

showed the parent peak at m/e 268, a small peak at 253 ($-\text{CH}_3$), and major peaks at 188 ($-\text{HBr}$), 173 ($-\text{HBr}$, $-\text{CH}_3$), 131 ($\text{C}_{10}\text{H}_{11}^+$), and 105 [$-(\text{CH}_2)_6\text{Br}$].

The phenyl-1-bromooctanes undergo three major modes of cleavage in the mass spectrograph. These are loss of either the alkyl or bromoalkyl group to yield the corresponding benzylic carbonium ions and the loss of both the alkyl group and HBr. Hence there are three distinctive mass spectral peaks associated with each isomer. Those observed are for the 4-phenyl isomer (m/e 211, 131, and 147), the 5-phenyl isomer (225, 145, and 133), the 6-phenyl isomer (239, 159, and 119), and the 7-phenyl isomer. The intensities of the observed peaks were qualitatively appropriate to the assignments made.

The peaks corresponding to the 3-phenyl isomer (m/e 197, 117, and 171) and the 2-phenyl isomer (183, 103, and 185) were not detected by this method or by vpc which would detect 0.1%.

Phenyl-1,1-dichlorooctanes.—7-Phenyl-1,1-dichlorooctane was trapped from the previously described Carbowax column. The nmr showed aromatic protons at 7.0, a triplet at 5.5 (CHCl_2), a sextuplet at 2.58 (benzylic methine), a multiplet at 2.04 (CH_2CCl_2), methylene protons at 1.5, and a doublet at 1.19 ppm (methyl β to phenyl).

The 6-phenyl-1,1-dichlorooctane was concentrated by vpc. The nmr showed aromatic protons at 7.0, a triplet at 5.5 (CHCl_2), a sextuplet at 2.58 (benzylic methine), a multiplet at 2.04 (CH_2CCl_2), methylene protons at 1.5, and a triplet at 0.75 ppm (methyl γ to phenyl).

The mass spectrum of the phenyldichlorooctane mixture showed peaks corresponding to alkyl or alkylidichloro group loss to form the corresponding benzylic carbonium ions and loss of both alkyl group and HCl. The observed peaks corresponded

to the 4-phenyl isomer (m/e 201, 147, and 165), the 5-phenyl isomer (215, 133, and 179), the 6-phenyl isomer (229, 119, and 193), and the 7-phenyl isomer (243, 105, and 207).

Phenyl-1,1,1-trichlorooctane.—The 7-phenyl isomer was recognized by the characteristic doublet at 1.15 ppm in the nmr. The mass spectrum showed the parent peak at m/e 292 and peaks at 256 ($-\text{HCl}$), 241 ($-\text{HCl}$, $-\text{CH}_3$), 131 ($\text{C}_{10}\text{H}_{11}^+$), and 105 [$-(\text{CH}_2)_6\text{CCl}_3$].

The 6-phenyl isomer showed a triplet in the nmr at 0.7 ppm characteristic of a methyl group γ to phenyl. The mass spectrum showed the parent peak at m/e 292 and peaks at 256 ($-\text{HCl}$), 227 ($-\text{HCl}$, $-\text{C}_2\text{H}_5$), 145 ($\text{C}_{11}\text{H}_{13}^+$), and 119 [$-(\text{CH}_2)_6\text{CCl}_3$].

The mass spectrum of the phenyl-1,1,1-trichlorooctane mixture showed peaks corresponding to the 5-phenyl isomer (m/e 249, 133, and 213) and the 4-phenyl isomer (235, 147, and 199).

The nmr of all isomers showed the $-\text{CH}_2\text{CCl}_3$ peak overlapping with the methine hydrogen.

Registry No.—Benzene, 71-43-2; 1,1-dichlorooctane, 20395-24-8; 1,1,1-trichlorooctane, 4905-79-7; 1,1,1,3-tetrachlorooctane, 18088-13-6; 1,1,1,6-tetrachlorooctane, 20414-34-0; 1,1,1,7-tetrachlorooctane, 20414-35-1; 1,1,1,8-tetrachlorooctane, 10311-13-4; 7-phenyl-1,1-dichlorooctane, 20414-37-3; 6-phenyl-1,1-dichlorooctane, 20414-38-4; 7-phenyl-1,1,1-trichlorooctane, 20414-39-5; 6-phenyl-1,1,1-trichlorooctane, 20414-40-8; 1,1,8-trichlorooctane, 20414-41-9; 1,1,3-trichlorooctane, 4905-80-0.

Application of the Linnett Electronic Theory to Organic Chemistry.

II. Introduction

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Received September 13, 1968

The double-quartet theory of Linnett is shown to account for a wide variety of typical organic structural phenomena. The concept of L strain, a unique corollary of the Linnett theory, is discussed and put on a semiquantitative basis. Examples of problems in geometry, stabilization, hyperconjugation, and configurational inversion are provided from among the classes alkanes, alkenes, alkynes, amines, carbanions, carbonium ions, radicals, and carbenes, and certain predictions are made.

