JOURNAL
OF THE AMERICAN CHEMICAL SOCIETY

VOLUME 101, NUMBER 4 FEBRUARY 14, 1979

Relationship between Olefinic π Complexes and Three-Membered Rings[1]

Michael J. S. Dewar* and George P. Ford

Contribution from the Department of Chemistry, The University of Texas, Austin, Texas 78712.

Received August 13, 1978

Abstract: Compounds with three-membered rings can be formulated either as such or as π complexes with back-coordination. Dewar first pointed out that olefin-transition metal complexes are best represented by the latter structure, a suggestion later confirmed by Chatt and Duncanson in the case of Zeise's salt. According to the π-complex theory, compounds of this type can show a continuous range of structures from the π-complex extreme at one end to a "pure" classical ring at the other, so a distinction can be drawn only on the basis of some property that changes along the range. Here we report detailed MNDO calculations for a number of species of this type which confirm the postulated continuous transition from π complex to classical ring and which show that the corresponding structural variations can be used to establish a fairly definite order of "π-complex character". It was originally suggested that the direction of ring opening in unsymmetrically substituted compounds with three-membered rings, brought about by nucleophiles, could be used to distinguish between species best regarded as π complexes and those best regarded as classical microcycles. A critical survey of the literature suggests that this criterion is generally consistent with the MNDO scale of π-complex character.

Introduction

The idea that unsaturated compounds might be able to use their π electrons to form dative bonds was first suggested by one of us[2] in 1945 to explain the benzidine-type rearrangements of 1,2-diarylhydrazines and it was later extended[2-4] to a number of other reactions of organic molecules. In particular, it was pointed out that olefins should be able to use their filled π MOs to form dative bonds to acceptors, analogous to the corresponding dative bonds formed by amines via the filled AOs of the nitrogen atoms in them. Electrophilic addition and rearrangements of the Wagner–Meerwein type were interpreted in terms of intermediate π complexes of this kind, the olefin being datively bound to the electrophile (e.g., **1**) or an alkyl cation (.g., **2**).

In 1947, Walsh[5] pointed out that similar π-complex structures, **3**, **4**, and **5**, could be written for cyclopropane, ethylene oxide, and the well-known adducts of olefins with silver salts, the acceptor being a neutral atom (O) or group (CH_2), or a silver cation (Ag^+). This suggestion was, however, strongly criticized by Robinson,[6] leading Walsh to withdraw it in favor of the MO description of cyclopropane now associated with his name ("Walsh orbitals"). The trouble with the π-complex representation is that none of these species shows the properties to be expected for the structures implied by **3**–**5**. Thus the chemistry of **3** and **4** corresponds well to that expected for strained three-membered rings (i.e., **6**, **7**) while **5** shows none of the reactivity to nucleophiles characteristic of the π-complex intermediates in the electrophilic addition to olefins (e.g., **1**). Similar problems occur in the case of other metal-olefin complexes, e.g., Zeise's salt, which contains an ion that could be represented as **8**.

Obviously all these species *can* be represented as π complexes. Why then do they fail to behave as such? This problem was solved by Dewar in 1951.[8] He pointed out that in these cases the acceptor (apical) group in the π complex has filled p or d AOs that can be used to form a reverse dative bond in which the empty antibonding π MO of the olefin (basal group) acts as the acceptor (Figure 1b). The olefin and acceptor are then doubly linked, by two opposed dative bonds. Since each of these transfers charge in opposite directions, the result is a great increase in overall bonding between the basal and apical groups in the π complex, combined with a decrease in overall charge transfer (cf. Figure 1).

This representation of transition metal-olefin π complexes has become generally accepted, being commonly referred to as the Dewar-Chatt-Duncanson theory. In the interests of historical accuracy, it should be pointed out that the theory was not due in any way or any part to Chatt or Duncanson, whose sole contibution was to provide experimental evidence in support of it 2 years later. Indeed, at about the same time that the original paper[8] was submitted, Chatt submitted one for publication (published in 1951[9]) in which he proposed a different and incorrect structure[10] for metal-olefin complexes. Later that year, having become aware of our suggestion, he referred[11] to it, with full acknowledgment, as more likely than his own. It should also be noted that Chatt and Duncanson did not even "adapt" the π-complex representation to the specific system considered by them since the original formulation explicitly referred to olefin complexes of transition metals in general. Indeed, the orbital diagram given by Chatt and Duncanson[12] is identical with the prototype,[8] apart from the shapes of the stylized curves used to represent orbitals and the addition of specific quantum numbers. Since this application represents

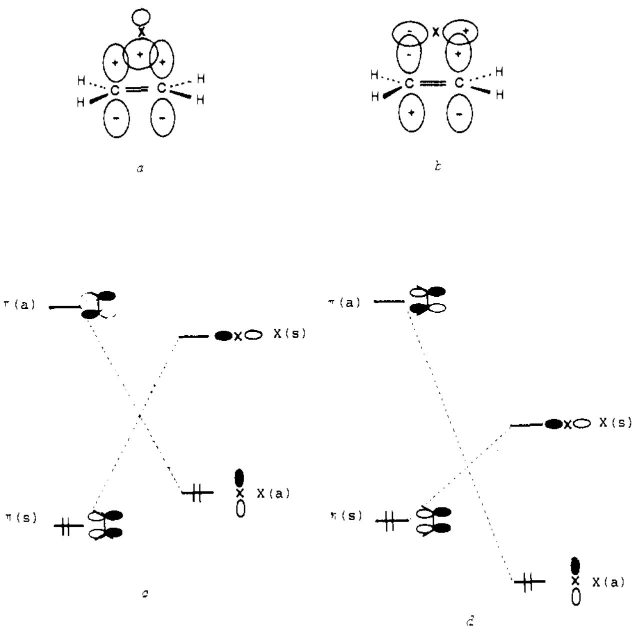


Figure 1. (a) Interaction between the filled olefinic π orbital and the vacant orbital of X. (b) Interaction between the vacant olefinic π* orbital and the filled orbital of X. (c) Orbital interactions of a weak π complex. Electron transfer π(s) → X(s) is approximately equal to X(a) → π(a). Systems of this type resemble classical three-membered rings. (d) Orbital interactions of a strong π complex. Electron transfer π(s) → X(s) greatly outweighs that in the reverse direction: X(a) → π(a).

only a special case of a more general theory, it would seem more appropriate to refer to it as the "π-complex theory of metal-olefin complexes" rather than to use any specific designation. However, if the latter is preferred, it seems inappropriate to include the names of Chatt and Duncanson in it.

In olefin π complexes where back-coordination is possible, the relative importance of forward and backward coordination must vary with the electronegativity of the apical group.[8] If the latter is extremely electronegative, back-coordination will be negligible and the resulting structure will behave like a simple π complex (cf. **2**). If, however, it is only weakly electronegative, back-coordination will become important and the basal and apical groups will then be linked by what is effectively a double bond. Dewar[8] noted that a π complex of the latter type is equivalent to a classical representation in terms of a three-membered ring, formed by three bent ("banana") bonds, and that there should consequently be a continuous transition, with changing electronegativity of the apical group, from species best represented as π complexes to ones best represented as classical microcycles. Those with "classical rings" should have CC bonds that are essentially single, whereas the π complexes should have ones that are intermediate in character between single and double bonds. The available data seem to suggest that the metal-olefin complexes do indeed follow this pattern. Those with weakly electronegative atoms (e.g., Pt(0), Ir(0), Fe(0), Ni(0)) have longer CC bonds, corresponding to cyclic structures, whereas complexes of more electronegative metals (e.g., Pt(II), Rh(I), Mn(I)) have shorter CC bonds. The former class also tend to exhibit lower CC stretching frequencies, although strong coupling with the CH_2 scissoring vibration makes this a less useful criterion of π-complex character than was previously thought.[13] Some examples are given in Table I.[14]

It should be noted that three-membered rings should also differ from the π complex in the hybridization of the basal carbon atoms,[15] a difference which should provide a potential distinction between the two extremes.

