Soc.* **1971**, *93*, 1206; Salinger; Mosher *J. Am. Chem. Soc.* **1964**, *86*, 1782; Kirmann; Hamelin; Hayes *Bull. Soc. Chim. Fr.* **1963**, 1395.

¹²¹Guggenberger; Rundle *J. Am. Chem. Soc.* **1968**, *90*, 5375; Stucky; Rundle *J. Am. Chem. Soc.* **1964**, *86*, 4825.

¹²²Weiss *Chem. Ber.* **1965**, *98*, 2805.

¹²³Ashby; Becker *J. Am. Chem. Soc.* **1963**, *85*, 118; Ashby; Smith *J. Am. Chem. Soc.* **1964**, *86*, 4363; Vreugdenhil; Blomberg *Recl. Trav. Chim. Pays-Bas* **1963**, *82*, 453, 461.

but not the other part; i.e., **15** is not present in measurable amounts. This was substantiated by ^{25}Mg nmr spectra of the ethyl Grignard reagent in THF, which showed the presence of three peaks, corresponding to EtMgBr , Et_2Mg , and MgBr_2 .¹²⁴ That the equilibrium between RMgX and R_2Mg lies far to the left for "ethylmagnesium bromide" in ether was shown by Smith and Becker, who mixed 0.1 *M* ethereal solutions of Et_2Mg and MgBr_2 and found that a reaction occurred with a heat evolution of 3.6 kcal/mol (15 kJ/mol) of Et_2Mg , and that the product was *monomeric* (by boiling-point-elevation measurements).¹²⁵ When either solution was added little by little to the other, there was a linear output of heat until almost a 1:1 molar ratio was reached. Addition of an excess of either reagent gave no further heat output. These results show that at least under some conditions the Grignard reagent is largely RMgX (coordinated with solvent) but that the equilibrium can be driven to R_2Mg by evaporation of all the ether or by addition of dioxane.

For some aryl Grignard reagents it has proved possible to distinguish separate nmr chemical shifts for ArMgX and Ar_2Mg .¹²⁶ From the area under the peaks it is possible to calculate the concentrations of the two species, and from them, equilibrium constants for the Schlenk equilibrium. These data show¹²⁶ that the position of the equilibrium depends very markedly on the aryl group and the solvent but that conventional aryl Grignard reagents in ether are largely ArMgX , while in THF the predominance of ArMgX is less, and with some aryl groups there is actually more Ar_2Mg present. Separate nmr chemical shifts have also been found for alkyl RMgBr and R_2Mg in HMPA¹²⁷ and in ether at low temperatures.¹²⁸ When Grignard reagents from alkyl bromides or chlorides are prepared in triethylamine the predominant species is RMgX .¹²⁹ Thus the most important factor determining the position of the Schlenk equilibrium is the solvent. For primary alkyl groups the equilibrium constant for the reaction as written above is lowest in Et_3N , higher in ether, and still higher in THF.¹³⁰

However, Grignard reagents prepared from alkyl bromides or iodides in ether at higher concentrations (0.5 to 1 *M*) contain dimers, trimers, and higher polymers, and those prepared from alkyl chlorides in ether at all concentrations are dimeric,¹³¹ so that **15** is in solution, probably in equilibrium with RMgX and R_2Mg ; i.e., the complete Schlenk equilibrium seems to be present.

The Grignard reagent prepared from 1-chloro-3,3-dimethylpentane in ether undergoes rapid inversion of configuration at the magnesium-containing carbon (demonstrated by nmr; this compound is not chiral).¹³² The mechanism of this inversion is not completely known.

It might be mentioned that matters are much simpler for organometallic compounds with less-polar bonds. Thus Et_2Hg and EtHgCl are both definite compounds, the former a liquid and the latter a solid.

The Generation and Fate of Carbanions

The two principal ways in which carbanions are generated are parallel with the ways of generating carbocations.

¹²⁴Benn; Lehmkuhl; Mehler; Ruffinska *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 534 [*Angew. Chem.* **96**, 521].

¹²⁵Smith; Becker *Tetrahedron* **1966**, *22*, 3027.

¹²⁶Evans; Khan *J. Chem. Soc. A* **1967**, 1643; Evans; Fazakerley *Chem. Commun.* **1968**, 974.

¹²⁷Ducom *Bull. Chem. Soc. Fr.* **1971**, 3518, 3523, 3529.

¹²⁸Ashby; Parris; Walker *Chem. Commun.* **1969**, 1464; Parris; Ashby, Ref. 120.

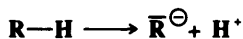
¹²⁹Ashby; Walker *J. Org. Chem.* **1968**, *33*, 3821.

¹³⁰Parris; Ashby, Ref. 120.

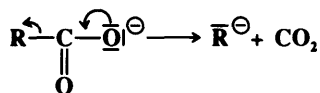
¹³¹Ashby; Smith, Ref. 123.

¹³²Whitesides; Witanowski; Roberts *J. Am. Chem. Soc.* **1965**, *87*, 2854; Whitesides; Roberts *J. Am. Chem. Soc.* **1965**, *87*, 4878. Also see Witanowski; Roberts *J. Am. Chem. Soc.* **1966**, *88*, 737; Fraenkel; Cottrell; Dix *J. Am. Chem. Soc.* **1971**, *93*, 1704; Pechhold; Adams; Fraenkel *J. Org. Chem.* **1971**, *36*, 1368; Maercker; Geuss *Angew. Chem. Int. Ed. Engl.* **1971**, *10*, 270 [*Angew. Chem.* **83**, 288].

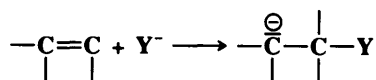
1. A group attached to a carbon leaves without its electron pair:



The leaving group is most often a proton. This is a simple acid–base reaction, and a base is required to remove the proton.¹³³ However, other leaving groups are known (see Chapter 12):

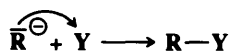


2. A negative ion adds to a carbon–carbon double or triple bond (see Chapter 15):

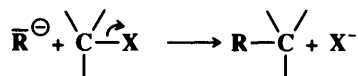


The addition of a negative ion to a carbon–oxygen double bond does not give a carbanion, since the negative charge resides on the oxygen.

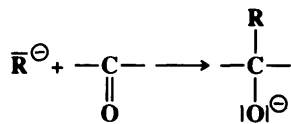
The most common reaction of carbanions is combination with a positive species, usually a proton, or with another species that has an empty orbital in its outer shell (a Lewis acid–base reaction):



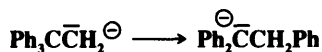
Carbanions may also form a bond with a carbon that already has four bonds, by displacing one of the four groups (S_N2 reaction, see Chapter 10):



Like carbocations, carbanions can also react in ways in which they are converted to species that are still not neutral molecules. They can add to double bonds (usually C=O double bonds; see Chapters 10 and 16),



or rearrange, though this is rare (see Chapter 18),



¹³³For a review of such reactions, see Durst, in Buncl; Durst, Ref. 70, pt. B, pp. 239-291.

or be oxidized to free radicals.¹³⁴ A system in which a carbocation $[\text{Ph}(p\text{-Me}_2\text{NC}_6\text{H}_4)_2\text{C}^+]$ oxidizes a carbanion $[(p\text{-NO}_2\text{C}_6\text{H}_4)_3\text{C}^-]$ to give two free radicals, reversibly, so that all four species are present in equilibrium, has been demonstrated.¹³⁵

Organometallic compounds that are not ionic but polar-covalent behave very much as if they were ionic and give similar reactions.

FREE RADICALS

Stability and Structure¹³⁶

A *free radical* (often simply called a *radical*) may be defined as a species that contains one or more unpaired electrons. Note that this definition includes certain stable inorganic molecules such as NO and NO₂, as well as many individual atoms, such as Na and Cl. As with carbocations and carbanions, simple alkyl radicals are very reactive. Their lifetimes are extremely short in solution, but they can be kept for relatively long periods frozen within the crystal lattices of other molecules.¹³⁷ Many spectral¹³⁸ measurements have been made on radicals trapped in this manner. Even under these conditions the methyl radical decomposes with a half-life of 10 to 15 min in a methanol lattice at 77 K.¹³⁹ Since the lifetime of a radical depends not only on its inherent stability, but also on the conditions under which it is generated, the terms *persistent* and *stable* are usually used for the different senses. A stable radical is inherently stable; a persistent radical has a relatively long lifetime under the conditions at which it is generated, though it may not be very stable.

Associated with the spin of an electron is a magnetic moment, which can be expressed by a quantum number of $+\frac{1}{2}$ or $-\frac{1}{2}$. According to the Pauli principle, any two electrons occupying the same orbital must have opposite spins, so the total magnetic moment is zero for any species in which all the electrons are paired. In radicals, however, one or more electrons are unpaired, so there is a net magnetic moment and the species is paramagnetic. Radicals can therefore be detected by magnetic-susceptibility measurements, but for this technique a relatively high concentration of radicals is required. A much more important technique is *electron spin resonance* (esr), also called *electron paramagnetic resonance* (epr).¹⁴⁰ The principle of esr is similar to that of nmr, except that electron spin is involved

¹³⁴For a review, see Guthrie, in Buncler; Durst, Ref. 70, pt. A, pp. 197-269.

¹³⁵Arnett; Molter; Marchot; Donovan; Smith *J. Am. Chem. Soc.* **1987**, *109*, 3788. See also Ref. 84.

¹³⁶For monographs, see Alfassi *Chemical Kinetics of Small Organic Radicals*, 4 vols.; CRC Press: Boca Raton, FL, 1988; Nonhebel; Tedder; Walton *Radicals*; Cambridge University Press: Cambridge, 1979; Nonhebel; Walton *Free-Radical Chemistry*; Cambridge University Press: Cambridge, 1974; Kochi *Free Radicals*, 2 vols.; Wiley: New York, 1973; Hay *Reactive Free Radicals*; Academic Press: New York, 1974; Pryor *Free Radicals*; McGraw-Hill: New York, 1966. For reviews, see Kaplan *React. Intermed. (Wiley)* **1985**, *3*, 227-303; **1981**, *2*, 251-314; **1978**, *1*, 163-196; Griller; Ingold *Acc. Chem. Res.* **1976**, *9*, 13-19; Huyser, in McManus, Ref. 1, pp. 1-59; Isaacs, Ref. 1, pp. 294-374.

¹³⁷For a review of the use of matrices to study radicals and other unstable species, see Dunkin *Chem. Soc. Rev.* **1980**, *9*, 1-23; Jacox *Rev. Chem. Intermed.* **1978**, *2*, 1-36. For a review of the study of radicals at low temperatures, see Mile *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 507-519 [*Angew. Chem.* **80**, 519-531].