In the past few years there has appeared a modified theory of chemical binding, developed by Linnett.^{1,2} Based on the principles of quantum mechanics, Linnett's theory nevertheless differs drastically in many cases from that held in recent decades by most chemists (the Lewis-Langmuir octet rule),³⁻⁵ while in other cases it agrees. Heretofore the chief area of application has been in inorganic chemistry with a few ventures into organic territory.

We have found that a detailed examination of structure and mechanism throughout organic chemistry in the light of the Linnett concepts can provide increased understanding. A portion of this work has already been presented in preliminary form.⁶ In this paper, which is intended as the introduction to a series of detailed surveys of mechanism, Linnett's structural concepts are extended, in the simplest possible way, to typi-

cal organic molecules and intermediates. For the most part, discussions will be limited to elements of atomic number below neon in the periodic table.

The Linnett Theory.—Inasmuch as a complete description has been published,^{1,2} only a few points will be repeated here. The principal innovation is the treatment of the outermost shell of electrons around the nucleus of an atom as an array, not of pairs with perhaps an odd electron, but of two spin sets, one of each spin. The disposition of the electrons in each spin set toward each other is rather firmly fixed, owing both to the Pauli principle and their mutual electrostatic repulsion, at that with the maximum mutual distance within the radius of the shell. (By the "position" of an electron, of course, "most probable position" is meant throughout.) Thus, a quartet occupies the corners of a regular tetrahedron, a trio the corners of an equilateral triangle, and a duo the ends of a straight line, all centered on the nucleus. The relative positions of the two spin sets are the most staggered possible (consistent with the maximization of binding energy), to minimize interelectronic repulsion. The second restriction is weaker than the first, however, because the Pauli principle is not involved.

(1) J. W. Linnett, *J. Amer. Chem. Soc.*, **83**, 2643 (1961).

(2) J. W. Linnett, "The Electronic Structure of Molecules," Methuen & Co. Ltd., London, 1964.

(3) G. N. Lewis, *J. Amer. Chem. Soc.*, **38**, 762 (1916).

(4) G. N. Lewis, "Valence and the Structure of Atoms and Molecules," The Chemical Catalog Co., New York, N. Y., 1923.

(5) I. Langmuir, *J. Amer. Chem. Soc.*, **38**, 2221 (1916).

(6) R. A. Firestone, *Tetrahedron Lett.*, 971 (1968).

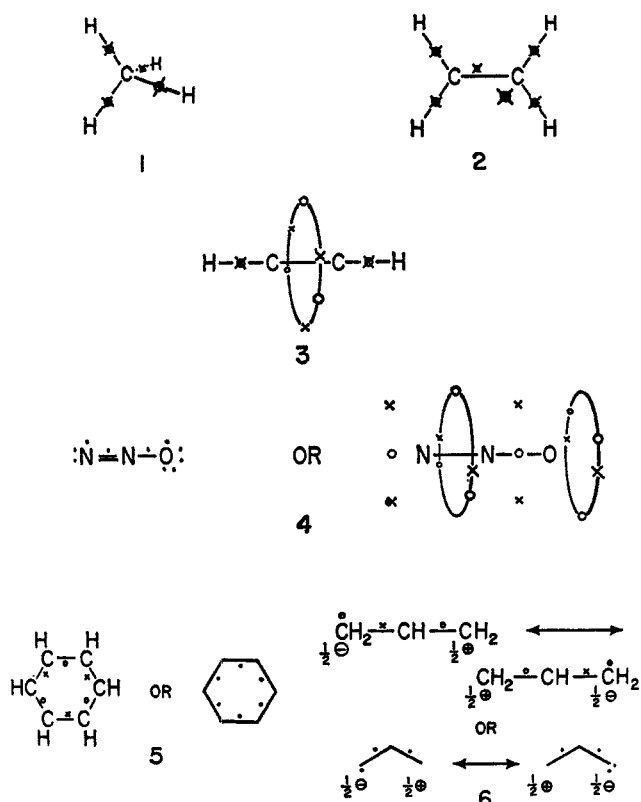


Figure 1.—1, methane; 2, ethylene; 3, acetylene; 4, nitrous acid; 5, benzene; 6, allyl radical.

A chemical bond between two atoms consists of one or more electrons between the nuclei, shared by both and as close to both as possible, allowing for the electrons' mutual repulsion and the Pauli principle. Thus a single bond has the two electrons close paired on the line connecting the two nuclei; their positions need not coincide, however. A double bond has four electrons which may or may not be close paired, and a triple bond has six electrons not close paired. Bonds with odd numbers of electrons are also permitted. The more electrons involved, the stronger the bond, although not necessarily in direct proportion. For nonbonding electrons, on the other hand (those not shared by more than one atom), the energy of the molecule is greater, the closer they lie to the internuclear line.

The chief innovation here is the deemphasis on the pair; a bond may contain any number of electrons, even or odd, up to six. In addition, great stress is laid upon the advantage of structures that have as few close pairs as possible, consonant with the other limitations. The relative ease with which the various types of atoms assume formal charges is also taken into account.