Table I. Representative CC Bond Lengths and Stretching Frequencies in Some Transition Metal Ethylene Complexes[a]

metal	oxidation state	ν(CC)	*d*(CC)	complex
Fe	0	1510	1.46	$Fe(CO)_4C_2H_4$
Ni	0	1490	1.431	$Ni(PCy_3)_3C_2H_4$; $Ni(PPh_3)_3C_2H_4$
Pd	0	1488		$Pd(PPh_3)_3C_2H_4$
Pt	0		1.43	$Pt(PPh_3)_3C_2H_4$
Ir	0		1.45[b]	$Ir(PPh_3)(PPh_2C_6H_4)C_2H_4$
Mn	1	1541	1.376	$[Mn(CO)_5C_2H_4]^+$
Cu	1	1534		$CuClC_2H_4$
Tc	1	1559		$[Tc(CO)_4(C_2H_4)_2]^+$
Rh	1	1520	1.376	$[RhCl(C_2H_4)_2]_2$
Ag	1	1584		$[Ag(C_2H_4)_2]^+$
Re	1	1582		$[Re(CO)_5C_2H_4]^+$
Fe	2	1527		$[C_5H_5Fe(CO)_2C_2H_4]^+$
Ru	2	1523		$[C_5H_5Ru(CO)_2C_2H_4]^+$
Pd	2	1527		$[PdCl_2(C_2H_4)_2]_2$
Os	2	1546		$[C_5H_5Os(CO)_2C_2H_4]^+$
Pt	2	1526	1.354	$[PtCl_3C_2H_4]^-$

[a] Data from ref 14a. [b] G. Perego, G. del Piero, M. Casari, M. G. Clerici, and E. Perrotti, *J. Organomet. Chem.*, **54**, C51 (1973).

While this qualitative picture of the relationship between π complexes and three-membered rings is satisfactory so far as it goes, there are important details that could be filled in only by a more quantitative treatment. In particular, one would like to know whether the distinction is clear cut, like that between covalent and ionic bonds, or sets in gradually over a range of electronegativity of the apical group.

No reliable procedure is as yet available for the quantitative study of transition metal compounds. On the other hand, work in these laboratories has led to the development of a semiempirical SCF MO method, MNDO,[16] which has proved to be remarkably successful in predicting a wide range of properties of organic molecules. We therefore decided to use it to study the structures of a variety of ethylene π complexes in which back-coordination involves a filled p AO of the apical group in the hope of throwing light on the relationship between π complexes and three-membered rings. Here we report our results.

Results and Discussion

A. Effect of Varying the Electronegativity of the Apical Group. Our first concern was to study the effect of varying the electronegativity of the apical atom in a π complex. For this we used a simple if somewhat artificial model, i.e., varying the MNDO parameters corresponding to the electronegativity of oxygen in calculations for ethylene oxide (**7**). We chose **7** as the basis for this study because, while **7** itself is best described in terms of a classical three-membered ring, its conjugate acid **9** is probably better formulated as a π complex (see ref 8 and below). Oxygen is therefore expected to play a pivotal role on the π complex vs. three-membered ring scale.

Since the various parameters in the MNDO method are highly interrelated, it is not immediately obvious how changes in the electronegativity can best be represented in a quantitative fashion. However, two of the parameters can reasonably be singled out as bearing a specific relationship to the usual notions of electronegativity, i.e., the one-center core-electron attraction integrals, U_s and U_p, and the orbital exponent, ζ. The former include the potential energy due to attractions between the electrons of a given atom and its nucleus, more electronegative atoms being characterized by more negative values of these quantities. The orbital exponent, ζ, determines the size of the orbital and therefore its ability to overlap with others. The more electronegative elements are characterized by larger values of ζ and thus more compact orbitals.

The effects of variations in these parameters on the CC bond length, CO bond length, the angle θ, and the electronic charge on the oxygen atom are shown in Table II. Here θ is the angle between the CH_2 plane and the CC bond (cf. **10**) and is a measure of the hybridization of the carbon atoms. In the iso-

Table II. Calculated (MNDO) Structural Variations in Ethylene Oxide with Simulated Electronegativity Changes of the Oxygen Atom

$\Delta U_s, \Delta U_p$	d(CC)	θ^a	d(CX)	q(O)^b
10.0	1.533	148.73	1.378	1.026
5.0	1.522	153.65	1.400	0.366
−5.0	1.510	163.75	1.442	−0.854
−10.0	1.514	166.80	1.476	−1.283
−20.0	1.528	169.88	1.564	−1.740
−30.0	1.541	171.04	1.647	−1.898
−50.0	1.551	171.98	1.745	−1.973
$\Delta\zeta$	d(CC)	θ	d(CX)	q(O)
−0.95	1.696	141.92	1.354	0.188
−0.70	1.621	147.14	1.353	0.045
−0.45	1.570	152.05	1.364	−0.084
−0.20	1.534	156.31	1.388	−0.200
0.05	1.508	159.86	1.427	−0.301
0.30	1.485	162.84	1.484	−0.387
0.55	1.459	165.75	1.577	−0.451

[a] For the definition of θ see **10**. [b] Net charge at the oxygen atom.

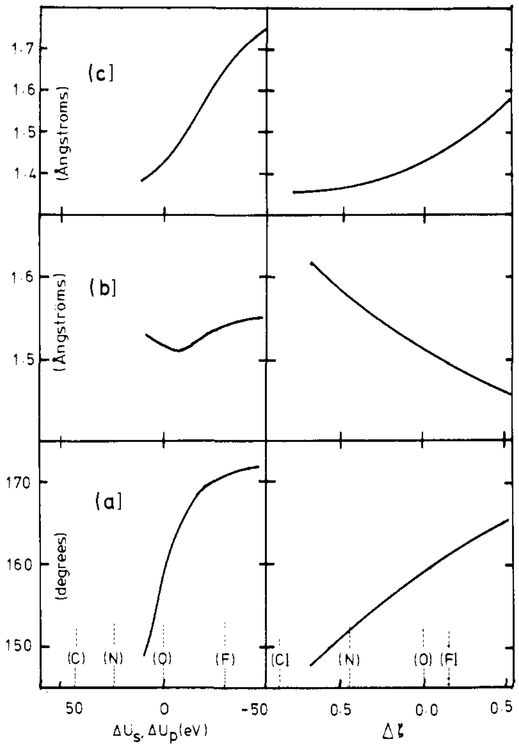


Figure 2. Effects of varying the electronegativity of the oxygen atom in oxirane on (a) the dihegral angle θ, (b) the CC bond length, and (c) the CO bond length.

lated olefin $\theta = 180°$ whereas in cyclopropane $\theta = 150°$. Intermediate values are expected[15] for molecules with π-complex character in which the apical group is more electronegative than carbon. These data are presented graphically in Figure 2. In each of the plots electronegativity increases from left to right. For convenience, the standard values of the parameters for the elements C, N, O, and F are recorded on the abscissa.

These results are in full accord with the conclusions from simple MO arguments[8,15] detailed above. Specifically, decreasing U_s and U_p, or increasing ζ, leads to (a) an increase in the CO bond distance; (b) a decrease in the CC bond distance; (c) an increase in the sp^2 character of the methylene groups; (d) an increase in the electron density associated with the apical (oxygen) atom, not shown in Figure 2. These changes appear to be continuous, there being no sudden transition from a three-membered ring to a π complex. Interestingly, the CC bond distance does not decrease smoothly with more negative values of U_s and U_p, although it does change in the expected direction with increasing values of ζ. Any shortening of the CC bond in molecules with π-complex character is therefore probably a consequence of reduced overlap between the apical group and the ethylene orbitals rather than to tighter binding of the electrons to the apical group.

