and 8 also hold in exact theory, in which all the quantities $(\partial E/\partial n_i)_{n_j}$ are equal to the electronegativity.[2,3,14]

Systematic extension of this whole line of analysis to the spin-polarized Xα method[4] is recommended. Applications to molecules are easy to carry through with presently available Xα technology.

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References and Notes

(1) P. Hohenberg and W. Kohn, *Phys. Rev. B*, **136**, 864 (1964).

(2) R. G. Parr, R. A. Donnelly, M. Levy, and W. E. Palke, *J. Chem. Phys.*, **68**, 380 (1978).

(3) R. A. Donnelly and R. G. Parr, *J. Chem. Phys.*, **69**, 4431 (1978).

(4) J. C. Slater, "The Self Consistent Field for Molecules and Solids", McGraw-Hill, New York, 1974. This book contains a complete bibliography of early work on the Xα method, which Slater invented.

(5) For a recent review of the Xα method, see J. W. D. Connolly in "Semiempirical Methods of Electronic Structure Calculation", Part A, Plenum Press, New York, 1977, pp 105–132.

(6) K. Schwartz, *J. Phys. B*, **11**, 1339 (1978).

(7) The atomic Xα program was kindly furnished us by Professor John Sabin of the University of Florida.

(8) (a) K. Schwartz, *Phys. Rev. B*, **5**, 2466 (1972); (b) *Theor. Chim. Acta*, **34**, 225 (1974).

(9) J. C. Slater and J. H. Wood, *Int. J. Quantum Chem., Symp.*, **4**, 3 (1971).

(10) See, however, the remarkable study by G. Simons, M. E. Zandler, and E. R. Talaty, *J. Am. Chem. Soc.*, **98**, 7869 (1976), in which electronegativities of the atoms H through Br were determined from calculations on molecular hydrides by the floating Gaussian orbital method.

(11) H. Hotop and W. C. Lineberger, *J. Phys. Chem. Ref. Data*, **4**, 539 (1975).

(12) W. E. Palke, private communication.

(13) J. Linderberg and Y. Ohrn, "Propagators in Quantum Chemistry," Academic Press, New York, 1973, p 64.

(14) R. A. Donnelly, *J. Chem. Phys.*, **71**, 2874 (1979).

Theoretical Study of Halobenzenium Ions

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Abstract: Electronic structures in the ab initio LCAO–SCF approximation are determined for benzene, fluorobenzene, and chlorobenzene and for benzenium and *o*, *m*, and *p*-fluoro- and chlorobenzenium ions. The reliability of the calculations, done in a double ζ contracted Gaussian basis, is affirmed by the agreement between predicted and observed proton affinities and ionization energies. Evidence is presented which supports the concept that the transition state for most electrophilic substitution reactions of monosubstituted benzenes is a σ complex, similar in structure to the Wheland intermediate and very different in its properties from the reactant molecules. Excellent correlation is found between positional selectivity of electrophilic substitution and the electronic properties of the model halobenzenium ions, whereas no correlation is found between selectivity and the properties of the parent monohalobenzene molecules.

Two types of intermediates are thought to occur in electrophilic aromatic substitution reactions, a π complex[1-3] (benzonium ion or encounter complex) and a σ complex[4] (benzenium ion or Wheland intermediate). The π complex is a loose association of an electrophile with an aromatic ring π-electron system. In the σ complex the electrophile is covalently bound to a ring carbon atom.

Wheland[4] proposed the σ complex as a model of the transition state for electrophilic aromatic substitution. Theoretical calculations,[5,6] low-temperature NMR spectra,[7,8] and the crystal structure of a salt of heptamethylbenzenium[9] have since shown the existence of stable σ complexes.

In this work protodeprotonation of halobenzenes is studied theoretically as a prototype electrophilic aromatic substitution reaction. Emphasis is on position selection in electrophilic substitution reactions of fluorobenzene and chlorobenzene. Ab initio single determinant LCAO–SCF calculations are performed in a flexible "double-ζ" basis on benzene, fluorobenzene, and chlorobenzene, as well as *o*-, *m*-, and *p*-fluorobenzenium and *o*-, *m*-, and *p*-chlorobenzenium ions. Orbital energies and σ, π, total, and frontier orbital[10] charge densities of the reactants and transition state models are assessed as reactivity indexes.[11] Because chemical shifts from nuclear magnetic resonance may give useful information about electron distributions in molecules, correlations between charge densities and proton and ^{13}C chemical shifts are also examined.