¹³⁸For a review of infrared spectra of radicals trapped in matrices, see Andrews *Annu. Rev. Phys. Chem.* **1971**, *22*, 109-132.

¹³⁹Sullivan; Koski *J. Am. Chem. Soc.* **1963**, *85*, 384.

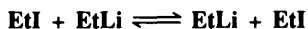
¹⁴⁰For monographs, see Wertz; Bolton *Electron Spin Resonance*; McGraw-Hill: New York, 1972 [reprinted by Chapman and Hall: New York, and Methuen: London, 1986]; Assenheim *Introduction to Electron Spin Resonance*; Plenum: New York, 1967; Bersohn; Baird *An Introduction to Electron Paramagnetic Resonance*; W. A. Benjamin: New York, 1966. For reviews, see Bunce *J. Chem. Educ.* **1987**, *64*, 907-914; Hirota; Ohya-Nishiguchi, in Bernasconi *Investigation of Rates and Mechanisms of Reactions*, 4th ed., pt. 2; Wiley: New York, 1986, pp. 605-655; Griller; Ingold *Acc. Chem. Res.* **1980**, *13*, 193-200; Norman *Chem. Soc. Rev.* **1980**, *8*, 1-27; Fischer, in Kochi, Ref. 136, vol. 2, pp. 435-491; Russell, in Nachod; Zuckerman *Determination of Organic Structures by Physical Methods*, vol. 3; Academic Press: New York, 1971, pp. 293-341; Rassat *Pure Appl. Chem.* **1971**, *25*, 623-634; Kevan *Methods Free-Radical Chem.* **1969**, *1*, 1-33; Geske *Prog. Phys. Org. Chem.* **1967**, *4*, 125-211; Norman; Gilbert *Adv. Phys. Org. Chem.* **1967**, *5*, 53-119; Schneider; Möbius; Plato *Angew. Chem. Int. Ed. Engl.* **1965**, *4*, 856-867 [*Angew. Chem.* **77**, 888-900]. For a review on the application of esr to photochemistry, see Wan *Adv. Photochem.* **1974**, *9*, 1-145. For a review of the related ENDOR method, see Kurreck; Kirste; Lubitz *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 173-194 [*Angew. Chem.* **96**, 171-193]. See also Poole *Electron Spin Resonance. A Comprehensive Treatise on Experimental Techniques*, 2nd ed.; Wiley: New York, 1983.

rather than nuclear spin. The two electron spin states ($m_s = \frac{1}{2}$ and $m_s = -\frac{1}{2}$) are ordinarily of equal energy, but in a magnetic field the energies are different. As in nmr, a strong external field is applied and electrons are caused to flip from the lower state to the higher by the application of an appropriate radio-frequency signal. Inasmuch as two electrons paired in one orbital must have opposite spins which cancel, an esr spectrum arises only from species that have one or more unpaired electrons, i.e., free radicals.

Since only free radicals give an esr spectrum, the method can be used to detect the presence of radicals and to determine their concentration. Furthermore, information concerning the electron distribution (and hence the structure) of free radicals can be obtained from the splitting pattern of the esr spectrum (esr peaks are split by nearby protons).¹⁴¹ Fortunately (for the existence of most free radicals is very short), it is not necessary for a radical to be persistent for an esr spectrum to be obtained. Esr spectra have been observed for radicals with lifetimes considerably less than 1 sec. Failure to observe an esr spectrum does not prove that radicals are not involved, since the concentration may be too low for direct observation. In such cases the *spin trapping* technique can be used.¹⁴² In this technique a compound is added that is able to combine with very reactive radicals to produce more persistent radicals; the new radicals can be observed by esr. The most important spin-trapping compounds are nitroso compounds, which react with radicals to give fairly stable nitroxide radicals:¹⁴³ $RN=O + R'\cdot \rightarrow RR'N-O\cdot$.

Because there is an equal probability that a given unpaired electron will have a quantum number of $+\frac{1}{2}$ or $-\frac{1}{2}$, radicals cause two lines or groups of lines to appear on an electronic spectrum, and are sometimes referred to as *doublets*.

Another magnetic technique for the detection of free radicals uses an ordinary nmr instrument. It was discovered¹⁴⁴ that if an nmr spectrum is taken during the course of a reaction, certain signals may be enhanced, either in a positive or negative direction; others may be reduced. When this type of behavior, called *chemically induced dynamic nuclear polarization*¹⁴⁵ (CIDNP), is found in the nmr spectrum of the product of a reaction, it means that *at least a portion of that product was formed via the intermediacy of a free radical*.¹⁴⁶ For example, the question was raised whether radicals were intermediates in the exchange reaction between ethyl iodide and ethyllithium (2-39):



Curve *a* in Figure 5.1¹⁴⁷ shows an nmr spectrum taken during the course of the reaction. Curve *b* is a reference spectrum of ethyl iodide (CH₃ protons at $\delta = 1.85$; CH₂ protons at

¹⁴¹For reviews of the use of esr spectra to determine structures, see Walton *Rev. Chem. Intermed.* **1984**, *5*, 249-291; Kochi *Adv. Free-Radical Chem.* **1975**, *5*, 189-317. For esr spectra of a large number of free radicals, see Bielski; Gebicki *Atlas of Electron Spin Resonance Spectra*; Academic Press: New York, 1967.

¹⁴²For reviews, see Janzen; Haire *Adv. Free Radical Chem. (Greenwich, Conn.)* **1990**, *1*, 253-295; Gasanov; Freidlina *Russ. Chem. Rev.* **1987**, *56*, 264-274; Perkins *Adv. Phys. Org. Chem.* **1980**, *17*, 1-64; Zubarev; Belevskii; Bugaenko *Russ. Chem. Rev.* **1979**, *48*, 729-745; Evans *Aldrichimica Acta* **1979**, *12*, 23-29; Janzen *Acc. Chem. Res.* **1971**, *4*, 31-40. See also the collection of papers on this subject in *Can. J. Chem.* **1982**, *60*, 1379-1636.

¹⁴³For a series of papers on nitroxide radicals, see *Pure Appl. Chem.* **1990**, *62*, 177-316.

¹⁴⁴Ward; Lawler *J. Am. Chem. Soc.* **1967**, *89*, 5518; Ward; Lawler; Cooper *J. Am. Chem. Soc.* **1969**, *91*, 746; Bargon; Fischer; Johnsen *Z. Naturforsch., Teil A* **1967**, *22*, 1551; Bargon; Fischer *Z. Naturforsch., Teil A* **1967**, *22*, 1556; Lepley *J. Am. Chem. Soc.* **1968**, *90*, 2710. **1969**, *91*, 749; Lepley; Landau *J. Am. Chem. Soc.* **1969**, *91*, 748.

¹⁴⁵For a monograph on CIDNP, see Lepley; Closs *Chemically Induced Magnetic Polarization*; Wiley: New York, 1973. For reviews, see Adrian *Rev. Chem. Intermed.* **1986**, *7*, 173-194; Closs; Miller; Redwine *Acc. Chem. Res.* **1985**, *18*, 196-202; Lawler; Ward; in Nachod; Zuckerman, Ref. 140, vol. 5, 1973, pp. 99-150; Ward, in Kochi, Ref. 136, vol. 1, pp. 239-273; *Acc. Chem. Res.* **1972**, *5*, 18-24; Closs *Adv. Magn. Reson.* **1974**, *7*, 157-229; Lawler *Acc. Chem. Res.* **1972**, *5*, 25-32; Kaptein *Adv. Free-Radical Chem.* **1975**, *5*, 319-380; Bethell; Brinkman *Adv. Phys. Org. Chem.* **1973**, *10*, 53-128.

¹⁴⁶A related technique is called chemically induced dynamic electron polarization (CIDEP). For a review, see Hore; Joslin; McLauchlan *Chem. Soc. Rev.* **1979**, *8*, 29-61.

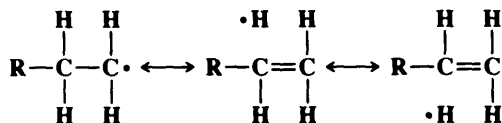
¹⁴⁷Ward; Lawler; Cooper, Ref. 144.



FIGURE 5.1¹⁴⁷ (a) Nmr spectrum taken during reaction between EtI and EtLi in benzene (the region between 2.5 and 3.5 δ was scanned with an amplitude twice that of the remainder of the spectrum). The signals at 1.0 to 1.6 δ are due to butane, some of which is also formed in the reaction. (b) Reference spectrum of EtI.

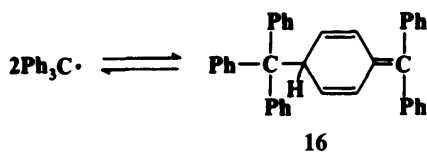
$\delta = 3.2$). Note that in curve *a* some of the ethyl iodide signals are enhanced; others go below the base line (*negative enhancement*; also called *emission*). Thus the ethyl iodide formed in the exchange shows CIDNP and hence was formed via a free-radical intermediate. CIDNP results when protons in a reacting molecule become dynamically coupled to an unpaired electron while traversing the path from reactants to products. Although the presence of CIDNP almost always means that a free radical is involved,¹⁴⁸ its absence does not prove that a free-radical intermediate is necessarily absent, since reactions involving free-radical intermediates can also take place without observable CIDNP. Also, the presence of CIDNP does not prove that *all* of a product was formed via a free-radical intermediate, only that some of it was.

As with carbocations, the stability order of free radicals is tertiary > secondary > primary, explainable by hyperconjugation, analogous to that in carbocations (p. 167):

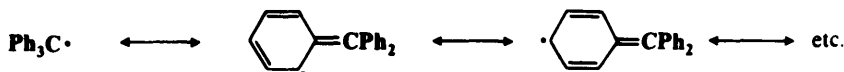


¹⁴⁸It has been shown that CIDNP can also arise in cases where *para* hydrogen (H_2 in which the nuclear spins are opposite) is present: Eisenschmid; Kirss; Deutsch; Hommeltoft; Eisenberg; Bargon; Lawler; Balch *J. Am. Chem. Soc.* **1987**, *109*, 8089.