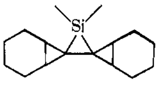
B. The π-Complex Order. In order to extend this study to a number of "real" molecules, the geometries of the isoelectronic series **11** were calculated with appropriate symmetry constraints. For convenience we use the three-membered ring notation, although some members of this series would be more appropriately described as π complexes. The calculations were

Table III. Comparison of Calculated and Experimental Data for the Neutral Compounds $\overline{CH_2CH_2X}^{a-c}$

X	ΔH_f	d(CC)	θ^d	d(CX)
CH_2	11.2 (12.7)	1.525 (1.510)	150.00 (150.00)	1.525 (1.510)
NH	25.1 (30.2)	1.516 (1.481)	154.95 (154)	1.479 (1.475)
O	−15.5 (−12.5)	1.513 (1.466)	159.23 (158.0)	1.417 (1.431)
SiH_2	6.4	1.555 (1.520^e)	137.85	1.811 (1.826^e)
PH	0.8	1.511 (1.502)	147.20 (149.5)	1.766 (1.867)
S	13.8 (19.7)	1.502 (1.484)	152.08 (151.81)	1.752 (1.815)

X	μ	q(X)^f	χ(X)^g	t^h	u^i
CH_2	0.00 (0.00)	0.00	2.35	0.00	1.0
NH	1.75 (1.89)	−1.45	3.16	0.15	1.2
O	1.92 (1.88)	−0.28	3.52	0.28	1.4
SiH_2	0.88	0.35	1.64	−0.31	0.72
PH	1.67 (1.12)	0.08	2.11	−0.01	0.91
S	2.24 (1.84)	−0.16	2.25	0.14	1.2

[a] Experimental values in parentheses. [b] Experimental heats of formation from J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York, N.Y., 1970. [c] Experimental structural data and dipole moments from J. Sheridan in "Physical Methods in Heterocyclic Chemistry", Vol. 6, A. R. Katritzky, Ed., Academic Press, New York, N.Y., 1974, p 53. [d] For the definition of θ, see **10**. [e] Data for



R. L. Lambert, C. K. Haas, and D. Seyferth, *J. Am. Chem. Soc.*, **98**, 1779 (1976). [f] Calculated charge on X. [g] Electronegativity; see ref 17. [h] For the definition of t see eq 1 and text. [i] For the definition of u see eq 2 and text.

Table IV. Heats of Formation and Relative Energies of $\overline{\mathrm{CH_2CH_2X}}^+$ and Isomeric Cations

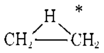
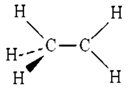
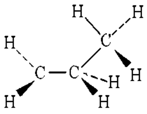
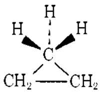
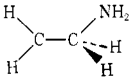
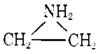
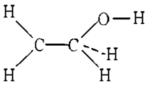
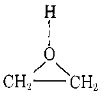
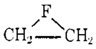
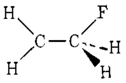
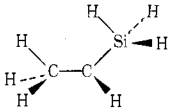
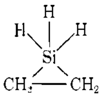
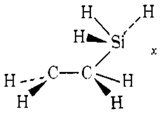
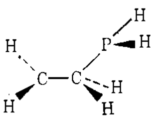
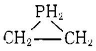
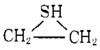
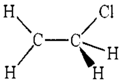
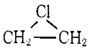
	point group and structure[a]		ΔH_f, kcal mol^{-1}		rel energies				
			exptl	MNDO	exptl	MNDO	STO3G	4-31G	other
$C_2H_5^+$	C_{2v}	 *		234.7[b]		15.0	11.4[c]	7.3[d]	−6.3[e]
	C_s		219[f]	219.7[g]		0.0	0.0	0.0	0.0
$C_3H_7^+$	C_s		208[h]	213.4	16	12.9	20.5[i]	16.9[i]	17.0[j]
	C_s		200[h,k]	229.5	8	28.7	22.8[i]	17.3[i]	13.0[j]
	C_{2v}	CH_3CHCH_3	192[h]	200.8[g]	0.0	0.0	0.0	0.0	0.0
$C_2H_6N^+$	C_s		~216[l]	223	~62	51.0	85.7[n]	72.1[n]	
	C_{2v}		173[o]	191.4	19	19.1	12.3[p]	29.5[p]	
	C_s	$CH_3CH{=}NH_2$	154[o]	172.3	0.0	0.0	0.0	0.0	
$C_2H_5O^+$	C_1		~189[q]	178.0	~46	38.2	57.9[r]	37.9[r]	
	C_s		169[s]	173.0	26	33.2			*t*
	C_s	$CH_3CH{=}OH$	143	139.8	0.0	0.0	0.0	0.0	
$C_2H_4F^+$	C_{2v}			206.0		41.3	16.7[u]	29.7[u]	*v*
	C_s			187.3		22.6	36.4[u]	18.3[u]	
	C_s	CH_3CHF	166[w]	164.7		0.0	0.0	0.0	
$C_2H_7Si^+$	C_s			206.9		23.6			
	C_s	 *		204.1		20.8			
	C_s	 *x*	~239[y]	198.3	~28	15.0			
	C_s	$CH_3CH_2SiH_2$	~211[y]	183.3	0.0	0.0			
$C_2H_6P^+$	C_s			212.3		12.1			
	C_s	$CH_3CH{=}PH_2$		206.6		6.4			
	C_{2v}			200.2		0.0			
C_2H_5S	C_s		~192[z]	211.7	~−5	7.8			*aa*
	C_s	$CH_3CH{=}SH$	197[bb]	203.9	0.0	0.0			
$C_2H_4Cl^+$	C_s			221.8		9.9	18.0[u]	13.7[u]	
	C_{2v}			216.2		4.3	−1.1[u]	4.5[u]	*cc*
	C_s	CH_3CHCl		211.9		0.0	0.0	0.0	

Table IV (*Continued*)

[a] All species are stable minima (diagonalization of the calculated force constant matrix reveals no negative eigenvalues) except those marked with an asterisk, which are transition states (one negative eigenvalue). [b] Unpublished calculations by H. S. Rzepa and W. Thiel, [c] Reference 25c. [d] Reference 25 b. [e] UMP2/6-31G* calculations, unpublished work by J. S. Binkley quoted in ref 25a: a UHF calculation at the 6-31G* level with second-order Møller–Plesset correlation energy correction; cf. C. Møller and M. S. Plesset, *Phys. Rev.*, **46**, 681 (1934). [f] Reference 18b. [g] Reference 16a. [h] Reference 19b. [i] References 26b. [j] UHF/6-31G* calculations from ref 25a. See also ref 26a. [k] It is not certain whether this value applies to the edge- or corner-protonated species. [l] Estimated value (cf. ref 20a) from $\Delta H_f[CH_3CH_2CH_2^+] = 208$,[h] $\Delta H_f[CH_3CH_2CH_3] = -24.9$,[m] and $\Delta H_f(CH_3CH_2NH_2] = -12.9$[m] and assuming an inductive stabilization of 4.0 kcal mol^{-1} due to the amino group.[24] [m] J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York, N.Y., 1970. [n] Calculated from data in ref 24; see also ref 27b. [o] Reference 20c. [p] Cyclic $C_2H_6N^+$ calculated to be 55.4 kcal mol$^-$ 1 more stable than $^+CH_2CH_2NH_2$ by an unspecified ab initio SCF-MO method.[27a] [q] Estimated value from ref 20a. [r] Calculated from data in ref 24. [s] Reference 21b. [t] Cyclic $C_2H_5O^+$ calculated to be 7.2 kcal mol^{-1} more stable than $^+CH_2CH_2OH$ by a double ζ ab initio SCF–MO method[27c] [u] Reference 28b. [v] Cyclic $C_2H_4F^+$ calculated to be 10.3 kcal mol^{-1} less stable than $^+CH_2CH_2F$ by an ab initio method using a double ζ basis set of 38 orbitals obtained by contraction from 88 primitive Gaussian functions. [w] Reference 23d. [x] The C_s structure was found to be a transition state for SiH_3 rotation. We did not attempt to accurately locate the stable minimum. [y] Estimated value from ref 22. [z] Estimated value from ref 23b. [aa] Ab initio calculations with various basis sets of the STO-NG and 4-31G types revealed (like the present calculations) that both rotamers of $^+CH_2CH_2SH$ are unstable with respect to collapse to the cyclic thiiranium ion.[29] [bb] Reference 23c. [cc] Cyclic $C_2H_4Cl^+$ calculated to be 9.4 kcal mol^{-1} more stable than $^+CH_2CH_2Cl$ by a double ζ ab initio SCF–MO method.[30]