This is the first detailed theoretical study of electrophilic substitution in monosubstituted benzenes in which all three of the benzenium ion isomers are included. Previous work has either been limited to one or two isomers[5,6,12] or has reported only proton affinities.[13]

Results and Discussion

Computational. The C, F, and H bases were the [9s,5p/4s] set of Huzinaga[14] contracted (4s,2p/2s) by Dunning.[15] The Cl set was Veillard's[16] [12s,9p] contracted (6s,4p) by Dunning.[17] The hydrogen set and part of the carbon were scaled to optimize the energy in a set of calculations on the ethylene molecule. The hydrogen scale factor was 1.3; the factor for the in-the-molecular-plane carbon p functions was 1.03 and that for the out-of-plane 0.98.

Electron-repulsion integrals over atomic functions were generated in a molecular fragment scheme. The principal fragments were a C_6H_5 benzene fragment (Figure 1) and a C_6H_4 benzenium ion fragment (Figure 2). To generate the integral file for one of the substituted benzenes, for example, a halogen atom was placed at the vacant position in the benzene fragment and integrals involving the functions centered at this atom were added to the files of integrals already evaluated for the main fragment and the substituent atom. Calculations were done with the POLYATOM system of programs[18] modified to incorporate an integral pretest and the machinery for assembling molecular fragments. The integral pretest is used to efficiently eliminate integrals with negligibly small values.

The geometric configurations of the species are shown in Figures 1 and 2. No geometry optimization was done. The structure of the benzene fragment is the experimentally determined[19] benzene structure less one hydrogen atom; that of

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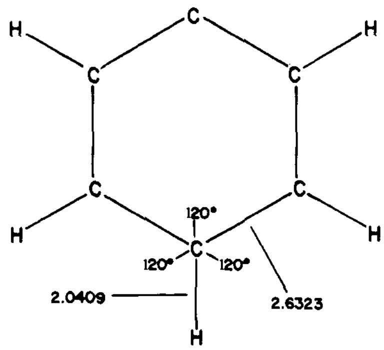

Figure 1. Geometric configuration of the benzene fragment. Bond lengths are in bohr. Fluorine and chlorine substitute at the top carbon with C-F = 2.5587 and C-Cl = 3.2125.

Table I. Energies of Substituted Benzenes and Benzenium Ions[a]

species	E_{total}	$\Delta E_{\text{parent-ion}}$
C_6H_6	−230.657	
$C_6H_7^+$	−230.949	0.292 (183)
C_6H_5F	−329.507	
o-$C_6H_6F^+$	−329.788	0.281 (177)
m-$C_6H_6F^+$	−329.777	0.270 (170)
p-$C_6H_6F^+$	−329.792	0.285 (179)
C_6H_5Cl	−689.541	
o-$C_6H_6Cl^+$	−689.816	0.275 (173)
m-$C_6H_6Cl^+$	−689.811	0.270 (169)
p-$C_6H_6Cl^+$	−689.829	0.288 (181)

[a] The units are hartrees with kcal/mol in parentheses.

the benzenium fragment is a plausible one derived from the previous theoretical optimizations of Ermler, Mulliken, and Clementi[6] and of Pople and Hehre.[5] The atoms in the benzenium fragment which are not part of the CH_2 group retain the positions they have in benzene. The carbon at the point of electrophilic attack is moved slightly farther from its neighbors in the benzenium ions as compared to benzene. This results in an elongation of the bonds to this carbon and a decrease in angle. The C-F bond[20] and C-Cl bond[19] lengths were taken from experimental determinations.

Energies. The computed total electronic energies are given in Table I. In previous work, Fischer-Hjalmars and Siegbahn[21] computed an energy of −230.658 hartrees for benzene using the same geometry and the same size basis used here. Clark and co-workers[22] used the same size basis and a geometry similar to that used here to compute an energy of −329.426 hartrees for fluorobenzene. Using a larger basis including polarization functions, Ermler and co-workers[6] found energies of −230.777 and −231.078 hartrees for benzene and benzenium ion. The Hartree-Fock limit for benzene has been estimated[21] at −230.82 hartrees.