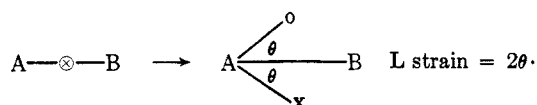
Another feature of Linnett's theory, though not a novelty, is that double bonds are seen as two-membered rings with bent bonds. The history and advantages of the bent-bond theory, particularly from the standpoint of rotational isomerism, have been adequately reviewed.⁷ It should be noted that triple bonds, while bent, are not simply two-membered bicyclic systems since they contain no close pairs.

A few structures are depicted in Figure 1 for illustration. We have adopted Linnett's convention of repre-

senting the two types of electrons by o's and x's, with simplified diagrams where possible, in which — represents a pair of electrons, one of each spin, without regard to whether or not they are close paired, and · represents one electron of either spin. Enough perspective drawings have been provided to illustrate at least one each of two-, three-, four-, five-, and six-electron bonds; in these particular illustrations, the lines connecting atoms, and some connecting electrons (*viz.*, five- and six-electron bonds), are there solely as aids to visualization. Space limitations preclude further discussion of Linnett's theory; ref 1 and 2 can be consulted for a full exposition.

L Strain.—One of the consequences of the double-quartet theory is that any event, at a given point in the valence shell of an atom, which alters the relative disposition of the two spin sets at that point will alter it at all other points as well, in a definite way. Thus all the bonds to that atom play a role in the reaction whether they appear to or not. This factor is distinct from the usual steric and electronic effects, and supplements but does not replace them.

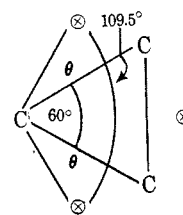
During a reaction, it is sometimes found that the two electrons in a single bond not directly involved are forced apart and off the internuclear line. This will



weaken the bond and, therefore, raise the activation energy, even though the bond may be intact and unstrained in both the reactants and the products. Bond weakening of this type constitutes a type of strain which we believe has not been invoked before and which we propose to call L strain. It may be exhibited by stable species as well as by transition states. Several examples of L strain have already been described.⁶

It is obvious that the strain energy will increase with θ , slowly at first and then more rapidly. An empirical relationship can be worked out using data from the literature.

(1) Cyclopropane suffers from L strain at each carbon atom. If we momentarily assume that all spin



sets are completely undistorted, the amount of L strain is seen to be 49.5° ; $\theta = ca. 25^\circ$. The angle strain in cyclopropane has been estimated to be about 21 kcal/mol,⁸ which provides a figure of 7 kcal/mol per C—C bond. Of course, the ring bonds will be stronger if the tetrahedra bend slightly so that the electrons can move a little inward.⁹ Thus 2θ in cyclopropane must be less

(8) K. W. Egger, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, **86**, 5420 (1964).

(9) That this is likely is indicated by the observed H—C—H angle in cyclopropane of $113.6 \pm 2^\circ$: O. Bastiensen and P. N. Skancke, *Advan. Chem. Phys.*, **3**, 323 (1960), p 349.

(7) E. A. Walters, *J. Chem. Educ.*, **43**, 134 (1966); E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, N. Y., 1965, pp 19–22.

than 49.5° , and our estimated strain energy for 49.5° somewhat low.

A correction must now be made for electron correlation, because the hypothetical reaction



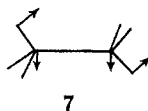
is exothermic, owing to the increase in interelectronic distance, even though the sum of the electronic deflections from the internuclear line is unchanged. A simple calculation of this correction can be made by setting the correlation energy proportional to $\sin \theta$. Perfect correlation (*i.e.*, maximum separation of electrons) is achieved at $2\theta = 70.5^\circ$, for a first-row atom whose valence shell is filled, because any further increase in θ necessarily involves the nearer approach of other electrons of the valence shell.¹⁰ From the "resonance energies" of benzene and carbon dioxide,² the approximate figure of 4 kcal/mol per electron pair can be derived for the maximum electron correlation energy, which is assigned to $2\theta = 70.5^\circ$. The correlation correction for cyclopropane, then, is about 3 kcal/mol per bond and the corrected L-strain energy for $2\theta = 49.5^\circ$ is 4 kcal/mol per electron pair.

(2) The strain energy of cyclobutane is almost the same as that of cyclopropane.¹¹ If the two also have similar total angle-strain energies, the L-strain energy for $2\theta \leq 19.5^\circ$ comes approximately to 4 kcal/mol per electron pair ($21 \div 4 - 1.2$ kcal).

(3) Ethylene can be looked upon as a strained two-membered ring with its four bonding electrons ideally 55° off the internuclear line but actually $<55^\circ$. The difference in bond energy between two single C-C bonds and one double bond is 19.4 kcal/mol.¹² If there is no correlation correction for $2\theta = 109.5^\circ$, the L-strain energy comes to 9.7 kcal/mol per electron pair; one could, however, assign up to half the maximum correction, or 2 kcal/mol, which would bring the L-strain energy to 7.7 kcal/mol.

(4) Acetylene has six well-correlated electrons in the C-C bond, each with $\theta \leq 70.5^\circ$. The difference in bond energy between three single bonds and one triple bond is 48.2 kcal/mol.¹² It is not clear whether a correlation correction should be made here; the figure would be 0.7 kcal/mol for an angular separation of 56° . With the correction, the L strain is $48.2 \div 3 - 0.7$, or 15.4 kcal/mol per electron pair and, without it, 16.1 kcal/mol.