carried out using the published[16] MNDO parameters and without the inclusion of d orbitals. Calculated heats of formation, geometries, and other properties of the neutral species are compared with the experimental data, where these are available, in Table III. Several of the open-chain analogues of the cationic species are expected to be comparable in stability with the corresponding cyclic isomers. Since this has an important bearing on the reactions of species potentially showing π-complex character, and since the properties and reactions of these small ions in the gas phase have recently been the subject of considerable experimental[18–23] and theoretical[24–30] interest, we report our results for some of the open-chain analogues together with those for the cyclic species in Table IV.

The criteria of π-complex character investigated in the previous section can be applied here with several minor modifications. Thus, while the angle between the plane of the CH_2 group and the CC bond axis (θ in **10**) was adequate in the artificial series based on ethylene oxide, here it is necessary to allow for variations in this angle due simply to the presence of apical groups with different bonding radii. In the species of this type which exhibits maximum three-membered ring character, i.e., cyclopropane, the planes containing the CH_2 groups bisect the internal ring angles. Deviations from this geometry can be described using eq 1 where the angles θ and ϕ are defined in structure **10**.

$$t = (\phi - \theta')/\phi; \qquad \theta' = 180 - \theta \tag{1}$$

While no rigorous relationship is implied here, t conveniently quantifies the intuition (supported by the MNDO calculations above) that the degree of π-complex character is reflected by the hybridization of the basal carbon atoms. On this basis the apical substituents (X in **11**) can be arranged in a series of decreasing π-complex character (smaller values of t) as shown in Scheme I.

Another measure of π-complex character can be derived from the electronic charge distributions. The simple magnitude of the charge at the apical atom does not in itself provide a useful insight because it is greatly influenced both by the polarity of the CX bond and by the charge carried by the molecule as a whole. A more appropriate index of π-complex character is suggested by an examination of Figure 1. In those species best represented as three-membered rings, the electron donation from the filled olefin π orbital to the apical group is almost balanced by electron donation in the reverse direction (Figure 1c). Conversely, in the case of strong π complexes, the forward donation greatly outweighs the reverse donation (Figure 1d). According to this reasoning, the appropriate measure of π-complex character is not the total electron density associated with the apical group but the *ratio* of electron transfer in the forward and reverse directions.

Many of the species studied here have C_{2v} symmetry, in which case the orbital interactions of Figures 1a and 1b belong to different symmetry classes (a_1 and b_1, respectively). In the present series one s and one p orbital of the apical group X, together with the appropriate components of the XH bonds present, contribute a total of two electrons to the a_1 orbitals of the apical group. Thus the electron density *gained* by the apical group by virtue of its interaction with the ethylene π bond will be $[q(a_1) - 2]$ where $q(a_1)$ is the contribution to the total electron density associated with the atom(s) of the apical group from the molecular orbitals of a_1 symmetry. Similarly, since the unperturbed p orbital of X contains two electrons, the electron density *lost* on interaction with the olefin π* orbital will be $[2 - q(b_1)]$. The required index of π-complex character should therefore be $[q(a_1) - 2]/[2 - q(b_1)]$. A number of species considered here have only C_s symmetry, in which case the orbital(s) of X perpendicular to the CXC plane (containing two electrons in the unperturbed moiety) cannot be distinguished from the orbitals characterizing the forward donation (Figure 1a) on symmetry grounds. Fortunately these orbitals seem to play little part in the π-complex interactions (judging from the calculations for the species having C_{2v} symmetry) so we have classified the orbitals in each system only by their behavior on reflection in the plane perpendicular to the CXC skeleton. The slightly modified ratio describing the expected degree of π-complex character is given by

$$u = (q' - 4)/(2 - q'') \tag{2}$$

where q' and q'' refer to orbitals which are respectively symmetric and antisymmetric with respect to this reflection. Since the apical group (H^+) in the cyclic ion C_2H_5 (**11**, X = H^+) has no electrons for back-donation, $u = \infty$ and the species corresponds to a "pure" π complex. The order of decreasing π-complex character (smaller values of u) defined in this way is given in Scheme II.

Numerical values for t and u are compiled in Tables III and V. Schemes I and II lead to almost identical orderings for the various species. The differences between them relate, moreover, to compounds near the center of each scale where less differentiation is predicted. The order within each scale (cationic

Scheme I

$H^+ > SiH_3^+ > F^+ > CH_3^+ > Cl^+$
$> OH^+ \sim SH^+ \sim O \sim NH_2^+$
$\sim NH \sim PH_2^+ \sim S > CH_2 \sim PH > SiH_2$

Scheme II

$H^+ > SiH_3^+ > CH_3^+ > Cl^+ > F^+$
$> OH^+ > SH^+ > NH_2^+ > PH_2^+$
$> O > S \sim NH > CH_2 > PH > SiH_2$

Table V. Calculated Data for Cationic Species $\overline{CH_2CH_2X}^+$

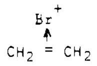
X^+	d(CC)[a]	θ[b]	d(CX)[a]	q(X)[c]	t[d]	u[e]
H[f]	1.419	170.69	1.375	0.11	0.68	∞
CH_3[f]	1.423	163.59	1.771	0.49	0.51	7.1
NH_2	1.517	158.00	1.518	0.34	0.27	2.1
OH	1.511	162.65	1.485	0.18	0.42	2.6
F	1.516	166.00	1.479	−0.03	0.53	3.6
SiH_3[f]	1.391	164.51	2.151	0.50	0.56	14
PH_2	1.519	151.90	1.797	0.39	0.14	2.0
SH	1.487	156.37	1.831	0.43	0.28	2.2
Cl	1.479	161.70	1.929	0.08	0.46	4.4

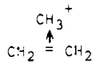
[a] Bond lengths in ångstrøms. [b] For the definition of θ (deg) see **10**. [c] Calculated charge on X. [d] For the definition of t see eq 1 and text. [e] For the definition of u see eq 2 and text. [f] Transition states for interconversion of classical structures.

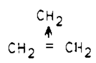
or neutral) also closely follows that of the electronegativities of the apical atoms, values[17] for which are shown in Table III. The position of X = PH and SiH_2 in both series is interesting. Since phosphorus and silicon are less electronegative than carbon, back-donation in these species is stronger than forward donation. Apart from $C_2H_5^+$, which is of course exceptional, our calculations predict a continuous transition from extreme π complex to "pure" three-membered ring, without any break that could be taken as a dividing point between the two extremes. This result is in complete agreement with the picture originally presented[8] on the basis of simple MO theory. Any criterion for deciding whether a given compound is better described as a π complex or as a classical microcycle must be essentially arbitrary and based solely on convenience in interpreting experimental data.