Energy differences between parent benzenoids and their benzenium ions are also listed in Table I. These may be compared to gas-phase proton affinities[23,24] observed to be 183.7, 182.9, and 182.7 kcal/mol for benzene, fluorobenzene, and chlorobenzene, respectively. The calculations of this study predict, in agreement with the experimental findings, that the proton affinities of the three molecules are nearly equal. The energy ordering by position on the aromatic ring correlates with experimental results of electrophilic substitutions; that is, the p-halobenzenium ion is lowest in energy followed by the ortho and the meta isomer.

The calculated orbital energies (Tables IS-VIS, available in microfilm edition) may, by Koopmans' theorem, be compared to first ionization potentials of the species. In Table II, comparison with ionization potentials from photoelectron spectra[25] shows good agreement. The first two ionization energies of fluorobenzene, for orbitals that correlate with the doubly degenerate e_{1g} orbital of benzene, are nearly equal and unresolved in the observed spectrum.

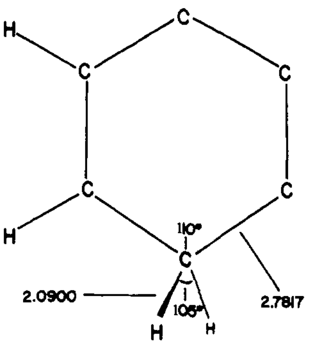

Figure 2. Geometry of the benzenium fragment. With the exception of the CH_2 carbon (at bottom), the carbon skeleton is that of benzene.

Table II. Comparison of Calculated and Experimental Ionization Potentials

	calcd		obsd	
	first IP, eV	second IP, eV	first IP, eV	second IP, eV
C_6H_6	9.24	9.24	9.24	9.24
C_6H_5F	9.54	9.78	9.86	9.86
C_6H_5Cl	9.30	9.74	9.31	9.71

The orbital energies of the benzenium ions (Tables IS-VIS) show evidence of interaction of the CH_2 group with the aromatic π system. Addition of a proton lowers all orbital energies, but those most lowered are π orbitals of the ring. This hyperconjugation effect has also been observed in studies of the benzenium[6] and p-toluenium[12] ions.

Table III. Gross Atomic Charges and Overlap Populations of Benzene and Fluoro- and Chlorobenzene[a]

	benzene	fluorobenzene	chlorobenzene
C_1	−0.180	0.456	−0.116
	0.000	0.000	−0.095
	−0.180	0.456	−0.211
C_2		−0.265	−0.094
		−0.037	0.007
		−0.302	−0.087
C_3		−0.156	−0.167
		0.017	0.011
		−0.139	−0.156
C_4		−0.180	−0.179
		−0.012	0.0
		−0.192	−0.179
X		−0.407	−0.133
		0.053	0.060
		−0.354	−0.073
C_1C_2	0.657	0.710	0.251
	0.305	0.302	0.302
	0.962	1.012	0.553
C_2C_3		0.596	0.654
		0.296	0.308
		0.892	0.962
C_3C_4		0.652	0.630
		0.306	0.302
		0.958	0.932
C_1X		0.366	0.780
		−0.041	−0.055
		0.325	0.725

[a] In each entry, the σ charge of population is given first followed by the π and total. The numbering begins with the halogenated carbon.

Table IV. Gross Atomic Charges and Overlap Populations of Benzenium and *o*-, *m*-, and *p*-Fluoro- and Chlorobenzenium Ions.[a]