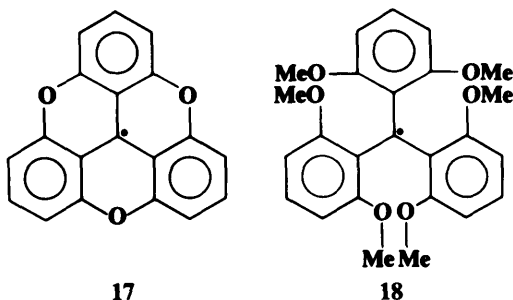
With resonance possibilities, the stability of free radicals increases;¹⁴⁹ some can be kept indefinitely.¹⁵⁰ Benzylic and allylic¹⁵¹ radicals for which canonical forms can be drawn similar to those shown for the corresponding cations (pp. 168, 169) and anions (p. 177) are more stable than simple alkyl radicals but still have only a transient existence under ordinary conditions. However, the triphenylmethyl and similar radicals¹⁵² are stable enough to exist in solution at room temperature, though in equilibrium with a dimeric form. The concen-



tration of triphenylmethyl radical in benzene solution is about 2% at room temperature. For many years it was assumed that $\text{Ph}_3\text{C}\cdot$, the first stable free radical known,¹⁵³ dimerized to hexaphenylethane ($\text{Ph}_3\text{C}-\text{CPh}_3$),¹⁵⁴ but uv and nmr investigations have shown that the true structure is **16**.¹⁵⁵ Although triphenylmethyl-type radicals are stabilized by resonance:



it is steric hindrance to dimerization and not resonance that is the major cause of their stability.¹⁵⁶ This was demonstrated by the preparation of the radicals **17** and **18**.¹⁵⁷ These



¹⁴⁹For a discussion, see Robaugh; Stein *J. Am. Chem. Soc.* **1986**, *108*, 3224.

¹⁵⁰For a monograph on stable radicals, including those in which the unpaired electron is not on a carbon atom, see Forrester; Hay; Thomson *Organic Chemistry of Stable Free Radicals*; Academic Press: New York, 1968.

¹⁵¹For an electron diffraction study of the allyl radical, see Vajda; Tremmel; Rozsondai; Hargittai; Maltsev; Kagramanov; Nefedov *J. Am. Chem. Soc.* **1986**, *108*, 4352.

¹⁵²For a review, see Sholle; Rozantsev *Russ. Chem. Rev.* **1973**, *42*, 1011-1020.

¹⁵³Gomberg *J. Am. Chem. Soc.* **1900**, *22*, 757, *Ber.* **1900**, *33*, 3150.

¹⁵⁴Hexaphenylethane has still not been prepared, but substituted compounds [hexakis(3,5-di-*t*-butyl-4-biphenyl)ethane and hexakis(3,5-di-*t*-butylphenyl)ethane] have been shown by x-ray crystallography to be nonbridged hexaarylethanes in the solid state: Stein; Winter; Rieker *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 692 [*Angew. Chem.* **90**, 737]; Kahr; Van Engen; Mislow *J. Am. Chem. Soc.* **1986**, *108*, 8305; Yannoni; Kahr; Mislow *J. Am. Chem. Soc.* **1988**, *110*, 6670. In solution, both dissociate into free radicals.

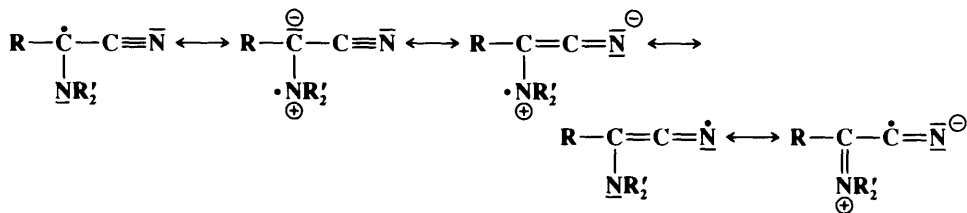
¹⁵⁵Lankamp; Nauta; MacLean *Tetrahedron Lett.* **1968**, 249; Staab; Brettschneider; Brunner *Chem. Ber.* **1970**, *103*, 1101; Volz; Lotsch; Schnell *Tetrahedron* **1970**, *26*, 5343; McBride *Tetrahedron* **1974**, *30*, 2009. See also Guthrie; Weisman *Chem. Commun.* **1969**, 1316; Takeuchi; Nagai; Tokura *Bull. Chem. Soc. Jpn.* **1971**, *44*, 753. For an example where a secondary benzylic radical undergoes this type of dimerization, see Peyman; Peters; von Schnering; Rüdhardt *Chem. Ber.* **1990**, *123*, 1899.

¹⁵⁶For a review of steric effects in free radical chemistry, see Rüdhardt *Top. Curr. Chem.* **1980**, *88*, 1-32.

¹⁵⁷Sabacky; Johnson; Smith; Gutowsky; Martin *J. Am. Chem. Soc.* **1967**, *89*, 2054.

radicals are electronically very similar, but **17**, being planar, has much less steric hindrance to dimerization than $\text{Ph}_3\text{C}^\bullet$, while **18**, with six groups in ortho positions, has much more. On the other hand, the planarity of **17** means that it has a maximum amount of resonance stabilization, while **18** must have much less, since its degree of planarity should be even less than $\text{Ph}_3\text{C}^\bullet$, which itself is propeller-shaped and not planar. Thus if resonance is the chief cause of the stability of $\text{Ph}_3\text{C}^\bullet$, **18** should dimerize and **17** should not, but if steric hindrance is the major cause, the reverse should happen. In the event, it was found¹⁵⁷ that **18** gave no evidence of dimerization, even in the solid state, while **17** existed primarily in the dimeric form, which is dissociated to only a small extent in solution,¹⁵⁸ indicating that steric hindrance to dimerization is the major cause for the stability of triarylmethyl radicals. A similar conclusion was reached in the case of $(\text{NC})_3\text{C}^\bullet$, which dimerizes readily though considerably stabilized by resonance.¹⁵⁹ Nevertheless, that resonance is still an important contributing factor to the stability of radicals is shown by the facts that (1) the radical $t\text{-Bu}(\text{Ph})_2\text{C}^\bullet$ dimerizes more than $\text{Ph}_3\text{C}^\bullet$, while $p\text{-PhCOC}_6\text{H}_4(\text{Ph})_2\text{C}^\bullet$ dimerizes less.¹⁶⁰ The latter has more canonical forms than $\text{Ph}_3\text{C}^\bullet$, but steric hindrance should be about the same (for attack at one of the two rings). (2) A number of radicals ($p\text{-XCOC}_6\text{H}_4)_3\text{C}^\bullet$, with X = F, Cl, O_2N , CN, etc. do not dimerize, but are kinetically stable.¹⁶¹ Completely chlorinated triarylmethyl radicals are more stable than the unsubstituted kind, probably for steric reasons, and many are quite inert in solution and in the solid state.¹⁶²

It has been postulated that the stability of free radicals is enhanced by the presence at the radical center of both an electron-donating and an electron-withdrawing group.¹⁶³ This is called the *push-pull* or *captodative effect* (see also pp. 129). The effect arises from increased resonance, e.g.:



There is some evidence in favor¹⁶⁴ of the captodative effect, some of it from esr studies.¹⁶⁵ However, there is also experimental¹⁶⁶ and theoretical¹⁶⁷ evidence against it. There is evidence that while FCH_2^\bullet and $\text{F}_2\text{CH}^\bullet$ are more stable than CH_3^\bullet , the radical CF_3^\bullet is less stable; that is, the presence of the third F destabilizes the radical.¹⁶⁸

¹⁵⁸Müller; Moosmayer; Ricker; Scheffler *Tetrahedron Lett.* **1967**, 3877. See also Neugebauer; Hellwinkel; Aulmich *Tetrahedron Lett.* **1978**, 4871.

¹⁵⁹Kaba; Ingold *J. Am. Chem. Soc.* **1976**, *98*, 523.

¹⁶⁰Zarkadis; Neumann; Marx; Uzick *Chem. Ber.* **1985**, *118*, 450; Zarkadis; Neumann; Uzick *Chem. Ber.* **1985**, *118*, 1183.

¹⁶¹Dünnebacke; Neumann; Penenory; Stewen *Chem. Ber.* **1989**, *122*, 533.

¹⁶²For reviews, see Ballester *Adv. Phys. Org. Chem.* **1989**, *25*, 267-445, pp. 354-405, *Acc. Chem. Res.* **1985**, *18*, 380-387. See also Hegarty; O'Neill *Tetrahedron Lett.* **1987**, *28*, 901.

¹⁶³For reviews, see Sustmann; Korth *Adv. Phys. Org. Chem.* **1990**, *26*, 131-178; Viehe; Janousek; Merényi; Stella *Acc. Chem. Res.* **1985**, *18*, 148-154.

¹⁶⁴For a summary of the evidence, see Pasto *J. Am. Chem. Soc.* **1988**, *110*, 8164. See also Ref. 163.

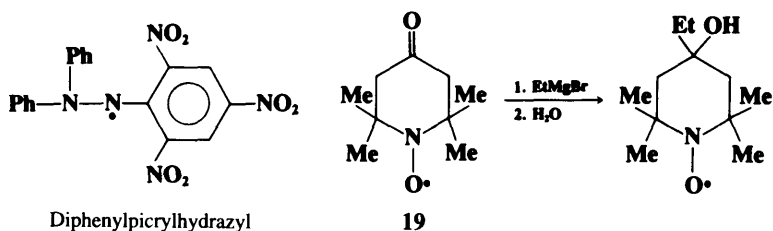
¹⁶⁵See, for example Korth; Lommes; Sustmann; Sylvander; Stella *New J. Chem.* **1987**, *11*, 365; Sakurai; Kyushin; Nakadaira; Kira *J. Phys. Org. Chem.* **1988**, *1*, 197; Rhodes; Roduner *Tetrahedron Lett.* **1988**, *29*, 1437; Viehe; Merényi; Janousek *Pure Appl. Chem.* **1988**, *60*, 1635; Creary; Sky; Mehrsheikh-Mohammadi *Tetrahedron Lett.* **1988**, *29*, 6839; Bordwell; Lynch *J. Am. Chem. Soc.* **1989**, *111*, 7558.

¹⁶⁶See, for example Beckhaus; Rüchardt *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 770 [*Angew. Chem.* *99*, 807]; Neumann; Penenory; Stewen; Lehnig *J. Am. Chem. Soc.* **1989**, *111*, 5845; Bordwell; Bausch; Cheng; Cripe; Lynch; Mueller *J. Org. Chem.* **1990**, *55*, 58; Bordwell; Harrelson *Can. J. Chem.* **1990**, *68*, 1714.

¹⁶⁷See Pasto. Ref. 164.

¹⁶⁸Jiang; Li; Wang *J. Org. Chem.* **1989**, *54*, 5648.