(5) Certain molecular vibration modes can yield L-strain data. For the vibration of ethane depicted in 7, the energy required for a 10° distortion is 3.1 kcal/



mol.¹³ This corresponds to a bent bond, as in cyclopropane and cyclobutane, with $\theta = 10^\circ$. The L-strain

(10) This point can be clarified if necessary by referring to the cubical array suggested by W. F. Luder, *J. Chem. Educ.*, **44**, 206 (1967) as a pictorial aid to the visualization of Linnett's structure for the neon configuration.

(11) J. D. Dunitz and V. Schomaker, *J. Chem. Phys.*, **20**, 1703 (1952).

(12) T. L. Cottrell, "The Strength of Chemical Bonds," 2nd Ed., Butterworth & Co. Ltd., London, 1958.

(13) J. W. Linnett, personal communication.

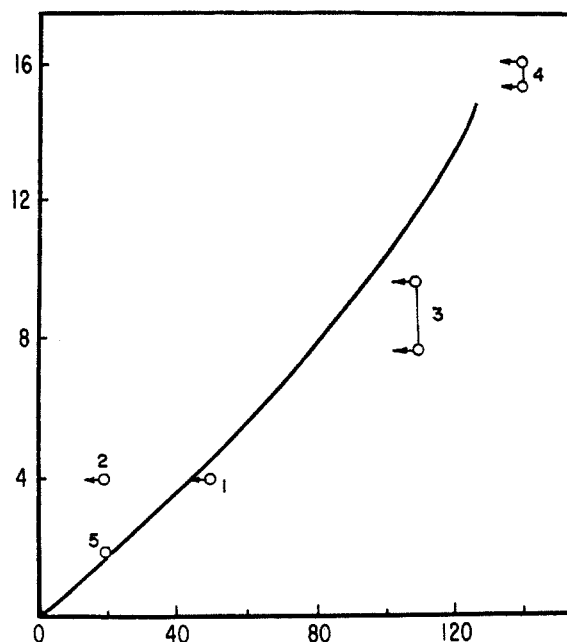
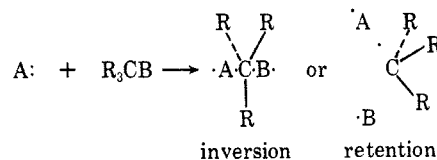


Figure 2.—L-Strain energies vs. angles for C-C bonds. Ordinate in kilocalories per mole; abscissa in degrees. For numbering of points, see text.

energy, then, comes to $3.1 - 1.2 = 1.9$ kcal/mol per electron pair.

These numbers are plotted in Figure 2. The arrows next to some of the points indicate that the actual L-strain angles must be smaller than the calculated ones by some unknown amount. Where the data permitted the adoption of two different L-strain energies, both are depicted. The line was sketched visually as the best smooth approximation to all the points except that for cyclobutane whose angle strain is unaccountably high. Although the curve is a crude one, it is good enough to use for the estimation of approximate L-strain energies.

Among the uses to which Figure 2 may be put is the estimation of the difference in L strain in the transition states of the S_N2 reaction for inversion and retention, according to the mechanism proposed in ref 6. For



inversion, the three C-R bonds suffer from 40° of L strain each and, for retention, 70.5° . The difference in L strain per C-R bond is $6.8 - 3.6$ or *ca.* 3.2 kcal/mol, so that inversion should be preferred to retention by *ca.* 10 kcal/mol. If $R = H$, this becomes *ca.* 11 kcal/mol after correcting for the difference between C-C and C-H bond energies.¹² If $R = CH_3$, secondary L strain within the CH_3 groups will raise the base figure still further, to an estimated 14 kcal/mol, based on the data¹⁴ for the successive replacement of H by CH_3 on carbon atoms undergoing S_N2 displacement.

For SE_2 reactions of the type $A^+ + CH_3B \rightarrow ACH_3 + B^+$, and for radical displacements $A\cdot + CH_3B \rightarrow ACH_3$

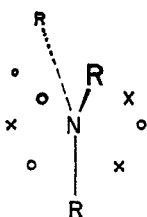
(14) D. Cook and A. J. Parker, *J. Chem. Soc., B* 142 (1968).

+ B, inversion should also be preferred.¹⁵ The effect of charge type on the energies of these transition states, which is expected to be significant, has been neglected in this discussion but will be taken up at a later time.

Typical Organic Structures. Tetravalent Saturated Carbon.—Methane (1) is depicted above. The two spin sets, both tetrahedra, coincide despite the creation of four close pairs because considerations of bond strength outweigh those of electron correlation.

Trivalent Saturated Nitrogen.—The two spin sets are anchored together at three points, leaving the fourth electrons a rather close pair also. Thus, amines are pyramidal in shape, equivalent to sp^3 hybridization.