	benzenium ion	*o*-F	*m*-F	*p*-F	*o*-Cl	*m*-Cl	*p*-Cl
C_1	−0.298	−0.306	−0.282	−0.295	−0.233	−0.289	−0.293
	−0.192	−0.227	−0.203	−0.202	−0.193	−0.199	−0.195
	−0.490	−0.533	−0.485	−0.497	−0.416	−0.488	−0.488
C_2	−0.287	0.336	−0.361	−0.269	−0.239	−0.193	−0.274
	0.325	0.288	0.293	0.332	0.176	0.332	0.320
	0.038	0.624	−0.068	0.063	0.063	0.139	0.046
C_3	−0.149	−0.250	0.510	−0.243	−0.066	−0.142	−0.061
	−0.069	−0.098	−0.089	−0.090	−0.056	−0.175	−0.063
	−0.218	−0.348	0.421	−0.333	−0.122	−0.317	−0.124
C_4	−0.313	−0.292	−0.413	0.354	−0.294	−0.224	−0.285
	0.383	0.384	0.364	0.325	0.375	0.394	0.232
	0.070	0.092	−0.049	0.679	0.081	0.170	−0.053
C_5		−0.154	−0.131		−0.149	−0.138	
		−0.067	−0.067		−0.071	−0.069	
		−0.221	−0.198		−0.220	−0.207	
C_6		−0.284	−0.291		−0.282	−0.284	
		0.309	0.338		0.318	0.336	
		0.025	0.047		0.036	0.052	
H_1	0.145	0.151	0.150	0.147	0.152	0.149	0.146
	0.149	0.162	0.154	0.152	0.154	0.153	0.148
	0.294	0.313	0.304	0.299	0.306	0.302	0.294
X		−0.364	−0.355	−0.358	−0.027	−0.005	−0.017
		0.088	0.056	0.089	0.143	0.075	0.152
		−0.276	−0.299	−0.269	0.116	0.070	0.135
C_1C_2	0.432	0.413	0.385	0.426	0.073	0.415	0.408
	0.046	0.046	0.053	0.045	−0.017	0.055	0.042
	0.478	0.459	0.438	0.471	0.056	0.470	0.450
C_2C_3	0.578	0.608	0.569	0.535	0.016	−0.086	0.585
	0.383	0.355	0.379	0.386	0.356	0.380	0.392
	0.961	0.963	0.948	0.921	0.372	0.294	0.977
C_3C_4	0.555	0.500	0.594	0.600	0.558	−0.046	0.010
	0.219	0.228	0.218	0.206	0.232	0.204	0.193
	0.774	0.728	0.812	0.806	0.790	0.158	0.203
C_4C_5		0.545	0.519		0.537	0.564	
		0.211	0.225		0.207	0.231	
		0.756	0.744		0.744	0.795	
C_5C_6		0.581	0.568		0.564	0.536	
		0.393	0.373		0.391	0.373	
		0.974	0.941		0.955	0.909	
C_6C_1		0.427	0.408		0.431	0.389	
		0.022	0.049		0.032	0.047	
		0.449	0.457		0.463	0.436	
C_1H_1	0.434	0.434	0.435	0.438	0.461	0.434	0.434
	0.334	0.331	0.330	0.333	0.335	0.331	0.336
	0.768	0.765	0.765	0.771	0.796	0.765	0.770
CX		0.345	0.418	0.362	0.675	0.859	0.788
		0.042	−0.052	0.049	0.120	−0.032	0.130
		0.387	0.366	0.411	0.795	0.827	0.918

[a] In each entry, the σ charge or population is given first followed by the π and total. The numbering begins with the protonated carbon and continues around the ring toward the halogen atom.

Energies of the inner-shell halogen orbitals in the halobenzenium ions are in the order $p < o < m$. This is a reflection of the amount of positive charge from the added proton that is delocalized onto the halogen atom through hyperconjugation and halogen lone pair donation. Greater charge delocalization in *p*-halobenzenium ion allows a smaller electron density at the halogen atom, hence less interelectron repulsion and lower core orbital energies. The ordering of the inner orbital energies correlates with the ordering of proton affinities, and so with the experimentally observed order of substitution rates.

Population Analysis. Mulliken population analysis,[26] which allows one to associate the electrons within a molecule with particular atoms or interatomic regions, is used to interpret the halogen substituent effects in fluorobenzene and chlorobenzene, to describe the effect of adding a proton to the aromatic systems, and to search for reactivity indexes in the electronic structures of parent molecules and reactive intermediates.