Certain radicals with the unpaired electron not on a carbon are also very stable.¹⁶⁹ Diphenylpicrylhydrazyl is a solid that can be kept for years. We have already mentioned nitroxide radicals. **19** is a nitroxide radical so stable that reactions can be performed on it



without affecting the unpaired electron¹⁷⁰ (the same is true for some of the chlorinated triarylmethyl radicals mentioned above¹⁷¹).

Dissociation energies (D values) of R—H bonds provide a measure of the relative inherent stability of free radicals R.¹⁷² Table 5.3 lists such values.¹⁷³ The higher the D value, the less stable the radical.

TABLE 5.3 D_{298} values for some R—H bonds¹⁷³
Free-radical stability is in the reverse order

R	D	
	kcal/mol	kJ/mol
Ph•	111	464
CF ₃ •	107	446
CH ₂ =CH•	106	444
cyclopropyl ¹⁷⁴	106	444
Me•	105	438
Et•	100	419
Me ₃ CCH ₂ •	100	418
Pr•	100	417
Cl ₃ C•	96	401
Me ₂ CH•	96	401
Me ₃ C ¹⁷⁵	95.8	401
cyclohexyl	95.5	400
PhCH ₂ •	88	368
HCO•	87	364
CH ₂ =CH—CH ₂ •	86	361

¹⁶⁹For reviews of radicals with the unpaired electron on atoms other than carbon, see, in Kochi, Ref. 136, vol. 2, the reviews by Nelson, pp. 527-593 (N-centered); Bentrude, pp. 595-663 (P-centered); Kochi, pp. 665-710 (O-centered); Kice, pp. 711-740 (S-centered); Sakurai, pp. 741-807 (Si, Ge, Sn, and Pb-centered).

¹⁷⁰Neiman; Rozantsev; Mamedova *Nature* **1963**, *200*, 256. For reviews of such radicals, see Aurich, in Patai *The Chemistry of Functional Groups, Supplement F*, pt. 1, Wiley: New York, 1982, pp. 565-622 [This review has been reprinted, and new material added, in Breuer; Aurich; Nielsen *Nitrones, Nitronates, and Nitroxides*; Wiley: New York, 1989, pp. 313-399]; Rozantsev; Sholle *Synthesis* **1971**, 190-202, 401-414.

¹⁷¹See Ballester; Veciana; Riera; Castañer; Armet; Rovira *Chem. Soc., Chem. Commun.* **1983**, 982.

¹⁷²It has been claimed that relative D values do not provide such a measure: Nicholas; Arnold *Can. J. Chem.* **1984**, *62*, 1850, 1860.

¹⁷³Except where noted, these values are from Kerr, in Weast *Handbook of Chemistry and Physics*, 69th ed.; CRC Press: Boca Raton, FL, 1988, p. F-183. For another list of D values, see McMillen; Golden *Annu. Rev. Phys. Chem.* **1982**, *33*, 493. See also Tsang *J. Am. Chem. Soc.* **1985**, *107*, 2872; Holmes; Lossing; Maccoll *J. Am. Chem. Soc.* **1988**, *110*, 7339; Holmes; Lossing *J. Am. Chem. Soc.* **1988**, *110*, 7343; Roginskii *J. Org. Chem. USSR* **1989**, *25*, 403.

¹⁷⁴For a review of cyclopropyl radicals, see Walborsky *Tetrahedron* **1981**, *37*, 1625-1651. See also Boche; Walborsky, Ref. 102.

¹⁷⁵This value is from Gutman *Acc. Chem. Res.* **1990**, *23*, 375-380.

There are two possible structures for simple alkyl radicals.¹⁷⁶ They might have sp^2 bonding, in which case the structure would be planar, with the odd electron in a p orbital, or the bonding might be sp^3 , which would make the structure pyramidal and place the odd electron in an sp^3 orbital. ESR spectra of CH_3^\bullet and other simple alkyl radicals as well as other evidence indicate that these radicals have planar structures.¹⁷⁷ This is in accord with the known loss of optical activity when a free radical is generated at a chiral carbon.¹⁷⁸ In addition, electronic spectra of the CH_3 and CD_3 radicals (generated by flash photolysis) in the gas phase have definitely established that under these conditions the radicals are planar or near-planar.¹⁷⁹ IR spectra of CH_3^\bullet trapped in solid argon led to a similar conclusion.¹⁸⁰

Evidence from studies on bridgehead compounds shows that though a planar configuration is more stable, pyramidal structures are not impossible. In contrast to the situation with carbocations, free radicals have often been generated at bridgeheads, although studies have shown that bridgehead free radicals are less rapidly formed than the corresponding open-chain radicals.¹⁸¹ In sum, the available evidence indicates that though simple alkyl free radicals prefer a planar, or near-planar shape, the energy difference between a planar and a pyramidal free radical is not great. However, free radicals in which the carbon is connected to atoms of high electronegativity, e.g., CF_3^\bullet , prefer a pyramidal shape;¹⁸² increasing the electronegativity increases the deviation from planarity.¹⁸³ Cyclopropyl radicals are also pyramidal.¹⁸⁴

Free radicals with resonance are definitely planar, though triphenylmethyl-type radicals are propeller-shaped,¹⁸⁵ like the analogous carbocations (p. 172).

A number of diradicals (also called biradicals) are known.¹⁸⁶ When the unpaired electrons of a diradical are widely separated, e.g., as in $\bullet\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2^\bullet$, the species behaves spectrally like two doublets. When they are close enough for interaction or can interact through an unsaturated system (as in trimethylenemethane,¹⁸⁷ they can have total spin numbers of $+1$, 0 , or -1 , since each electron could be either $+\frac{1}{2}$ or $-\frac{1}{2}$. Spectroscopically

¹⁷⁶For a review, see Kaplan, in Kochi, Ref. 136, vol. 2, pp. 361-434.

¹⁷⁷See, for example, Cole; Pritchard; Davidson; McConnell *Mol. Phys.* **1958**, *1*, 406; Fessenden; Schuler *J. Chem. Phys.* **1963**, *39*, 2147; Symons *Nature* **1969**, 222, 1123, *Tetrahedron Lett.* **1973**, 207; Bonazzola; Leray; Roncin *J. Am. Chem. Soc.* **1977**, *99*, 8348; Giese; Beckhaus *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 594 [*Angew. Chem.* **90**, 635]; Ref. 98. See, however, Paddon-Row; Houk *J. Am. Chem. Soc.* **1981**, *103*, 5047.

¹⁷⁸There are a few exceptions. See p. 682.

¹⁷⁹Herzberg; Shoosmith *Can. J. Phys.* **1956**, *34*, 523; Herzberg *Proc. R. Soc. London, Ser. A* **1961**, 262, 291. See also Tan; Winer; Pimentel *J. Chem. Phys.* **1972**, *57*, 4028; Yamada; Hirota; Kawaguchi *J. Chem. Phys.* **1981**, *75*, 5256.

¹⁸⁰Andrews; Pimentel *J. Chem. Phys.* **1967**, *47*, 3637; Milligan; Jacox *J. Chem. Phys.* **1967**, *47*, 5146.

¹⁸¹Lorand; Chodroff; Wallace *J. Am. Chem. Soc.* **1968**, *90*, 5266; Fort; Franklin *J. Am. Chem. Soc.* **1968**, *90*, 5267; Humphrey; Hodgson; Pincock *Can. J. Chem.* **1968**, *46*, 3099; Oberlinner; Rüchardt *Tetrahedron Lett.* **1969**, 4685; Danen; Tipton; Saunders *J. Am. Chem. Soc.* **1971**, *93*, 5186; Fort; Hiti *J. Org. Chem.* **1977**, *42*, 3968; Lomas *J. Org. Chem.* **1987**, *52*, 2627.

¹⁸²Fessenden; Schuler *J. Chem. Phys.* **1965**, *43*, 2704; Rogers; Kispert *J. Chem. Phys.* **1967**, *46*, 3193; Pauling *J. Chem. Phys.* **1969**, *51*, 2767.

¹⁸³For example, 1,1-dichloroalkyl radicals are closer to planarity than the corresponding 1,1-difluoro radicals, though still not planar: Chen; Tang; Montgomery; Kochi *J. Am. Chem. Soc.* **1974**, *96*, 2201. For a discussion, see Krusic; Bingham *J. Am. Chem. Soc.* **1976**, *98*, 230.

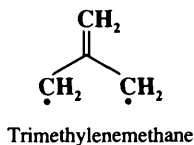
¹⁸⁴See Deycard; Hughes; Luszyk; Ingold *J. Am. Chem. Soc.* **1987**, *109*, 4954.

¹⁸⁵Adrian *J. Chem. Phys.* **1958**, *28*, 608; Andersen *Acta Chem. Scand.* **1965**, *19*, 629.

¹⁸⁶For a monograph, see Borden *Diradicals*; Wiley, New York, 1982. For reviews, see Johnston; Scaiano *Chem. Rev.* **1989**, *89*, 521-547; Doubleday; Turro; Wang *Acc. Chem. Res.* **1989**, *22*, 199-205; Scheffer; Trotter *Rev. Chem. Intermed.* **1988**, *9*, 271-305; Wilson *Org. Photochem.* **1985**, *7*, 339-466; Borden *React. Intermed. (Wiley)* **1985**, *3*, 151-188, **1981**, *2*, 175-209; Borden; Davidson *Acc. Chem. Res.* **1981**, *14*, 69-76; Salem; Rowland *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 92-111 [*Angew. Chem.* **84**, 86-106]; Salem *Pure Appl. Chem.* **1973**, *33*, 317-328; Jones *J. Chem. Educ.* **1974**, *51*, 175-181; Morozova; Dyatkina *Russ. Chem. Rev.* **1968**, *37*, 376-391. See also Döhnert; Koutecký *J. Am. Chem. Soc.* **1980**, *102*, 1789. For a series of papers on diradicals, see *Tetrahedron* **1982**, *38*, 735-867.

¹⁸⁷For reviews of trimethylenemethane, see Borden; Davidson *Ann. Rev. Phys. Chem.* **1979**, *30*, 125-153; Bergman; in Kochi, Ref. 136, vol. 1, pp. 141-149.

they are called *triplets*,¹⁸⁸ since each of the three possibilities is represented among the molecules and gives rise to its own spectral peak. In triplet *molecules* the two unpaired

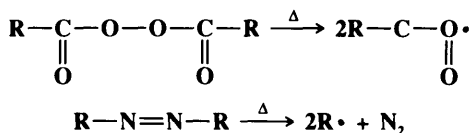


electrons have the same spin. Radicals with both unpaired electrons on the same carbon are discussed under carbenes.