The easy inversion of amines occurs through the transition state 8. The three bonds suffer from L



strain (2θ) of 40° each and the lone pair is now well correlated. The estimated activation energy from L strain considerations alone comes to approximately 7 kcal/mol.¹⁶ The experimental value is ca. 6 kcal/mol for NH_3 .¹⁷ The activation energy is expected to increase with methylation owing to secondary L strain in the methyl groups.¹⁸

Divalent Saturated Oxygen.—Here the two tetrahedra are fastened together at only two corners. The four nonbonded electrons are still, therefore, formally close paired, but with considerably more freedom to spread than those in amines.¹⁹

Alkyl Halides.—The two spin sets around the halogen atom are now joined at only one point and the nonbonded electrons are well correlated. The noble gas configuration, with its optimal electron correlation, is nevertheless not attainable.

Carbanions.—These are isoelectronic with amines and the same considerations apply.

Carbonium Ions.—The structures should be planar, with R-C-R angles of 120° , since both spin sets are equilateral triangles centered on the nucleus. This agrees with current thinking, based mainly on the slow

(15) There are few examples of S_N2 reactions not involving heavy atoms or small rings. Of particular interest is the formation of *t*-butyl cation from both neopentane and 2,2,3,3-tetramethylbutane in super acids, reported by H. Hogeveen and A. F. Bickel, *Chem. Comm.*, 635 (1967), and by G. A. Olah and R. H. Schlosberg, *J. Amer. Chem. Soc.*, **90**, 2726 (1968). Taking into account both the steric inaccessibility of neopentyl carbon and the fact that free protons cannot exist even in super acids, one is forced to conclude that these S_N2 reactions occur with inversion. Whether this is a general rule remains to be seen.

(16) Calculated from Figure 2, allowing 4 kcal/mol for the lone pair. Since N-H bonds are somewhat stronger and N-C bonds somewhat weaker than C-C bonds,¹² no bond strength correction was made in this case.

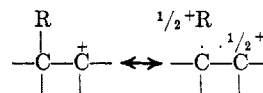
(17) G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., New York, N. Y., 1945; D. M. Dennison and G. E. Uhlenbeck, *Phys. Rev.*, **41**, 313 (1932); C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy," McGraw-Hill, Book Co., Inc., N. Y., 1955.

(18) In this example, and others like it to follow, it should not be inferred that L strain alone is responsible for the activation energy. The intention is simply to show that the energetics of many phenomena are commensurate with those anticipated from L strain and, therefore, that it must be reckoned an important factor in these cases.

(19) The deviations of bond angles from 109.5° in many compounds are ascribed, in large part, to this "spreading" tendency of unshared valence electrons: C. E. Mellish and J. W. Linnett, *Trans. Faraday Soc.*, **50**, 657 (1954).

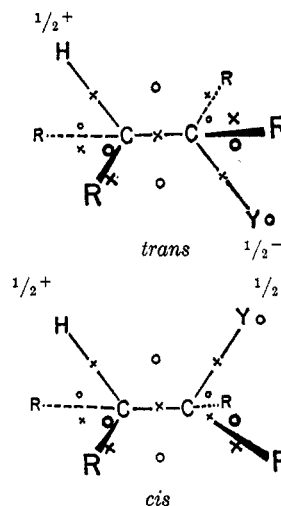
rate of formation of carbonium ions at bridgeheads.^{20,21} The degree of rigidity with which carbonium ions apparently adhere to planarity²¹ is not so easily accounted for, however; distortion of a spin set would be expected to be easier the fewer electrons it contains, because severe Pauli "repulsion" ought to come into play only as the interelectronic angle gets down near 109.5° .

Hyperconjugation.—This is a stabilizing factor in carbonium ions²² which can be depicted in the following way. It is apparent from this picture why C-H



hyperconjugates better than C-C,²³ since not only does hydrogen bear a positive charge more easily than carbon, but also there is a certain amount of L strain associated with a carbon atom that has only seven valence electrons, e.g., when $R = CH_3$ (*vide infra*), but absent when $R = H$.

Another phenomenon can also be rationalized. Shiner and coworkers have shown that the secondary β -deuterium isotope effect on solvolysis is subject to a steric restriction, with the *trans*-coplanar conformation apparently preferred^{24,25}; yet, in the solvolysis of cyclopentyl tosylate, a β -*cis* deuterium has a larger retarding effect ($k_H/k_D = 1.22$) than a *trans* ($k_H/k_D = 1.16$).²⁶ The situation is reminiscent of the observation by dePuy's group that, in cyclopentyl systems, E2 eliminations also exhibit larger *cis/trans* ratios than normal.²⁷ From these and other data, Shiner and Humphrey²⁵ conclude that hyperconjugative assistance to solvolysis is maximized in both *cis*- and *trans*-coplanar arrange-



(20) P. D. Bartlett and L. H. Knox, *J. Amer. Chem. Soc.*, **61**, 3184 (1939).

(21) W. von E. Doering, M. Levitz, A. Sayigh, M. Sprecher, and W. P. Whelan, Jr., *ibid.*, **75**, 1008 (1953).