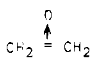
In the case of the metal–olefin complexes, such a distinction can be drawn on the basis of molecular geometry or CC stretching frequencies. In the case of organic compounds of this type, a distinction can also be drawn, this time on the basis of their ring-opening reactions with nucleophiles.

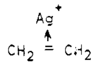
C. Nucleophilic Ring Opening of Unsymmetrically Substituted Three-Membered Rings. An unsymmetrically substituted three-membered heterocycle can in principle be cleaved in two directions. For example, alcoholysis of propane oxide (**12**) may give rise to either a primary (**13**) or a secondary (**14**) alcohol. If the reaction involved a nucleophilic attack of one of the carbon atoms, this would be a typical S_N2 reaction and, in the case of **12**, should take place at the primary carbon atom with inversion of configuration to give **14** rather than **13**. This stereochemistry is indeed observed in the base-catalyzed ring opening of **12**[31] and other[32] unsymmetrically alkyl-substituted epoxides by alcohols (ROH) where ring opening is brought about by a nucleophile corresponding to the alkoxide ion (RO^-). Similar regioselectivity is observed in the acid-catalyzed methanolysis of propeneimine[33] and the ring opening of propene sulfide by the ethyl mercaptide ion[34] (propene sulfide is unreactive toward alcohols in the presence of either acidic or basic catalysts[35]). On the other hand, a number of compounds containing apparently analogous three-membered rings behave in a different manner. This, for example, is true of the acid-catalyzed methanolysis of **12** which leads to approximately equal amounts of the two isomeric hydroxy ethers.[36] Further examples are provided by the nucleophilic ring openings of substituted ethylene chloronium[37] and bromonium[38] ions by methanol which lead to mixtures of *vic*-halo ethers composed largely of the product resulting from attack at the more highly substituted carbon atom; cf. eq 4–6.

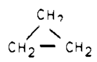

1

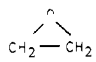

2

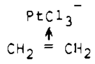

3

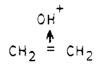

4

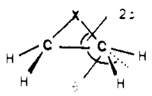

5


6

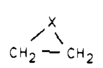

7


8

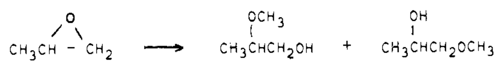

9

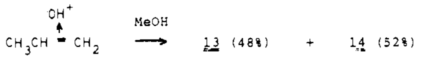


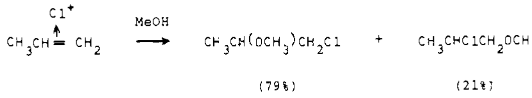
10

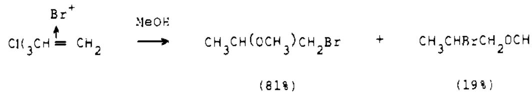

11

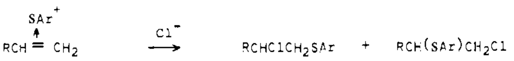
X = H^+, CH_2, CH_3^+, NH, NH_2^+, O, OH^+, F^+
SiH_2, SiH_3^-, PH, PH_2^+, S, SH^+, Cl^+


$$\underset{\mathbf{12}}{CH_3CH\overset{O}{-}CH_2} \longrightarrow \underset{\mathbf{13}}{CH_3\overset{OCH_3}{C}HCH_2OH} + \underset{\mathbf{14}}{CH_3\overset{OH}{C}HCH_2OCH_3}$$


$$CH_3CH\overset{OH^+}{\overset{\uparrow}{=}}CH_2 \xrightarrow{MeOH} \mathbf{13}\ (48\%) + \mathbf{14}\ (52\%) \quad (4)$$


$$CH_3CH\overset{Cl^+}{\overset{\uparrow}{=}}CH_2 \xrightarrow{MeOH} \underset{(79\%)}{CH_3CH(OCH_3)CH_2Cl} + \underset{(21\%)}{CH_3CHClCH_2OCH_3} \quad (5)$$

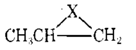
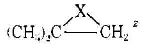

$$CH_3CH\overset{Br^+}{\overset{\uparrow}{=}}CH_2 \xrightarrow{MeOH} \underset{(81\%)}{CH_3CH(OCH_3)CH_2Br} + \underset{(19\%)}{CH_3CHBrCH_2OCH_3} \quad (6)$$


$$RCH\overset{SAr^+}{\overset{\uparrow}{=}}CH_2 \xrightarrow{Cl^-} RCHClCH_2SAr + RCH(SAr)CH_2Cl \quad (7)$$

15a:	R = Me, Ar = 4-Cl-C_6H_4-	**16a** (38%)	**17a** (62%)	ref 39
15b:	R = Et, -	**16b** (23%)	**17b** (77%)	
15c:	R = iPr, -	**16c** (0%)	**17c** (100%)	
15d:	R = Bu, Ar = 2-NO_2-C_6H_4-	**16d** (54%)	**17d** (44%)	ref 46
15e:	- Ar = 2,4-NO_2-C_6H_4-	**16e** (61%)	**17e** (38%)	
15f:	- Ar = 2-NO_2-4-Me-C_6H_4-	**16f** (51%)	**17f** (47%)	
15g:	- Ar = 2-NO_2-4-OMe-C_6H_4-	**16g** (47%)	**17g** (52%)	

The results available in the literature for the reactions of a variety of nucleophiles with several 2-methyl- and 2,2-dimethyl-substituted heterocycles of this type are summarized in Table VI. These results were, as far as was possible, selected from studies in which careful product analyses were carried out and in which the product proportions appeared to be under kinetic control. Several generalizations follow from these results. Thus, under otherwise similar conditions, increasing the

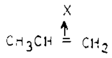
Table VI. Percentage of Normal Product Formed in the Ring Cleavage of 2-Methyl and 2,2-Dimethyl Substituted Three-Membered Heterocyclic Systems with Various Nucleophiles

X	NHR_2	CH_3CO_2H	CH_3OH	H_2O	Cl^-(aq)	Cl^-(anhyd)	AlH_4^-
							
Cl^+			20^a	10^b			
SH^+		55^c				$76^{d,e}$ $62^{f,g}$	
OH^+	$100^{h,i}$	67^c	52^j	30^k	$40^{l,m}$ $61^{o,p}$	$84^{m,n}$ $67^{f,g}$	
NH_2^+	$>85^{q,r}$		$\sim100^s$	66^t		$86^{f,g}$	
O	$100^{h,i}$		100^u	80^k	$91^{o,p}$		100^v
S	$100^{w,x}$						$>99^e$
			 ^{z}				
SH^+						$66^{d,e}$	
OH^+				0.5^k	$25^{l,m}$	$62^{m,n}$	
NH_2^+	$>85^{q,r}$		$\sim50^s$	10^t	86^y		
O				91^k			$>95^v$
S	$100^{h,x}$						