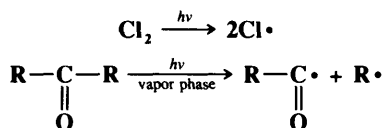
The Generation and Fate of Free Radicals¹⁸⁹

Free radicals are formed from molecules by breaking a bond so that each fragment keeps one electron.¹⁹⁰ The energy necessary to break the bond is supplied in one of two ways.

1. *Thermal cleavage.* Subjection of any organic molecule to a high enough temperature in the gas phase results in the formation of free radicals. When the molecule contains bonds with *D* values of 20 to 40 kcal/mol (80 to 170 kJ/mol), cleavage can be caused in the liquid phase. Two common examples are cleavage of diacyl peroxides¹⁹² and of azo compounds;¹⁹³



2. *Photochemical cleavage* (see p. 236). The energy of light of 600 to 300 nm is 48 to 96 kcal/mol (200 to 400 kJ/mol), which is of the order of magnitude of covalent-bond energies. Typical examples are photochemical cleavage of chlorine and of ketones;



¹⁸⁸For discussions of the triplet state, see Wagner; Hammond *Adv. Photochem.* **1968**, *5*, 21-156; Turro *J. Chem. Educ.* **1969**, *46*, 2-6. For a discussion of esr spectra of triplet states, see Wasserman; Hutton *Acc. Chem. Res.* **1977**, *10*, 27-32.

¹⁸⁹For a summary of methods of radical formation, see Giese *Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds*; Pergamon: Elmsford, NY, 1986, pp. 267-281. For a review on formation of free radicals by thermal cleavage, see Brown *Pyrolytic Methods in Organic Chemistry*; Academic Press: New York, 1980, pp. 44-61.

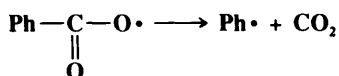
¹⁹⁰It is also possible for free radicals to be formed by the collision of two nonradical species. For a review, see Harmony *Methods Free-Radical Chem.* **1974**, *5*, 101-176.

¹⁹¹For a review of homolytic cleavage of carbon-metal bonds, see Barker; Winter, in Hartley; Patai, Ref. 107, pp. 151-218.

¹⁹²For a review of free radical mechanisms involving peroxides in solution, see Howard, in Patai *The Chemistry of Peroxides*; Wiley: New York, 1983, pp. 235-258. For a review of pyrolysis of peroxides in the gas phase, see Batt; Liu, in the same volume, pp. 685-710. See also Chateaucneuf; Luszyk; Ingold *J. Am. Chem. Soc.* **1988**, *110*, 2877, 2886.

¹⁹³For a review of the cleavage of azoalkanes, see Engel *Chem. Rev.* **1980**, *80*, 99-150. For summaries of later work, see Adams; Burton; Andrews; Weisman; Engel *J. Am. Chem. Soc.* **1986**, *108*, 7935; Schmittel; Ruchardt *J. Am. Chem. Soc.* **1987**, *109*, 2750.

Radicals are also formed from other radicals, either by the reaction between a radical and a molecule (which *must* give another radical, since the total number of electrons is odd) or by cleavage of a radical to give another radical, e.g.,



Radicals can also be formed by oxidation or reduction, including electrolytic methods.

Reactions of free radicals either give stable products (termination reactions) or lead to other radicals, which themselves must usually react further (propagation reactions). The most common termination reactions are simple combinations of similar or different radicals:

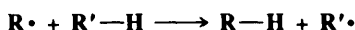


Another termination process is disproportionation:¹⁹⁴

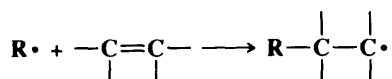


There are four principal propagation reactions, of which the first two are most common:

1. *Abstraction of another atom or group, usually a hydrogen atom* (see Chapter 14):



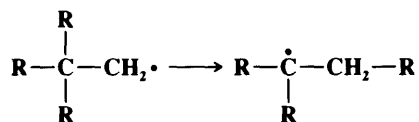
2. *Addition to a multiple bond* (see Chapter 15):



The radical formed here may add to another double bond, etc. This is one of the chief mechanisms for vinyl polymerization.

3. *Decomposition*. This can be illustrated by the decomposition of the benzyloxy radical (above).

4. *Rearrangement*:



This is less common than rearrangement of carbocations, but it does occur (though not when R = alkyl or hydrogen; see Chapter 18).

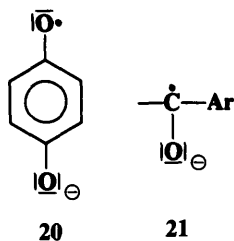
Besides these reactions, free radicals can be oxidized to carbocations or reduced to carbanions.¹⁹⁵

¹⁹⁴For reviews of termination reactions, see Pilling *Int. J. Chem. Kinet.* **1989**, *21*, 267-291; Khudyakov; Levin; Kuz'min *Russ. Chem. Rev.* **1980**, *49*, 982-1002; Gibian; Corley *Chem. Rev.* **1973**, *73*, 441-464.

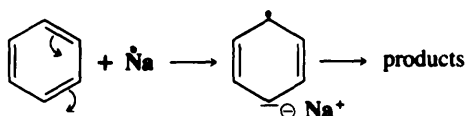
¹⁹⁵For a review of the oxidation and reduction of free radicals, see Khudyakov and Kuz'min *Russ. Chem. Rev.* **1978**, *47*, 22-42.

Radical Ions¹⁹⁶

Several types of radical anions are known with the unpaired electron or the charge or both on atoms other than carbon. Important examples are semiquinones¹⁹⁷ (20) and ketyls¹⁹⁸



(21). Reactions in which alkali metals are reducing agents often involve radical anion intermediates, e.g., reaction 5-10:



Several types of radical cation are also known.¹⁹⁹

CARBENES

Stability and Structure²⁰⁰

Carbenes are highly reactive species, practically all having lifetimes considerably under 1 sec. With exceptions noted below (p. 200), carbenes have been isolated only by entrapment in matrices at low temperatures (77 K or less).²⁰¹ The parent species CH_2 is usually called

¹⁹⁶For a monograph, see Kaiser; *Kevan Radical Ions*; Wiley: New York, 1968. For reviews, see Gerson; *Huber Acc. Chem. Res.* **1967**, *20*, 85-90; Todres *Tetrahedron* **1985**, *41*, 2771-2823; Russell; Norris, in McManus, Ref. 1, pp. 423-448; Holy; Marcum *Angew. Chem. Int. Ed. Engl.* **1971**, *10*, 115-124 [*Angew. Chem.* **83**, 132-142]; Bilevich; Okhlobystin *Russ. Chem. Rev.* **1968**, *37*, 954-968; Szwarc *Prog. Phys. Org. Chem.* **1968**, *6*, 322-438. For a related review, see Chanon; Rajzmann; Chanon *Tetrahedron* **1990**, *46*, 6193-6299. For a series of papers on this subject, see *Tetrahedron* **1986**, *42*, 6097-6349.

¹⁹⁷For a review of semiquinones, see Depew; Wan, in Patai; Rappoport *The Chemistry of the Quinonoid Compounds*, vol. 2, pt. 2; Wiley: New York, 1988, pp. 963-1018.

¹⁹⁸For a review of ketyls, see Russell, in Patai; Rappoport *The Chemistry of Enones*, pt. 1; Wiley: New York, 1989, pp. 471-512.

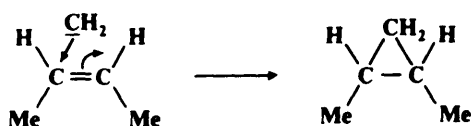
¹⁹⁹For reviews, see Roth *Acc. Chem. Res.* **1987**, *20*, 343-350; Courtneidge; Davies *Acc. Chem. Res.* **1987**, *20*, 90-97; Hammerich; Parker *Adv. Phys. Org. Chem.* **1984**, *20*, 55-189; Symons *Chem. Soc. Rev.* **1984**, *13*, 393-439; Bard; Ledwith; Shine *Adv. Phys. Org. Chem.* **1976**, *13*, 155-278.

²⁰⁰For monographs, see Jones; Moss *Carbenes*, 2 vols.; Wiley: New York, 1973-1975; Kirmse *Carbene Chemistry*, 2nd ed.; Academic Press: New York, 1971; Rees; Gilchrist *Carbenes, Nitrenes, and Arynes*; Nelson: London, 1969. For reviews, see Minkin; Simkin; Glukhovtsev *Russ. Chem. Rev.* **1989**, *58*, 622-635; Moss; Jones *React. Intermed. (Wiley)* **1985**, *3*, 45-108, **1981**, *2*, 59-133, **1978**, *1*, 69-115; Isaacs, Ref. 1, pp. 375-407; Bethell *Adv. Phys. Org. Chem.* **1969**, *7*, 153-209; Bethell, in McManus, Ref. 1, pp. 61-126; Closs *Top. Stereochem.* **1968**, *3*, 193-235; Herold; Gaspar *Fortschr. Chem. Forsch.* **1966**, *5*, 89-146; Rozantsev; Fainzil'berg; Novikov *Russ. Chem. Rev.* **1965**, *34*, 69-88. For a theoretical study, see Liebman; Simons *Mol. Struct. Energ.* **1986**, *1*, 51-99.

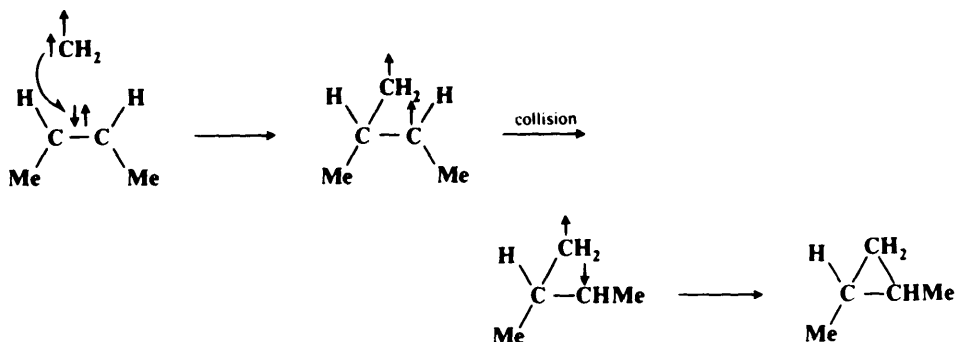
²⁰¹For example, see Murray; Trozzolo; Wasserman; Yager *J. Am. Chem. Soc.* **1962**, *84*, 3213; Brandon; Closs; Hutchison *J. Chem. Phys.* **1962**, *37*, 1878; Milligan; Mann; Jacox; Mitsch *J. Chem. Phys.* **1964**, *41*, 1199; Nefedov; Maltsev; Mikaelyan *Tetrahedron Lett.* **1971**, 4125; Wright *Tetrahedron* **1985**, *41*, 1517. For reviews, see Zuev; Nefedov *Russ. Chem. Rev.* **1989**, *58*, 636-643; Sheridan *Org. Photochem.* **1987**, *8*, 159-248, pp. 196-216; Trozzolo *Acc. Chem. Res.* **1968**, *1*, 329-335.

methylene, though derivatives are more often named by the carbene nomenclature. Thus CCl_2 is generally known as dichlorocarbene, though it can also be called dichloromethylene.