(22) See, *inter alia*, (a) V. J. Shiner, Jr., W. E. Buddenbaum, B. L. Murr, and G. Lamaty, *ibid.*, **90**, 418 (1968), and earlier papers; (b) H. C. Brown and R. A. Wirkkala, *ibid.*, **88**, 1453 (1966); (c) K. L. Servis, S. Borcic and D. E. Sunko, *Tetrahedron*, **24**, 1247 (1968); (d) T. Yonezawa, H. Nakatsuji and H. Kato, *J. Amer. Chem. Soc.*, **90**, 1239 (1968).

(23) M. Ballester and J. Riera, *Tetrahedron*, **20**, 2217 (1964), and references contained therein.

(24) V. J. Shiner, Jr., B. L. Murr, and G. Heinemann, *J. Amer. Chem. Soc.*, **85**, 2413 (1963).

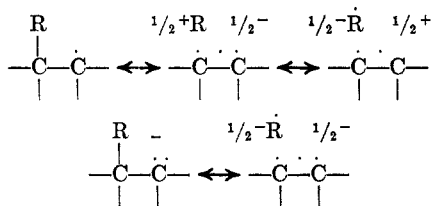
(25) V. J. Shiner, Jr., and J. S. Humphrey, Jr., *ibid.*, **85**, 2416 (1963).

(26) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey, and S. Suzuki, *ibid.*, **80**, 2326 (1958).

(27) C. H. DePuy, G. F. Morris, J. S. Smith, and R. J. Smat, *ibid.*, **87**, 2421 (1965).

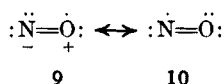
ments, and absent at 90°. In conformity with these ideas, our transition state for hyperconjugation-assisted solvolysis, like that for the E2 reaction,⁶ has two preferred planar conformations, of which the *trans* is slightly better with respect to electron correlation.

Hyperconjugation of radicals and anions is also ex-

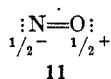


pected. There is evidence for the former,^{28a} but the latter goes counter to the general belief that anion stability decreases in the order primary, secondary, tertiary. We suggest that this order, if correct, is a solution phase phenomenon, and predict that in the gas phase it will be reversed.^{28b}

Organic Radicals.—Molecules such as CH₃· and *t*-BuO· are generally treated as *unsaturated* structures containing at least one atom with an incomplete valence shell. The low activation energies for dimerization of methyl and *t*-butoxy radicals²⁹ fit this description. However, by abandoning the fixed idea that electrons must be paired whenever possible, Linnett has shown that many radicals can be written with *saturated* structures, in particular those whose formally unsaturated atom is directly bonded to one possessing unshared electrons. Although these molecules still have an odd electron, they contain no atoms with incomplete valence shells. A good example is nitric oxide, NO.³⁰ Two canonical Lewis forms can be written, 9 and 10, each



with the odd electron on an unsaturated atom. Since dimerization, for example, to O=N—N=O, would create a new bond without cost to the existing ones, the failure of NO to dimerize is difficult to understand. In the Linnett structure 11, on the other hand, the mole-



cule as a whole is saturated because both atoms have filled valence shells; dimerization would consequently lead to no increase in the number of bonding electrons, but would lead to increased interelectronic repulsion owing to the creation of close pairs. Many other examples of this type have also been discussed.^{1,2}

Formally unsaturated organic radicals are stabilized by adjacent sulfur³¹ or chlorine.³² The resonance forms

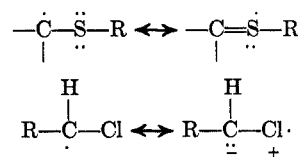
(28) (a) B. Mile, *Angew. Chem. Intern. Ed. Engl.*, **7**, 507 (1968). (b) Anionic hyperconjugation has been discussed by R. A. Mulliken, *Tetrahedron* **5**, 253 (1959), and draws possible experimental support from the report by W. M. Schubert, R. B. Murphy, and J. Robins, *ibid.*, **17**, 199 (1962), that *p*-alkyl groups lower the energies of the uv transitions of both anilines and nitrobenzenes.

(29) R. Gomer and G. B. Kistiakowsky, *J. Chem. Phys.*, **19**, 85 (1951); D. J. Carlsson, J. A. Howard and K. U. Ingold, *J. Amer. Chem. Soc.*, **88**, 4725 (1966).

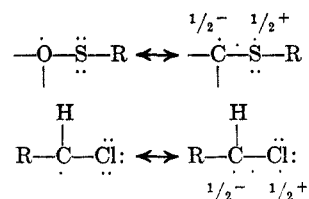
(30) Reference 2, pp 43, 58.

(31) C. C. Price and S. Oae, "Sulfur Bonding," Ronald Press, New York, N. Y., 1962, p 27.