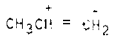
[a] Reference 37. [b] Reference 42a, p 111. [c] N. S. Isaacs and K. Neelakantan, *Can. J. Chem.*, **46**, 1043 (1968). [d] Et_2O solution. [e] Reference 34. [f] Toluene solution. [g] H. Kakiuchi and T. Iijima, *Bull. Chem. Soc. Jpn.*, **46**, 1568 (1973). [h] Reaction with piperidine. [i] T. Colclough, J. I. Cunneen, and C. G. Moore, *Tetrahedron*, **15**, 187 (1961). [j] Reference 36. [k] F. A. Long and J. G. Pritchard, *J. Am. Chem. Soc.*, **78**, 2663 (1956). [l] 1:1 $EtOH/H_2O$ solution. [m] G. Lamaty, R. Maloq, C. Selve, A. Sivade, and J. Wylde, *J. Chem. Soc., Perkin Trans 2*, 1119 (1975). [n] THF solution. [o] 9:1 H_2O/dioxane solution. [p] J. K. Addy and R. E. Parker, *J. Chem. Soc.*, 915 (1963). [q] Reaction with morpholine. [r] Data for 2-ethylaziridine: L. B. Clapp, *J. Am. Chem. Soc.*, **70**, 184 (1948). [s] Reference 33. [t] J. F. Bunnett, R. L. McDonald, and F. P. Olsen, *J. Am. Chem. Soc.*, **96**, 2855 (1974). [u] Reference 31. [v] E. L. Eliel and M. N. Rerick, *J. Am. Chem. Soc.*, **82**, 1362 (1960). [w] Reaction with $NHMe_2$. [x] S. D. Turk, R. P. Louthan, R. L. Cobb, and C. R. Bresson, *J. Org. Chem.*, **29**, 974 (1964). [y] V. B. Schatz and L. B. Clapp, *J. Am. Chem. Soc.*, **77**, 5113 (1955). [z] No data are given for the 2,2-dimethylethylenechloronium ion since there is evidence that the stable form of this ion in weakly nucleophilic solvents is the classical open-chain tertiary carbonium ion: G. A. Olah and J. M. Bollinger, *J. Am. Chem. Soc.*, **90**, 947 (1968).

steric bulk of the nucleophile leads to a greater proportion of the product arising by attack at the less highly substituted carbon atom. In accordance with current usage we describe this as the "normal" product.[32] For example, methanolysis consistently leads to a greater proportion of normal product than does hydrolysis. In one case, the acid-catalyzed alcoholysis of **12**, it has been further demonstrated that increasing the steric bulk of the alcohol leads to progressively larger amounts of the normal product.[36] The effect of varying the 2-alkyl substituent has not been systematically studied for any of the systems in Table VI. However, parallel studies of the electrophilic addition of aryl sulfenyl chlorides to olefins (eq 7), which involves nucleophilic attack on an intermediate which may be formally represented as a substituted thiiranium ion **15**, reveal a similar tendency favoring the normal (i.e., anti-Markownikoff) product (cf. **17a–c**) as the steric bulk of the substituent R is increased.[39] Comparing the data in Table VI for the 2-methyl and 2,2-dimethyl substrates under the same conditions reveals that *less* of the normal product is obtained in all cases, except the alkaline hydrolysis of propene oxide (**12**). In several other cases the normal isomer only was detected in the reactions of both the mono- and disubstituted substrates. For a given nucleophile under comparable conditions, the ratio of normal to abnormal products obtained from a particular substrate depends in a consistent fashion on the nature of the heteroatom present. Accordingly the rows of Table VI have been arranged so that the proportion of normal isomer increases on proceeding down the columns. Since insufficient data were available, the order of the entries corresponding to the nonprotonated oxiranes and thiiranes is arbitrary.

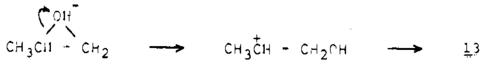
It was suggested at one time that the acid-catalyzed reaction of epoxides (e.g., eq 4) might involve an S_N1 (overall A-1) process, the ring opening to form an intermediate 2-hydroxyethyl cation (eq 8). This would of course take place in the manner indicated to give a secondary rather than a primary carbonium ion. Such a mechanism is, however, excluded by the fact that the ring opening takes place with complete inversion of stereochemistry, regardless of whether the carbon atom involved is primary, secondary, or tertiary.[32,40,41] Typically, stereochemical studies of this type have been restricted to those systems in which inversion of configuration at a secondary carbon atom was demonstrated. This is true for the ring opening of alkyl-substituted ethylene chloronium,[42] ethylene bromonium,[42] aziridinium,[43] and thiiranium[44] ions with a variety of nucelophiles. Whether an S_N1 reaction can be definitely excluded in any of these cases where a classical tertiary carbonium ion is possible is uncertain (see footnote *z*, Table VI). Nevertheless the tendency of the monosubstituted rings to produce abnormal products clearly requires an explanation in terms other than the intervention of an S_N1 type of process.



18



19



(8)

This tendency is very easily understood in terms of the π-complex theory, as Dewar indeed pointed out in his original formulation of it.[8] Consider, for example, a π complex (**18**) formed by addition of an acceptor X to the π bond of propene. It is generally supposed (and theoretical studies have confirmed[45]) that the π molecular orbital of propene is polarized by electron-releasing groups in the manner indicated in **19**. Addition of X should not qualitatively alter this asymmetry, so the resulting π complex should be asymmetrical, X being closer to the unsubstituted carbon atom than to the one bearing the methyl group (Figure 3). Attack by a nucleophile should

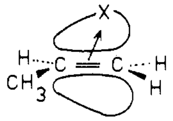


Figure 3. Distortion of the pseudo-π bond in a 2-alkyl substituted π complex should lead to unequal CX distances.

therefore tend to take place at the latter, because it is more positive than the methylene carbon, because less motion of X is needed to form the corresponding adduct, and because the bond between X and the methyl-bearing carbon is longer and so presumably weaker than that to the methylene group. Furthermore, since the propene-like moiety of **18** should be more nearly planar, the methyl group will offer much less steric hindrance to the approach of a nucleophile than it must do in the corresponding S_N2 ring opening of a classical microcycle such as **12**. The mode of ring opening of species of this kind should therefore serve to distinguish between those having substantial π-complex character, which react with nucleophiles to give significant amounts of abnormal product or, in the case of overall electrophilic addition, Markownikoff addition, and those best represented with classical three-membered rings to give normal or anti-Markownikoff products.

Since the degree of π-complex character in such compounds depends, as we have seen, on the electronegativity of the apical atom, we may expect a progressive increase in the electronegativity of the apical atom of an initially "classical" molecule to lead to a species which reacts with progressively more of the character of a π complex. This effect is clearly seen in a study[46] in which a series of 4-substituted 2-nitrobenzenesulfenyl chlorides were added to 4-methylpent-1-ene in acetic acid. When the 4 substituent was hydrogen, the intermediate episulfonium ion (**15d**) opened to give 54% of the Markownikoff product (**16d**), but when the substituent in this position was NO_2, the additional electron-withdrawing effect (which causes the apical atom to be effectively more electronegative) led to a greater (61%) proportion of the Markownikoff product. Conversely, electron-releasing groups in the 4 position led to less of the Markownikoff product (cf. eq 7). Although not explained in such terms by the authors,[46] we believe that these effects are readily understood in terms of π-complex theory. A similar effect is seen on changing the apical atom in **18**. While the paucity of data precludes any really quantitative analysis (Table IV), these results nevertheless seem to lead consistently to a π-complex order similar to that of Scheme II. Indeed, the only clear exception is the inversion of **18** (X = OH^+) and **18** (X = SH^+). While both MO criteria suggest that the π-complex character of the conjugate acid of ethylene oxide (**9**) is greater than that of the corresponding conjugate acid of ethylene sulfide (**11**, X = SH^+), the present criterion suggests the reverse. We will return to this point presently.