The two nonbonded electrons of a carbene can be either paired or unpaired. If they are paired, the species is spectrally a *singlet*, while, as we have seen (p. 193), two unpaired electrons appear as a *triplet*. An ingenious method of distinguishing between the two possibilities was developed by Skell,²⁰² based on the common reaction of addition of carbenes to double bonds to form cyclopropane derivatives (5-50). If the singlet species adds to *cis*-2-butene, the resulting cyclopropane should be the *cis* isomer since the movements of



the two pairs of electrons should occur either simultaneously or with one rapidly succeeding another. However, if the attack is by a triplet species, the two unpaired electrons cannot both go into a new covalent bond, since by Hund's rule they have parallel spins. So one of the unpaired electrons will form a bond with the electron from the double bond that has the opposite spin, leaving two unpaired electrons that have the same spin and therefore cannot form a bond at once but must wait until, by some collision process, one of the



electrons can reverse its spin. During this time, there is free rotation about the C—C bond and a mixture of *cis*- and *trans*-1,2-dimethylcyclopropanes should result.²⁰³

The results of this type of experiment show that CH_2 itself is usually formed as a singlet species, which can decay to the triplet state, which consequently has a lower energy (molecular-orbital calculations and experimental determinations show that the difference in energy between singlet and triplet CH_2 is about 8 to 10 kcal/mol or 33 to 42 kJ/mol²⁰⁴). However, it is possible to prepare triplet CH_2 directly by a photosensitized decomposition of diazomethane.²⁰⁵ CH_2 is so reactive²⁰⁶ that it generally reacts as the singlet before it has

²⁰²Skell; Woodworth *J. Am. Chem. Soc.* **1956**, *78*, 4496; Skell *Tetrahedron* **1985**, *41*, 1427.

²⁰³These conclusions are generally accepted though the reasoning given here may be oversimplified. For discussions, see Closs, Ref. 200, pp. 203-210; Bethell *Adv. Phys. Org. Chem.*, Ref. 200, pp. 194-200; Hoffmann *J. Am. Chem. Soc.* **1968**, *90*, 1475.

²⁰⁴See, for example, Hay; Hunt; Goddard *Chem. Phys. Lett.* **1972**, *13*, 30; Dewar; Haddon; Weiner *J. Am. Chem. Soc.* **1974**, *96*, 253; Frey; Kennedy *J. Chem. Soc., Chem. Commun.* **1975**, 233; Lucchese; Schaefer *J. Am. Chem. Soc.* **1977**, *99*, 6765; Roos; Siegbahn *J. Am. Chem. Soc.* **1977**, *99*, 7716; Lengel; Zare *J. Am. Chem. Soc.* **1978**, *100*, 7495; Borden; Davidson, Ref. 187, pp. 128, 134; Leopold; Murray; Lineberger *J. Chem. Phys.* **1984**, *81*, 1048.

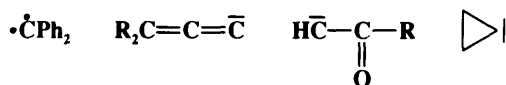
²⁰⁵Kopecky; Hammond; Leermakers *J. Am. Chem. Soc.* **1961**, *83*, 2397, **1962**, *84*, 1015; Duncan; Cveticanić *J. Am. Chem. Soc.* **1962**, *84*, 3593.

²⁰⁶For a review of the kinetics of CH_2 reactions, see Laufer *Rev. Chem. Intermed.* **1981**, *4*, 225-257.

a chance to decay to the triplet state.²⁰⁷ As to other carbenes, some react as triplets, some as singlets, and others as singlets or triplets, depending on how they are generated.

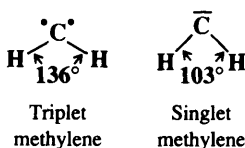
There is a limitation to the use of stereospecificity of addition as a diagnostic test for singlet or triplet carbenes.²⁰⁸ When carbenes are generated by photolytic methods, they are often in a highly excited singlet state. When they add to the double bond, the addition is stereospecific; but the cyclopropane formed carries excess energy; i.e., it is in an excited state. It has been shown that under certain conditions (low pressures in the gas phase) the excited cyclopropane may undergo cis-trans isomerization *after* it is formed, so that triplet carbene may seem to be involved although in reality the singlet was present.²⁰⁹

The most common carbenes are CH₂ and CCl₂,²¹⁰ but many others have been reported, e.g.,²¹¹



Studies of the ir spectrum of CCl₂ trapped at low temperatures in solid argon indicate that the ground state for this species is the singlet.²¹²

The geometrical structure of triplet methylene can be investigated by esr measurements,²¹³ since triplet species are diradicals. Such measurements made on triplet CH₂ trapped in matrices at very low temperatures (4 K) show that triplet CH₂ is a bent molecule, with an angle of about 136°.²¹⁴ Epr measurements cannot be made on singlet species, but from electronic spectra of CH₂ formed in flash photolysis of diazomethane it was concluded that singlet CH₂ is also bent, with an angle of about 103°.²¹⁵ Singlet CCl₂²¹² and CBr₂²¹⁶ are also



bent, with angles of 100 and 114°, respectively. It has long been known that triplet aryl carbenes are bent.²¹⁷

²⁰⁷Decay of singlet and triplet CH₂ has been detected in solution, as well as in the gas phase: Turro; Cha; Gould *J. Am. Chem. Soc.* **1987**, *109*, 2101.

²⁰⁸For other methods of distinguishing singlet from triplet carbenes, see Hendrick; Jones *Tetrahedron Lett.* **1978**, 4249; Creary *J. Am. Chem. Soc.* **1980**, *102*, 1611.

²⁰⁹Rabinovitch; Tschuikow-Roux; Schlag *J. Am. Chem. Soc.* **1959**, *81*, 1081; Frey *Proc. R. Soc. London, Ser. A* **1959**, *251*, 575. It has been reported that a singlet carbene (CBr₂) can add nonstereospecifically: Lambert; Larson; Bosch *Tetrahedron Lett.* **1983**, *24*, 3799.

²¹⁰For reviews of halocarbenes, see Burton; Hahnfeld *Fluorine Chem. Rev.* **1977**, *8*, 119-188; Margrave; Sharp; Wilson *Fort. Chem. Forsch.* **1972**, *26*, 1-35, pp. 3-13.

²¹¹For reviews of unsaturated carbenes, see Stang *Acc. Chem. Res.* **1982**, *15*, 348-354; *Chem. Rev.* **1978**, *78*, 383-403. For a review of carbalkoxycarbenes, see Marchand; Brockway *Chem. Rev.* **1974**, *74*, 431-469. For a review of arylcarbenes, see Schuster *Adv. Phys. Org. Chem.* **1986**, *22*, 311-361. For a review of carbenes with neighboring hetero atoms, see Taylor *Tetrahedron* **1982**, *38*, 2751-2772.

²¹²Andrews *J. Chem. Phys.* **1968**, *48*, 979.

²¹³The technique of spin trapping (p. 187) has been applied to the detection of transient triplet carbenes: Forrester; Sadd *J. Chem. Soc., Perkin Trans. 2* **1982**, 1273.

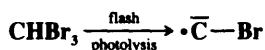
²¹⁴Wasserman; Kuck; Hutton; Yager *J. Am. Chem. Soc.* **1970**, *92*, 7491; Wasserman; Yager; Kuck *Chem. Phys. Lett.* **1970**, *7*, 409; Wasserman; Kuck; Hutton; Anderson; Yager *J. Chem. Phys.* **1971**, *54*, 4120; Bernheim; Bernard; Wang; Wood; Skell *J. Chem. Phys.* **1970**, *53*, 1280, **1971**, *54*, 3223.

²¹⁵Herzberg; Shoosmith *Nature* **1959**, *183*, 1801; Herzberg *Proc. R. Soc. London, Ser. A* **1961**, *262*, 291; Herzberg; Johns *Proc. R. Soc. London, Ser. A* **1967**, *295*, 107, *J. Chem. Phys.* **1971**, *54*, 2276.

²¹⁶Ivey; Schulze; Leggett; Kohl *J. Chem. Phys.* **1974**, *60*, 3174.

²¹⁷Trozzolo; Wasserman; Yager *J. Am. Chem. Soc.* **1965**, *87*, 129; Senthilnathan; Platz *J. Am. Chem. Soc.* **1981**, *103*, 5503; Gilbert; Griller; Nazran *J. Org. Chem.* **1985**, *50*, 4738.

Flash photolysis of CHBr_3 produced the intermediate CBr^{218}

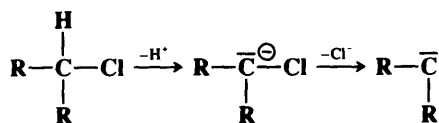


This is a *carbyne*. The intermediates CF and CCl were generated similarly from CHFBr_2 and CHClBr_2 , respectively.

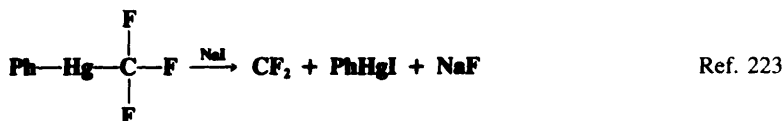
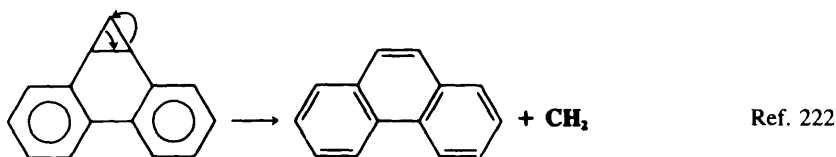
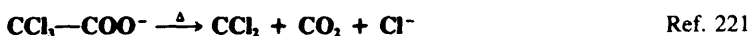
The Generation and Fate of Carbenes²¹⁹

Carbenes are chiefly formed in two ways, though other pathways are also known.