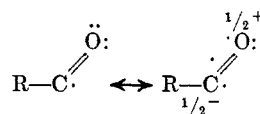
depicted below were proposed to account for this stabilization. We now suggest that these are actually ex-



amples of saturated radicals, shown below. The stabili-



zation of acyl radicals³² can be explained similarly. By this reasoning, one would expect that any atom bearing unshared electrons could stabilize an adjacent radical in



the same way. In the case of oxygen, there is ample evidence for such stabilization.³³ Many studies have shown that the α C—H bond in ethers is especially activated to attack by oxygen,^{33–35} nitrogen,³⁶ and carbon³⁷ radicals. The α C—H bond in amines is similarly activated.^{38,39} While it could be argued that these are all kinetic effects arising from the attacking radicals' being of the acceptor type, the reduced dissociation energies of C—H bonds next to oxygen,⁴⁰ and the large stabilization energies of XCH₂· radicals compared with CH₃·, when X bears unshared valence electrons,⁴¹ support our interpretation. For example, these comparisons among bond dissociation energies (in kilocalories/mole) may be made⁴⁰: H—CH₂OH, 92; and H—CH₃, 104; H—CH(CH₃)OH, 90; and H—Et, 98. For radicals XCH₂·, the following stabilization energies, in kilocalories/mole relative to CH₃·, are reported⁴¹: X = F, 13; Cl, 14; Br, 19; OCH₃, 20. In comparison, the value for X = CN is only 11.

The transfer of formal charge implied in the preceding description of radical stabilization manifests itself in the increased acidity of OH bonds next to radical centers. In general, R₂COH is much more acidic than R₂CHOH.⁴²

(32) C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc., New York, N. Y., 1957, p 51; J. S. Shirk and G. C. Pimentel, *J. Amer. Chem. Soc.*, **90**, 3349 (1968).

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(35) C. Walling and M. J. Mintz, *J. Amer. Chem. Soc.*, **89**, 1515 (1967).

(36) R. Partch, *Tetrahedron Lett.*, 1361 (1966).

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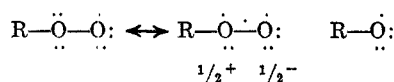
(39) M. M. Nazarova and L. K. Freidlin, *Bull. Acad. Sci. USSR, Div. Chem. Sci., Engl. Transl.*, 1754 (1966).

(40) J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).

(41) R. H. Martin, F. W. Lampe, and R. W. Taft, *J. Amer. Chem. Soc.*, **88**, 1353 (1966).

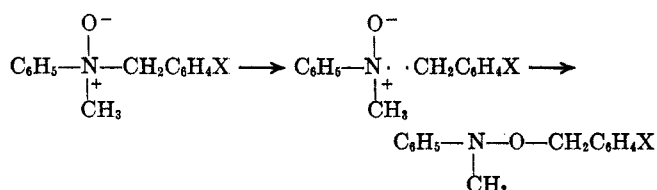
(42) G. Porter and F. Wilkinson, *Trans. Faraday Soc.*, **57**, 1686 (1961); R. Stewart, "Oxidation Mechanisms," W. A. Benjamin, Inc., New York, N. Y., 1964, p 66.

In like manner, peroxy radicals can be pictured as saturated, in contrast with alkoxy radicals, which are unsaturated.² It is thus understandable why peroxy

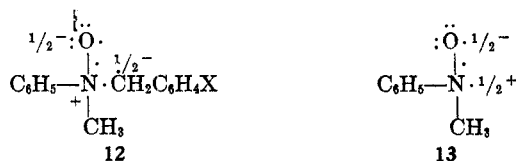


radicals are much less reactive than alkoxy toward dimerization⁴³ and hydrogen abstraction.⁴⁴

A number of 1,2 rearrangements, formerly thought to be heterolytic in nature, are now recognized as proceeding *via* radical cleavage-recombination. It is difficult to rationalize these homolyses on conventional grounds. For example, the following reaction⁴⁵ proceeds readily at 30–45° which, as the authors point out, is a surprisingly low temperature for homolysis of a C–N bond.

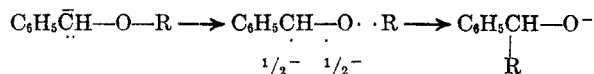


Electron-withdrawing substituents in the benzyl ring increase the reaction rate. These facts can be accommodated with the three-electron bonded structures 12 and 13 for the transition state and nitroxyl intermediate, respectively. In a parallel investigation, another



example of the same type has also been shown to have the same mechanism.⁴⁶

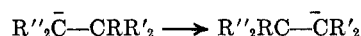
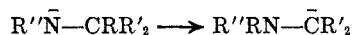
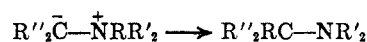
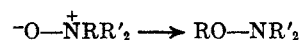
Radicals may be stabilized not only by hetero atoms, but also by carbon if it possesses unshared electrons. Thus, removal of a proton from carbon facilitates homolysis at neighboring oxygen, as in the Wittig rearrangement.⁴⁷



A similar mechanism has also been proposed by Schöllkopf, *et al.*,⁴⁸ for the related Stevens rearrangement.⁴⁸