The fluoro and chloro substituents both withdraw charge from an aromatic ring by virtue of their large electronegativity and donate to the ring by interaction of their lone pairs with the π system of the ring; however, there are important differences in their electronic effects. In Table III, the σ, π, and total gross charges and overlap populations for fluoro- and chlorobenzene are shown. Both halogens withdraw electrons from the σ system, both donate to the π system, and both are net withdrawers. The σ-inductive effect dominates the π-resonance effect. The fluoro substituent is a more powerful electron withdrawer than the chloro. The C–F bond is highly polar; the

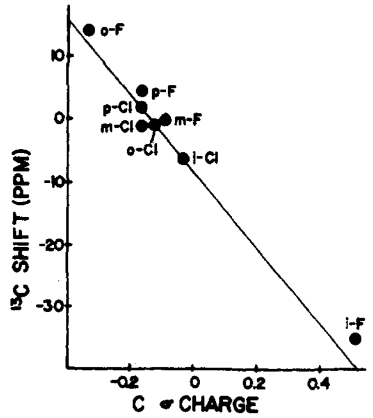

Figure 3. Correlation between ^{13}C NMR chemical shift (relative to benzene) and gross atomic σ charge at positions in fluorobenzene and chlorobenzene.

atoms have opposite charges and the overlap is rather small. In contrast, the C–Cl bond appears to be nonpolar. In chlorobenzene, the C–C bonds immediately adjacent to the C–Cl are markedly depleted of overlap population, whereas the same bonds in the fluoro species are little affected (slightly enhanced). In comparison with other systems, it is interesting that there is more similarity between the electron distributions of toluene[12] and fluorobenzene than there is between those of the two halobenzenes.

The effect of protonating the benzenes (Table IV) is marked in both the σ and π systems, but is greater in the π system. The overlap populations show marked alternation with almost no π character in the bonds to the CH_2 carbon. This agrees with the classical picture that this atom is tetrahedral,[4] surrounded by four bonds of single-bond strength and no longer a participant in the aromatic system. The effect of protonation on the electronic structure is greater than the substituent effects of halogens.

In comparative studies of electrophilic substitution in benzenoid compounds, correlations have been found between charge densities and reaction rates of positions meta and para to a substituent; such correlations do not work at the ortho position. This "ortho effect",[27] which has received little direct theoretical treatment, may be related to unique features seen in the electron distributions of the *o*-halobenzenium ions. In five of the seven benzenium ions studied here, the charge on the tetrahedral carbon atom is −0.491 ± 0.006 unit. The gross charge on this atom in *o*-chlorobenzenium ion is only −0.416, while in the *o*-fluorobenzenium ion it is −0.533. Aside from this discrepancy, *o*-fluorobenzenium ion has an electron distribution similar to those of the other fluorobenzenium ions. In *o*-chlorobenzenium ion, however, the bond between the tetrahedral carbon and the C–Cl carbon has a nearly zero overlap population. Consequently, we predict that bond to be long and weak and the transition state for electrophilic substitution at the ortho position to be very different from that for substitution at other positions. The chloro substituent reduces σ populations in adjacent C–C bonds and the CH_2 group reduces σ and π population in adjacent bonds; therefore, when the two groups are ortho to each other, population in the intervening bond is reduced to a very small value.

Correlations are successful between reaction rates and molecular electronic structure for a series of reactants when the reaction paths and transition states are similar throughout the series. The combined effects of two adjacent groups on the intervening bond may, as in *o*-chlorobenzenium ion, produce a unique transition state for ortho substitution and thus contribute to the ortho effect.

The chemical shift of nuclear magnetic resonance spectra is a reflection of the electronic environment of the resonating nuclei and should correlate with electron populations. To be most useful, the correlation should work for all positions, including the ipso and ortho. Figure 3 shows that the relation between carbon σ gross charge in benzene, fluorobenzene, and chlorobenzene and ^{13}C chemical shift[28] is fairly linear. There is little correlation between chemical shift and π charge, which is not surprising since the π orbitals have a node in the plane of the nuclei. The ^{1}H shifts[28,29] correlate better (Figure 4) with the sum of the σ charges on the hydrogen and the carbon to which it is attached (the σ-site charge) than with the σ charge on the hydrogen alone. Because hydrogen has no core contribution to the nuclear shielding, contributions from neighboring atoms are important.