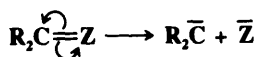
1. In α elimination, a carbon loses a group without its electron pair, usually a proton, and then a group with its pair, usually a halide ion:²²⁰



The most common example is formation of dichlorocarbene by treatment of chloroform with a base (see reaction 0-3), but many other examples are known, a few of which are



2. Disintegration of compounds containing certain types of double bonds:



²¹⁸Ruzsicska; Jodhan; Choi; Strausz *J. Am. Chem. Soc.* **1983**, *105*, 2489.

²¹⁹For reviews, see Jones *Acc. Chem. Res.* **1974**, *7*, 415-421; Kirmse, in Bamford; Tipper *Comprehensive Chemical Kinetics*, vol. 9; Elsevier: New York, 1973, pp. 373-415; Ref. 200. For a review of electrochemical methods of carbene generation, see Petrosyan; Niyazymbetov *Russ. Chem. Rev.* **1969**, *58*, 644-653.

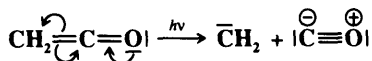
²²⁰For a review of formation of carbenes in this manner, see Kirmse *Angew. Chem. Int. Ed. Engl.* **1965**, *4*, 1-10 [*Angew. Chem.* *77*, 1-10].

²²¹Wagner *Proc. Chem. Soc.* **1959**, 229.

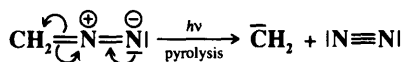
²²²Richardson; Durrett; Martin; Putnam; Slaymaker; Dvoretzky *J. Am. Chem. Soc.* **1965**, *87*, 2763. For reviews of this type of reaction, see Hoffmann *Angew. Chem. Int. Ed. Engl.* **1971**, *10*, 529, 537 [*Angew. Chem.* *83*, 595-603]; Griffin *Angew. Chem. Int. Ed. Engl.* **1971**, *10*, 537-547 [*Angew. Chem.* *83*, 604-613]. See also Hoffmann *Acc. Chem. Res.* **1985**, *18*, 248-253.

²²³Seyferth; Hopper; Darragh *J. Am. Chem. Soc.* **1969**, *91*, 6536; Seyferth *Acc. Chem. Res.* **1972**, *5*, 65-74.

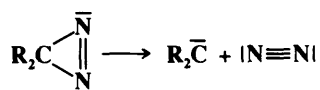
The two most important ways of forming CH_2 are examples: the photolysis of ketene



and the isoelectronic decomposition of diazomethane.²²⁴



Diazirines (isomeric with diazoalkanes) also give carbenes:²²⁵

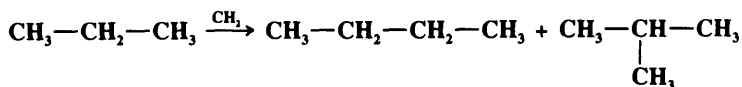


Because most carbenes are so reactive, it is often difficult to prove that they are actually present in a given reaction. In many instances where a carbene is *apparently* produced by an α elimination or by disintegration of a double-bond compound there is evidence that no free carbene is actually involved. The neutral term *carbenoid* is used where it is known that a free carbene is not present or in cases where there is doubt. α -Halo organometallic compounds R_2CXM are often called carbenoids because they readily give α elimination reactions²²⁶ (for example, see 2-39).

The reactions of carbenes are more varied than those of the species previously discussed in this chapter.

1. Additions to carbon-carbon double bonds have already been mentioned. Carbenes also add to aromatic systems, but the immediate products rearrange, usually with ring enlargement (see 5-50). Additions of carbenes to other double bonds, such as $\text{C}=\text{N}$ (6-61 and 6-62), and to triple bonds have also been reported.

2. An unusual reaction of carbenes is that of insertion into $\text{C}-\text{H}$ bonds (2-20). Thus CH_2 reacts with methane to give ethane and with propane to give *n*-butane and isobutane.



This reaction is virtually useless for synthetic purposes but illustrates the extreme reactivity of carbene. Treatment in the liquid phase of an alkane such as pentane with carbene formed from the photolysis of diazomethane gives the three possible products in statistical ratios²²⁷ demonstrating that carbene is displaying no selectivity. For many years, it was a generally accepted principle that the lower the selectivity the greater the reactivity; however, this

²²⁴For a review, see Regitz; Maas *Diazo Compounds*; Academic Press: New York, 1986, pp. 170-184.

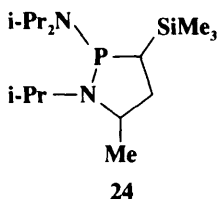
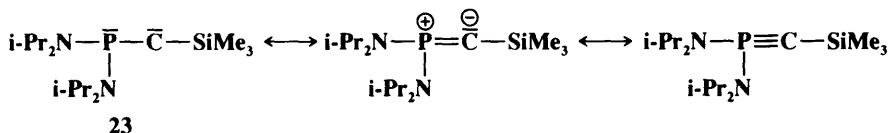
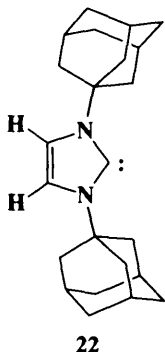
²²⁵For a treatise, see Liu *Chemistry of Diazirines*, 2 vols.; CRC Press: Boca Raton, FL, 1987. For reviews, see Liu *Chem. Soc. Rev.* **1982**, *11*, 127-140; Frey *Adv. Photochem.* **1966**, *4*, 225-256.

²²⁶For a review, see Nefedov; D'yachenko; Prokof'ev *Russ. Chem. Rev.* **1977**, *46*, 941-966.

²²⁷Doering; Buttery; Laughlin; Chaudhuri *J. Am. Chem. Soc.* **1956**, *78*, 3224; Richardson; Simmons; Dvoretzky *J. Am. Chem. Soc.* **1961**, *83*, 1934; Halberstadt; McNesby *J. Am. Chem. Soc.* **1967**, *89*, 3417.

principle is no longer regarded as general because many exceptions have been found.²²⁸ Singlet CH₂ generated by photolysis of diazomethane is probably the most reactive organic species known, but triplet CH₂ is somewhat less reactive, and other carbenes are still less reactive. The following series of carbenes of decreasing reactivity has been proposed on the basis of discrimination between insertion and addition reactions: CH₂ > HCCOOR > PhCH > BrCH ≈ ClCH.²²⁹ Dihalocarbenes generally do not give insertion reactions at all. Insertion of carbenes into other bonds has also been demonstrated, though not insertion into C—C bonds.^{229a}

Two carbenes that are stable at room temperature have been reported.²³⁰ These are **22** and **23**. In the absence of oxygen and moisture **22** exists as stable crystals with a melting point of 240-241°C.^{230a} Its structure was proved by x-ray crystallography. **23**, which is in resonance with an ylide form and with a form containing a P≡C bond, is a red oil that



²²⁸For reviews of this question, see Buncel; Wilson *J. Chem. Educ.* **1987**, *64*, 475-480; Johnson *Tetrahedron* **1980**, *36*, 3461-3480; *Chem. Rev.* **1975**, *75*, 755-765; Giese *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 125-136 [*Angew. Chem.* *89*, 162-173]; Pross *Adv. Phys. Org. Chem.* **1977**, *14*, 69-132. See also Ritchie; Sawada *J. Am. Chem. Soc.* **1977**, *99*, 3754; Argile; Ruasse *Tetrahedron Lett.* **1980**, *21*, 1327; Godfrey *J. Chem. Soc., Perkin Trans. 2* **1981**, 645; Kurz; El-Nasr *J. Am. Chem. Soc.* **1982**, *104*, 5823; Srinivasan; Shunmugasundaram; Arumugam *J. Chem. Soc., Perkin Trans. 2* **1985**, *17*; Bordwell; Branca; Cripe *Isr. J. Chem.* **1985**, *26*, 357; Formosinho *J. Chem. Soc., Perkin Trans. 2* **1988**, 839; Johnson; Stratton *J. Chem. Soc., Perkin Trans. 2* **1988**, 1903. For a group of papers on this subject, see *Isr. J. Chem.* **1985**, *26*, 303-428.

²²⁹Closs; Coyle *J. Am. Chem. Soc.* **1965**, *87*, 4270.

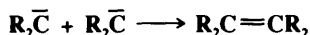
^{229a}See, for example, Doering; Knox; Jones *J. Org. Chem.* **1959**, *24*, 136; Franzen *Liebigs Ann. Chem.* **1959**, 627; Bradley; Ledwith *J. Chem. Soc.* **1961**, 1495; Frey; Voisey *Chem. Commun.* **1966**, 454; Seyferth; Damrauer; Mui; Jula *J. Am. Chem. Soc.* **1968**, *90*, 2944; Tomioka; Ozaki; Izawa *Tetrahedron* **1985**, *41*, 4987; Frey; Walsh; Watts *J. Chem. Soc., Chem. Commun.* **1989**, 284.

²³⁰For a discussion, see Regitz *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 674 [*Angew. Chem.* *103*, 691].

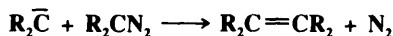
^{230a}Arduengo; Harlow; Kline *J. Am. Chem. Soc.* **1991**, *113*, 361.

undergoes internal insertion (the carbene carbon inserts into one of the C—H bonds of an isopropyl group to give **24**) when heated to 300°C.²³¹

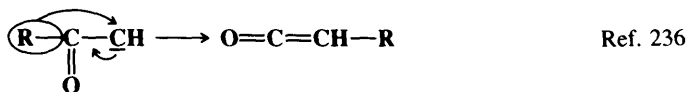
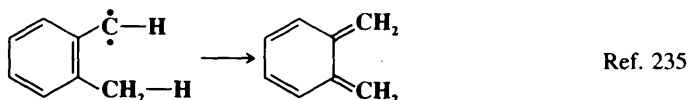
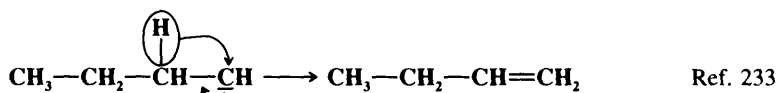
3. It would seem that dimerization should be an important reaction of carbenes



but it is not, because the reactivity is so great that the carbene species do not have time to find each other and because the dimer generally has so much energy that it dissociates again. Apparent dimerizations have been observed, but it is likely that the products in many reported instances of "dimerization" do not arise from an actual dimerization of two carbenes but from attack by a carbene on a molecule of carbene precursor, e.g.,



4. Alkylcarbenes can undergo rearrangement, with migration of alkyl or hydrogen.^{231a} Indeed these rearrangements are generally so rapid²³² that additions to multiple bonds and insertion reactions, which are so common for CH₂, are seldom encountered with alkyl or dialkyl carbenes. Unlike rearrangement of the species previously encountered in this chapter, most rearrangements of carbenes directly give stable molecules. Some examples are



The rearrangement of acylcarbenes to ketenes is called the Wolff rearrangement (**8-8**). A few rearrangements in which carbenes rearrange to other carbenes are also known.²³⁷ Of course, the new carbene must stabilize itself in one of the ways we have mentioned.