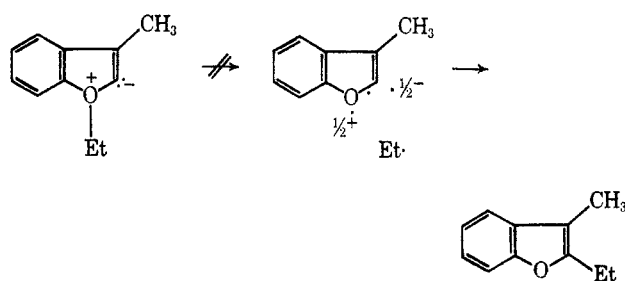
It can be predicted, then, that an important factor in the ease with which this sort of rearrangement will take place is the increase in binding energy of the AB bond which accompanies the change $\overset{\cdot}{\text{A}}-\text{B}-\text{C} \rightarrow \overset{\cdot}{\text{A}}-\overset{\cdot}{\text{B}} + \overset{\cdot}{\text{C}}$. For each AB combination, this increase can be estimated by interpolating on the smooth plot of bond energy *vs.* multiplicity for two-, four-, and six-electron bonds. After minor corrections for differences in elec-

tron correlation and L strain have been made, it should be possible to calculate the activation energy differences within series such as the following. Within each series,



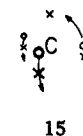
groups R and R' must be chosen so that R· is a good radical and the reactions are thermodynamically favorable.

It is significant that $\text{R}''\bar{\text{N}}-\text{NRR}'_2 \rightarrow \text{R}''\text{RN}-\text{NR}'_2$ does not occur readily,⁴⁹ since the difference between the energies of N–N and N–N bonds is particularly small, only 27 kcal/mol, *vs.* C–C, 33, C–N, 34, or C–O, 45. Steric inhibition of assisted homolysis is also possible, as illustrated below.⁵⁰ Although the zwitterionic interme-



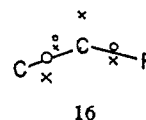
mediate seems exceptionally well suited for Wittig rearrangement, none of the normal Wittig product was observed.⁵¹ This is expected because the intermediate radical is highly strained; the $\overset{\cdot}{\text{O}}-\overset{\cdot}{\text{C}}=\text{C}$ angle must be *ca.* 108° but wants to be *ca.* 152°.

The geometry of trivalent carbon with a septet of electrons can be predicted in simple terms from the Linnett structure 14. Since one spin set is a triangle and the other a tetrahedron, both centered on the nucleus, all three bonds are L strained by *ca.* 19.5°. The



molecule will be a flattened pyramid, not quite planar, but easily inverted by rotating one spin set as in 15. This picture agrees with current opinion.⁵²

Vinyl radicals are described by a similar picture, 16.



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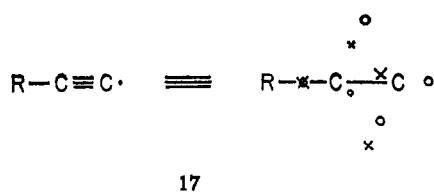
(50) H. H. Wasserman and J. M. Fernandez, *J. Amer. Chem. Soc.*, **90**, 5322 (1968).

(51) H. H. Wasserman, personal communication.

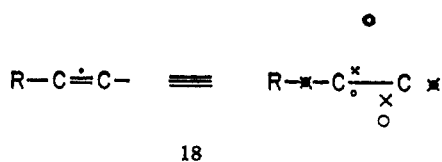
(52) W. A. Pryor, *Chem. Eng. News*, **46** [3], 74 (1968).

They should be slightly bent, but easily inverted. This geometry is known to be correct.⁵³ The estimated C-C-R angle is 152°, close to the experimental value.^{28a}

Acetylenic radicals are unusual in that the simple structure 17 is a poor one according to the Linnett



theory, because the triangular spin set on the right-hand carbon atom is centered far off the nucleus. While this is not forbidden for a trio, it must increase the energy of the radical considerably. An alternative formulation is 18, in which the trio is now centered prop-



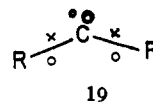
erly, but the carbon-carbon bond has lost one bonding electron. This too must increase the energy; and, in fact, acetylenic radicals are destabilized relative to their alkyl and vinyl counterparts, as shown by the data in Table I.^{40,54}

Carbenes.—For singlet carbenes, the idealized representation is that of two coincident triangular spin sets; the R-C-R angle is 120°. Allowing for the tendency of the unshared electrons to “spread,”¹⁹ one expects a somewhat smaller angle. The experimental value is *ca.* 103°.⁵⁵ Triplet carbenes, on the other hand, have one quartet and one duo. If these are

TABLE I

Bond	D	Ref
H—CH ₃	104	40
H—Et	98	40
H—CHCH ₂	104	40
H—CCH	~125	54
H—CN	129	40
CH ₃ —CH ₃	88	40
Et—Et	87	40
CH ₂ CH—CHCH ₂	100	54
CHC—CCH	150	54
CN—CN	145	40
CH ₃ —Et	85	40
CH ₃ —CCH	117	54
CH ₃ —CN	122	54
Et—CN	128	54

arranged to minimize L strain in the two C—R bonds, as in 19, an R-C-R angle of about 145° is predicted with undistorted spin sets; slightly less when the greater flexibility of a duo, compared with a quartet, is taken into account. This rather peculiar angle is not far from the latest experimental figure of about 150°.⁵⁶



This brief survey of organic structural types demonstrates the power of the Linnett theory to correlate a large body of diverse facts by means of a relatively small number of very simple concepts. In future papers of the series, the ideas presented here will be applied in depth to problems in organic reaction mechanisms.

Acknowledgment.—The advice and encouragement of Professor Linnett have been of great assistance in this work.

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