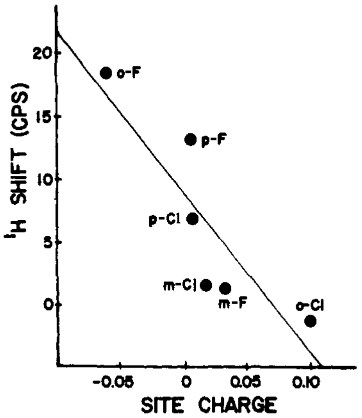

Figure 4. Correlation between ^{1}H NMR chemical shift (relative to benzene) and σ site charge (defined in text) at positions in fluorobenzene and chlorobenzene.

Reactivity Indexes. Electrophilic substitution in fluoro- and chlorobenzene[30] occurs predominantly at the para position; smaller yields of the ortho product are produced and meta substitution is rare. The reactivity indexes that were evaluated and the positional selectivity predicted by each of them are summarized in Table V.

It is often assumed that the electrophile attacks the most negatively charged ring carbon atom and that positional selectivity is indicated by the gross atomic charges of the reactants. The gross charges on fluoro- and chlorobenzene (Table III), however, predict substitution at the ortho and ipso positions, respectively, to dominate. Neither σ nor π populations

Table V. Reactivity Indexes

reactivity index	substitutional preference for fluorobenzene	substitutional preference for chlorobenzene
From Reactant		
highest core orbital energy of C	*p, o, m, i*	*p, m, o, i*
highest total electron density on C	*o, p, m, i*	*i, p, m, o*
highest σ-electron density on C	*o, p, m, i*	*p, m, i, o*
highest π-electron density on C	*o, p, i, m*	*i, p, o, m*
frontier b_2 orbital electron density	*p, i, o, m*	*p, i, o, m*
frontier b_2 + a_2 orbital densities	*o, p, m, i*	*o, p, m, i*
From σ Complex		
protonation energy	*p, o, m*	*p, o, m*
least negative halogen atom	*p, o, m*	*p, o, m*
most π donation by halogen atom	*p, o, m*	*p, o, m*
core orbital energy of halogen	*p, o, m*	*p, o, m*

considered separately correctly predict the position of substitution. In fact, no reactivity index reliable for both molecules was found in the population analyses of the reactant wave functions.

Electron distribution in the highest occupied, or frontier, orbital has been proposed[10] to be a significant factor in the outcome of electrophilic substitution reactions. The highest occupied orbitals in fluoro- and chlorobenzene are the b_2 and a_2 orbitals derived from the degenerate 3_{1g} orbitals of benzene. The b_2 orbital atomic populations (not shown) predict the order of substitution correctly, with the exception that the ipso population appears second to para; furthermore, there is a near degeneracy with the a_2 orbital which has a node at the ipso and para carbons. When the populations in the a_2 and b_2 orbitals are added, the predicted order of substitution is also incorrect.

Core orbital energies of the ring carbon atoms of aromatic reactants are commonly employed to predict the preferred position for electrophilic substitution.[22,31] The use of these energies to predict reactivity is based on the dual assumptions that a more negative carbon atom has a higher core orbital energy and that electrophilic substitution takes place at the most negative position, that is, at the carbon with the highest energy core orbital. The association holds for fluorobenzene (Table IIS and ref 22), but not for chlorobenzene.

It was shown in the section on energies that there is a correlation between the stability of a benzenium ion and substitutional preference. It is not surprising, then, that there are trends in the electron populations of the ions that correlate with the rates of reaction. The gross atomic charges of the benzenium ions (Table IV) show that the positive charge of the proton is distributed among the peripheral atoms, the hydrogens and the halogen. There are only small differences between the ions in their hydrogen charges, but there is a systematic variation in their halogen charges. The halogen atom with the least negative charge is in the *p*-halobenzenium ion followed by that in the *o*-halobenzenium ion. The halogen in *m*-halobenzenium ion is considerably more negative than the others. The π overlap populations and gross σ charges are in the same order. The π overlap population is negative in *m*-halobenzenium ion.

The ability of the halogen to participate in the π system of the ring determines the stability of a particular benzenium ion, which in turn relates to the tendency of a substituted benzene to undergo protonation at the corresponding site. The traditional quinoid structures for the σ complex,[4] derived from resonance theory, are consistent with this interpretation, except that they do not distinguish between ortho and para species.