²³¹Igau; Grutzmacher; Baccaredo; Bertrand *J. Am. Chem. Soc.* **1991**, *113*, 6463; Igau; Baccaredo; Trinquier; Bertrand *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 621 [*Angew. Chem.* *101*, 617]. See also Gillette; Baccaredo; Bertrand *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1429 [*Angew. Chem.* *102*, 1486].

^{231a}For reviews of carbene and nitrene rearrangements, see Brown, Ref. 189, pp. 115-163; Wentrup *Adv. Heterocycl. Chem.* **1981**, *28*, 231-361, *React. Intermed. (Plenum)* **1980**, *1*, 263-319, *Top. Curr. Chem.* **1976**, *62*, 173-251; Jones, in de Mayo, Ref. 91, vol. 1, pp. 95-160; Schaefer *Acc. Chem. Res.* **1979**, *12*, 288-296; Kirmse, Ref. 200, pp. 457-496.

²³²The activation energy for the 1,2-hydrogen shift has been estimated at 1.1 kcal/mole (4.5 kJ/mol), an exceedingly low value; Stevens; Liu; Soundararajan; Paik *Tetrahedron Lett.* **1989**, *30*, 481.

²³³Kirmse; Doering *Tetrahedron* **1960**, *11*, 266. For kinetic studies of the rearrangement: Cl- \bar{C} -CHR₂ → ClCH=CR₂, see Liu; Bonneau *J. Am. Chem. Soc.* **1989**, *111*, 6873; Jackson; Soundararajan; White; Liu; Bonneau; Platz *J. Am. Chem. Soc.* **1989**, *111*, 6874; Ho; Krogh-Jespersen; Moss; Shen; Sheridan; Subramanian *J. Am. Chem. Soc.* **1989**, *111*, 6875; LaVilla; Goodman *J. Am. Chem. Soc.* **1989**, *111*, 6877.

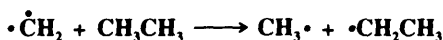
²³⁴Friedman; Shechter *J. Am. Chem. Soc.* **1960**, *82*, 1002.

²³⁵McMahon; Chapman *J. Am. Chem. Soc.* **1987**, *109*, 683.

²³⁶Friedman; Berger *J. Am. Chem. Soc.* **1961**, *83*, 492, 500.

²³⁷For a review, see Jones *Acc. Chem. Res.* **1977**, *10*, 353-359.

5. Triplet carbenes can abstract hydrogen or other atoms to give free radicals, e.g.,



This is not surprising, since triplet carbenes are free radicals. But singlet carbenes can also give this reaction, though in this case only halogen atoms are abstracted, not hydrogen.²³⁸

NITRENES

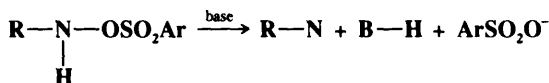
Nitrenes,²³⁹ R—N, are the nitrogen analogs of carbenes, and most of what we have said about carbenes also applies to them. Nitrenes are too reactive for isolation under ordinary conditions. Alkyl nitrenes have been isolated by trapping in matrices at 4 K,²⁴⁰ while aryl nitrenes, which are less reactive, can be trapped at 77 K.²⁴¹ The ground state of NH, and probably of most nitrenes,²⁴² is a triplet, though nitrenes can be generated in both triplet and singlet states. In additions of EtOOC—N to C=C double bonds two species are involved,



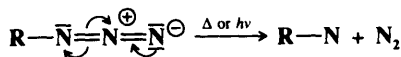
one of which adds stereospecifically and the other not. By analogy with Skell's proposal involving carbenes (p. 196) these are taken to be the singlet and triplet species, respectively.²⁴³

The two principal means of generating nitrenes are analogous to those used to form carbenes.

1. *Elimination.* An example is



2. *Breakdown of certain double-bond compounds.* The most common method of forming nitrenes is photolytic or thermal decomposition of azides,²⁴⁴



²³⁸Roth *J. Am. Chem. Soc.* **1971**, *93*, 1527, 4935, *Acc. Chem. Res.* **1977**, *10*, 85-91.

²³⁹For monographs, see Scriven *Azides and Nitrenes*; Academic Press: New York, 1984; Lwowski *Nitrenes*; Wiley: New York, 1970. For reviews, see Scriven *React. Intermed. (Plenum)* **1982**, *2*, 1-54; Lwowski *React. Intermed. (Wiley)* **1985**, *3*, 305-332, **1981**, *2*, 315-334, **1978**, *1*, 197-227, *Angew. Chem. Int. Ed. Engl.* **1967**, *6*, 897-906 [*Angew. Chem.* **79**, 922-931]; Abramovitch, in McManus, Ref. 1, pp. 127-192; Hünig *Helv. Chim. Acta* **1971**, *54*, 1721-1747; Belloli *J. Chem. Educ.* **1971**, *48*, 422-426; Kuznetsov; Ioffe *Russ. Chem. Rev.* **1989**, *58*, 732-746 (N- and O-nitrenes); Meth-Cohn *Acc. Chem. Res.* **1987**, *20*, 18-27 (oxycarbonylnitrenes); Abramovitch; Sutherland *Fortsch. Chem. Forsch.* **1970**, *16*, 1-33 (sulfonyl nitrenes); Ioffe; Kuznetsov *Russ. Chem. Rev.* **1972**, *41*, 131-146 (N-nitrenes).

²⁴⁰Wasserman; Smolinsky; Yager *J. Am. Chem. Soc.* **1964**, *86*, 3166. For the structure of CH₃-N, as determined in the gas phase, see Carrick; Brazier; Bernath; Engelking *J. Am. Chem. Soc.* **1987**, *109*, 5100.

²⁴¹Smolinsky; Wasserman; Yager *J. Am. Chem. Soc.* **1962**, *84*, 3220. For a review, see Sheridan, Ref. 201, pp. 159-248.

²⁴²A few nitrenes have been shown to have singlet ground states. See Sigman; Autrey; Schuster *J. Am. Chem. Soc.* **1988**, *110*, 4297.

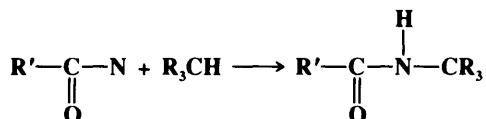
²⁴³McConaghy; Lwowski *J. Am. Chem. Soc.* **1967**, *89*, 2357, 4450; Mishra; Rice; Lwowski *J. Org. Chem.* **1968**, *33*, 481.

²⁴⁴For reviews, see Dyllal, in Patai; Rappoport *The Chemistry of Functional Groups, Supplement D*, pt. 1; Wiley: New York, 1983, pp. 287-320; Dürr; Kober *Top. Curr. Chem.* **1976**, *66*, 89-114; L'Abbé *Chem. Rev.* **1969**, *69*, 345-363.

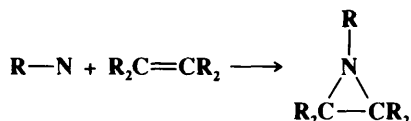
The unsubstituted nitrene NH has been generated by photolysis of or electric discharge through NH_3 , N_2H_4 , or HN_3 .

The reactions of nitrenes are also similar to those of carbenes.²⁴⁵ As in that case, many reactions in which nitrene intermediates are suspected probably do not involve free nitrenes. It is often very difficult to obtain proof in any given case that a free nitrene is or is not an intermediate.

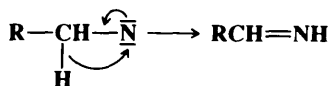
1. *Insertion* (see 2-12). Nitrenes, especially acyl nitrenes and sulfonyl nitrenes, can insert into C—H and certain other bonds, e.g.,



2. *Addition to C=C bonds* (see 5-42):

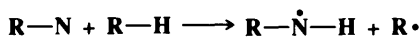


3. *Rearrangements*.^{231a} Alkyl nitrenes do not generally give either of the two preceding reactions because rearrangement is more rapid, e.g.,



Such rearrangements are so rapid that it is usually difficult to exclude the possibility that a free nitrene was never present at all, i.e., that migration takes place at the same time that the nitrene is formed²⁴⁶ (see p. 1091).

4. *Abstraction*, e.g.,



5. *Dimerization*. One of the principal reactions of NH is dimerization to diimide N_2H_2 . Azobenzenes are often obtained in reactions where aryl nitrenes are implicated:²⁴⁷



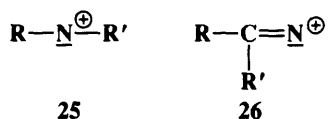
It would thus seem that dimerization is more important for nitrenes than it is for carbenes, but again it has not been proved that free nitrenes are actually involved.

²⁴⁵For a discussion of nitrene reactivity, see Subbaraj; Subba Rao; Lwowski *J. Org. Chem.* **1989**, *54*, 3945.

²⁴⁶For example, see Moriarty; Reardon *Tetrahedron* **1970**, *26*, 1379; Abramovitch; Kyba *J. Am. Chem. Soc.* **1971**, *93*, 1537.

²⁴⁷See, for example, Leyva Platz; Pery; Wirtz *J. Am. Chem. Soc.* **1986**, *108*, 3783.

At least two types of *nitrenium ions*, the nitrogen analogs of carbocations, can exist as intermediates, though much less work has been done in this area than on carbocations. In one type (**25**) the nitrogen is bonded to two atoms and in the other (**26**) to only one atom.²⁴⁸



When R = H in **25** the species is a protonated nitrene. Like carbenes and nitrenes, nitrenium ions can exist in singlet or triplet states.²⁴⁹

²⁴⁸For reviews of **25**, see Abramovitch; Jeyaraman, in *Scriven Azides and Nitrenes*, Ref. 239, pp. 297-357; Gassman *Acc. Chem. Res.* **1970**, 3, 26-33. For a review of **26**, see Lansbury, in *Lwowski Nitrenes*, Ref. 239, pp. 405-419.

²⁴⁹Gassman; Cryberg *J. Am. Chem. Soc.* **1969**, 91, 5176.