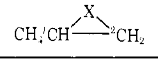
As a check of these qualitative interpretations, we have carried out MNDO calculations for **18** (X = Cl^+, SH^+, OH^+, NH_2^+, S, O, NH). We have also, for comparison, carried out minimum basis set (STO-3G) RH calculations for these species, using the MNDO optimized geometries. The geometries and calculated charge distributions are shown in Table VII. It will be seen that the lengths of the CX bonds in **18** differ in the manner predicted for a π complex, and that the differences (cf. Table VII, column 5) increase in the same order as that expected on the basis of the direction of nucleophilic ring opening (Table VI). The STO-3G calculations also clearly indicate that the charge on the carbon atom bearing the methyl group is positive relative to that on the primary carbon atom. The magnitude of this polarization (cf. Table VII, columns 9 and 12) is moreover greater in those species for which the nucleophilic ring opening reactions indicate substantial π-complex character. Interestingly, both the geometry and charge distributions in **18** (X = OH^+) and **18** (X = SH^+) are in accord with the observation that the latter leads to the greater proportion of products formed by abnormal ring opening with nucleophiles.

It has hitherto been tacitly assumed that the changes in geometry and in formal charges induced by the attached methyl group should increase monotonically with increasing π-complex character. While this undoubtedly is broadly true, the magnitude of the perturbation also depends on other properties of the heteroatom. Thus in the particular case of **18** (X = SH^+), the relatively weak carbon–sulfur bonds are apparently more readily distorted than would have been anticipated simply from the degree of π-complex character associated with the conjugate acid of ethylene sulfide.

The π-complex theory thus seems to provide a very satisfactory interpretation of the nucleophilic ring opening reactions undergone by compounds of this type. While no unique scale of π-complex character can be established for them, the resulting uncertainties are relatively unimportant. In view of this success, it seems surprising that the π-complex theory has been largely ignored by organic chemists, both in this and in other connections, especially in view of the recognized importance of π complexes in organometallic chemistry.

The main reason for this neglect was that the π-complex theory was developed at a time (1945–1951) when few organic chemists were familiar with MO concepts or even willing to explore them. Any MO explanation of the behavior of organic compounds therefore tended to be discounted[47] or translated into supposedly equivalent statements in earlier terminology. Thus the ring-opening reactions considered here have been generally interpreted in terms of a model first suggested by Parker and Isaacs,[32] to explain the formation of abnormal products from unsymmetrical epoxides under acidic conditions. Parker and Isaacs supposed that in these cases breaking of the CO bond has proceeded to a greater extent in the transition state than has formation of the new bond to the nucleophile, leading to a positive charge on the relevant carbon atom of the epoxide and hence to acceleration of the reaction by electron-releasing groups at that position. This could be regarded

Table VII. Calculated Geometries and Charge Distributions[a]



	MNDO								STO-3G[b]		
X	$d(CC)$	$d(C_1X)$	$d(C_2X)$	$\Delta\%$[c]	θ[d]	q_1	q_2	Δq[e]	q_1	q_2	Δq[e]
Cl^+	1.483	2.115	1.855	13	99.5	0.276	0.096	0.180	0.186	−0.036	0.204
SH^+	1.493	1.866	1.804	3.4	105.1	0.034	0.017	0.017	−0.027	−0.147	0.120
OH^+	1.517	1.500	1.477	1.5	100.9	0.122	0.154	−0.032	0.126	0.040	0.086
NH_2^+	1.524	1.528	1.510	1.2	106.3	0.067	0.105	−0.038	0.092	0.007	0.085
S	1.509	1.762	1.746	0.9	110.8	−0.071	−0.013	−0.058	−0.122	−0.207	0.085
O	1.521	1.423	1.413	0.7	104.9	0.007	0.071	−0.064	0.040	−0.038	0.078
NH	1.523	1.484	1.475	0.6	104.6	−0.062	0.001	−0.063	0.015	−0.066	0.081

[a] Bond lengths in ångstroms. [b] STO-3G calculation on the MNDO optimized geometry. [c] Percentage asymmetry: $[d(C_1X) - d(C_2X)]/\frac{1}{2}[d(C_1X) + d(C_2X)] \times 100$. [d] Dihedral angle CCCX (deg). [e] $\Delta q = q_1 - q_2$.

as a reasonable translation of the π-complex theory into the terminology of prequantum organic chemistry. As such, it provides correspondingly less insight.

Acknowledgments. This work was supported by the Air Force Office of Scientific Research (Grant AFOSR 75-2749) and the Robert A. Welch Foundation (Grant F-126). The calculations were carried out using the CDC 6400/6600 computer at The University of Texas Computation Center.

Supplementary Material Available: Table VIII, MNDO optimized geometries (12 pages). Ordering information is given on any current masthead page.

References and Notes

(1) A preliminary account of this work was given at the Zeise Symposium, Meeting of the American Chemical Society, New Orleans, La., March 21, 1977.

(2) M. J. S. Dewar, *Nature* (*London*), **156**, 748 (1945); *J. Chem. Soc.*, 406, 777 (1946); "The Electronic Theory of Organic Chemistry", Clarendon Press, Oxford, 1949.

(3) M. J. S. Dewar and A. P. Marchand, *Annu. Rev. Phys. Chem.*, **16**, 321 (1965).

(4) M. J. S. Dewar, R. C. Haddon, A. Komornicki, and H. S. Rzepa, *J. Am. Chem. Soc.*, **99**, 377 (1977); M. J. S. Dewar and W. Thiel, *ibid.*, **99**, 3898 (1977); N. Bodor, M. J. S. Dewar, and Z. B. Maksic, *ibid.*, **95**, 5245 (1973); M. J. S. Dewar and M. C. Kohn, *ibid.*, **94**, 2704 (1972).

(5) A. D. Walsh, *Nature* (*London*), **159**, 165 (1947).

(6) R. Robinson, *Nature* (*London*), **159**, 400 (1947); **160**, 162 (1947).

(7) A. D. Walsh, *Nature* (*London*), **159**, 712 (1947).

(8) M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, C71 (1951).

(9) J. Chatt, *Research* (*London*), **4**, 180 (1951).

(10) The structure proposed by Chatt[9] required a hydrogen migration to form an ethylidine link; cf. i.

$$[\mathrm{Cl_3Pt = CHCH_3}]^-$$

(11) J. Chatt in "Cationic Polymerization and Related Complexes", P. H. Plesch, Ed., Heffer, Cambridge, 1953.

(12) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

(13) D. C. Andrews, G. Davidson, and D. A. Duce, *J. Organomet. Chem.*, **101**, 113 (1975); G. Davidson, *Organomet. Chem. Rev., Sect. A*, **8**, 303 (1972).

(14) For recent discussion of bonding in transition metal olefin complexes see (a) M. Herberhold, "Metal π-Complexes", Vol. 2, Elsevier, Amsterdam, 1974; (b) N. Rösch, R. P. Messmer, and K. H. Johnson, *J. Am. Chem. Soc.*, **96**, 3855 (1974); (c) F. R. Hartley, *Angew. Chem., Int. Ed. Engl.*, 11, 596 (1972).

(15) M. J. S. Dewar and R. C. Dougherty, "The PMO Theory of Organic Chemistry", Plenum Press, New York, N.Y., 1975, p 300.

(16) (a) M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **99**, 4899, 4907 (1977); (b) M. J. S. Dewar and M. L. McKee, *ibid.*, **99**, 5231 (1977); (c) M. J. S. Dewar and H. S. Rzepa, *ibid.*, **100**, 58 (1978); M. J. S. Dewar and W. Thiel, *Theor. Chim. Acta*, **46**, 89 (1977); (d) M. J. S. Dewar, M. L. McKee, and H. S. Rzepa, *J. Am. Chem. Soc.*, **100**, 3607 (1978).

(17) G. Simons, M. E. Zandler, and E. R. Talaty, *J. Am. Chem. Soc.*, **98**, 7869 (1976).

(18) (a) P. Ausloos, R. E. Rebbart, L. W. Sieck, and T. O. Tiernan, *J. Am. Chem. Soc.*, **94**, 8939 (1972); (b) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, **No. 26** (1969).

(19) (a) G. P. K. Smith, J. Weiner, M. Saunders, and R. J. Cross Jr., *J. Am. Chem. Soc.*, **97**, 3593 (1975); (b) S-L. Chong and J. L. Franklin, *ibid.*, **94**, 6347 (1972); (c) D. J. McAdoo, F. W. McLafferty, and P. F. Bente III, *ibid.*, **94**, 2027 (1972); (d) S. G. Lias, R. E. Rebbert, and P. Ausloos, *ibid.*, **92**, 6430 (1970).

(20) (a) R. D. Bowen, D. H. Williams, and G. Hvistendahl, *J. Am. Chem. Soc.*, **99**, 7509 (1977); (b) K. Levsen and F. W. McLafferty, *ibid.*, **96**, 139 (1974); (c) B. H. Solka and M. E. Russell, *J. Phys. Chem.*, **78**, 1268 (1974).

(21) (a) R. D. Bowen, J. R. Kalman, and D. H. Williams, *J. Am. Chem. Soc.*, **99**, 5481 (1977); (b) R. H. Staley, R. R. Corderman, M. S. Foster, and J. L. Beachamp, *ibid.*, **96**, 1260 (1974).

(22) W. N. Allen and F. W. Lampe, *J. Am. Chem. Soc.*, **99**, 6816 (1977).

(23) (a) B. van der Graaf and F. W. McLafferty, *J. Am. Chem. Soc.*, **99**, 6806 (1977); (b) J. K. Kim, M. C. Findlay, W. G. Henderson, and M. C. Caserio, *ibid.*, **95**, 2184 (1973); (c) B. G. Keyes and A. G. Harrison, *ibid.*, **90**, 5671 (1968); (d) D. P. Ridge, *ibid.*, **97**, 5670 (1975).

(24) Y. Apeloig, P. von R. Schleyer, and J. A. Pople, *J. Am. Chem. Soc.*, **99**, 1291, 5901 (1977).

(25) (a) J. A. Pople, *Int. J. Mass Spectrom. Ion Phys.*, **19**, 89 (1976); (b) P. C. Hariharan, W. A. Lathan, and J. A. Pople, *Chem. Phys. Lett.*, **14**, 385 (1972); (c) W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, **93**, 808 (1971); (d) D. T. Clark and D. M. J. Lilley, *J. Chem. Soc., Chem. Commun.*, 549 (1970); (e) R. Sustman, J. E. Williams, M. J. S. Dewar, L. C. Allen, and P. von R. Schleyer, *J. Am. Chem. Soc.*, **91**, 5350 (1969).

(26) (a) P. C. Hariharan, L. Radom, J. A. Pople, and P. von R. Schleyer, *J. Am. Chem. Soc.*, **96**, 599 (1974); (b) L. Radom, J. A. Pople, V. Buss, and P. von R. Schleyer, *ibid.*, **94**, 311 (1972); **93**, 1813 (1971).

(27) (a) A. C. Hopkinson, M. H. Lien, K. Yates, and I. G. Csizmadia, unpublished work quoted by K. Yates, *Adv. Theor. Chem.*, **2**, 269 (1976); (b) F. Jordan, *J. Phys. Chem.*, **80**, 76 (1976); A. C. Hopkinson, M. H. Lien, I. G. Csizmadia, and K. Yates, *Theor. Chim. Acta*, **47**, 97 (1978).

(28) (a) A. C. Hopkinson, M. H. Lien, K. Yates, and I. G. Csizmadia, *Theor. Chim. Acta*, **38**, 21 (1975); (b) W. J. Hehre and P. C. Hiberty, *J. Am. Chem. Soc.*, **96**, 2665 (1974); (c) D. T. Clark and D. M. J. Lilley, *J. Chem. Soc., Chem. Commun.*, 603 (1970); (d) M. J. S. Dewar and G. P. Ford, *J. Mol. Struct.*, in press.

(29) J. W. Gordon, G. H. Schmid, and I. G. Csizmadia, *J. Chem. Soc., Perkin Trans. 2*, 1722 (1975).

(30) A. C. Hopkinson, M. H. Lien, K. Yates, and I. G. Csizmadia, *Theor. Chim. Acta*, **44**, 389 (1977).

(31) W. Reeve and A. Sadle, *J. Am. Chem. Soc.*, **72**, 1251 (1950).

(32) R. A. Wohl, *Chimia*, **28**, 1 (1974); R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 737 (1959); A. Rosowsky in "Heterocyclic Compounds with Three- and Four-Membered Rings", A. Weissberger, Ed., Interscience, New York, N.Y., 1964.

(33) U. Harder, E. Pfeil, and K.-F. Zenner, *Chem. Ber.*, **97**, 510 (1964).

(34) N. V. Schwartz, *J. Org. Chem.*, **33**, 2895 (1968).

(35) D. D. Reynolds and D. L. Fields in "Heterocyclic Compounds with Three- and Four-Membered Rings", A. Weissberger, Ed., Interscience, New York, N.Y., 1964; H. R. Snyder, J. M. Stewart, and J. B. Ziegler, *J. Am. Chem. Soc.*, **69**, 2675 (1947).

(36) J. Biggs, N. B. Chapman, and V. Wray, *J. Chem. Soc. B*, 66 (1971).

(37) Ch. Duschek, M. Hampel, and W. Pritzkov, *J. Prakt. Chem.*, **317**, 335 (1975).

(38) J.-E. Dubois and J. R. Chretien, *J. Am. Chem. Soc.*, **100**, 3506 (1978).

(39) G. H. Schmid, C. L. Dean, and D. G. Garratt, *Can. J. Chem.*, **54**, 1253 (1976).

(40) Frequently cited as evidence for the intermediacy of free carbonium ions in the hydrolysis of epoxides containing tertiary carbon atoms is the report that the hydrolysis of tetramenthyloxirane leads to substantial rearrangement to pinacolone: Y. Pocker, *Chem. Ind.* (*London*), 332 (1959). This result has recently been shown to be in error: M. D. Carr and C. D. Stevenson, *J. Chem. Soc., Perkin Trans. 2*, 518 (1973).

(41) Excluded from this generalization are those compounds which possess an aryl or acyl group attached directly to the epoxide ring. Here, the possibility of neighboring group participation often leads to a double inversion mechanism with overall retention of configuration; cf. ref 32.

(42) (a) P. B. D. de la Mare, "Electrophilic Halogenation", Cambridge University Press, New York, N.Y., 1976; (b) R. C. Fahey, *Top. Stereochem.*, **3**, 237 (1968).

(43) O. C. Dermer and G. E. Ham, "Ethyleneimine and Other Aziridines", Academic Press, New York, N.Y., 1969, p 208; H. M. Wenghoefer, K. T. Lee, R. M. Srivastava, G. Srimannarayana, and L. B. Clapp, *J. Heterocycl. Chem.*, 7, 1407 (1970).

(44) Data in this series are limited to S-substituted thiiranium ions: W. A. Smit, M. Z. Krimer, and E. A. Vorob'eva, *Tetrahedron Lett.*, 2451 (1975); M. Z. Vorob'eva, M. Z. Krimer, and W. A. Smit, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2832 (1974); *Chem. Abstr.*, **82**, 97896a (1975).

(45) W. J. Hehre and J. A. Pople, *J. Am. Chem. Soc.*, **92**, 2191 (1970); L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *ibid.*, **93**, 5339 (1971).

(46) G. M. Beverly, D. R. Hogg, and J. H. Smith, *Chem. Ind.* (*London*), 1403 (1968); D. R. Hogg, *Q. Rep. Sulfur Chem.*, **2**, 339 (1967).

(47) See, for example, Winstein's comments in the discussion[8] following the presentation[8] of the π-complex theory in its final form.