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Supplementary Material Available: Tables of orbital energies for all species studied (Tables IS–VS) (4 pages). Ordering information is given on any current masthead page.

References and Notes

(1) M. J. S. Dewar, *J. Chem. Soc.*, 406, 777 (1946).
(2) G. A. Olah, *J. Am. Chem. Soc.*, **94**, 808 (1972).
(3) L. M. Stock, *Prog. Phys. Org. Chem.*, **12**, 21 (1976).
(4) G. W. Wheland, *J. Am. Chem. Soc.*, **64**, 900 (1942).
(5) W. J. Hehre and J. A. Pople, *J. Am. Chem. Soc.*, **94**, 6901 (1972).
(6) W. C. Ermler, R. S. Mulliken, and E. Clementi, *J. Am. Chem. Soc.*, **98**, 388 (1976).
(7) G. A. Olah, R. H. Schlosberg, R. D. Porter, Y. K. Mo, D. P. Kelley, and G. D. Mateescu, *J. Am. Chem. Soc.*, **94**, 2034 (1972).
(8) G. A. Olah and T. E. Klovsky, *J. Am. Chem. Soc.*, **89**, 5692 (1967).
(9) N. C. Baenziger and A. D. Nelson, *J. Am. Chem. Soc.*, **90**, 6602 (1968).
(10) K. Fukui, T. Yonezawa, and H. Shingu, *J. Chem. Phys.*, **20**, 722 (1952).
(11) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists", Wiley, New York, 1961.
(12) W. C. Ermler and R. S. Mulliken, *J. Am. Chem. Soc.*, **100**, 1647 (1978).
(13) W. J. Hehre, R. T. McIver, Jr., J. A. Pople, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **96**, 7162 (1974).
(14) S. Huzinaga, *J. Chem. Phys.*, **42**, 1293 (1965).
(15) T. H. Dunning, *J. Chem. Phys.*, **53**, 2823 (1970).
(16) A. Veillard, *Theor. Chim. Acta*, **12**, 405 (1968).
(17) T. H. Dunning, *Chem. Phys. Lett.*, **7**, 423 (1970).
(18) D. B. Neumann, H. Basch, R. L. Kornegay, L. C. Snyder, J. W. Moskowitz, C. Hornback, and S. P. Liebmann, Program 199, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.
(19) L. E. Sutton, "Tables of Interatomic Distances", *Chem. Soc., Spec. Publ.* **No. 18** (1965).
(20) L. Nygaard, I. Bojesen, T. Pedersen, and J. Rastrup-Andersen, *J. Mol. Struct.*, **2**, 209 (1968).
(21) I. Fischer-Hjalmars and P. Siegbahn, *Theor. Chim. Acta*, **31**, 1 (1973).
(22) D. T. Clark, D. Kilcast, D. B. Adams, and I. Scanlan, *J. Electron Spectrosc. Relat. Phenom.*, **1**, 153 (1972/3).
(23) Y. K. Lau and P. Kebarle, *J. Am. Chem. Soc.*, **98**, 1320 (1976).
(24) R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc.*, **98**, 7452 (1976).
(25) A. D. Baker, D. P. May, and D. W. Turner, *J. Chem. Soc. B*, 22 (1968).
(26) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).
(27) T. Fujita and T. Nishioka, *Prog. Phys. Org. Chem.*, **12**, 49 (1976).
(28) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961).
(29) G. L. Nelson and E. A. Williams, *Prog. Phys. Org. Chem.*, **12**, 229 (1976).
(30) R. O. C. Norman and R. Taylor, "Electrophilic Substitution in Benzenoid Compounds", American Elsevier, New York, 1965.
(31) R. J. Buenker and S. D. Peyerimhoff, *Chem. Phys. Lett.*, **3**, 37 (1969).

Metallacyclopentanes and Bisolefin Complexes

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Abstract: The reaction path for the bisethylene metallacyclopentane interconversion is explored, for the specific case of two olefins coordinated to a trigonal bipyramidal iron tricarbonyl. If the ethylene is unsymmetrically substituted, the reaction should proceed stereoselectively, placing the substituents so that the ethylene π^* enters the reaction with its largest lobe β to the metal in the product metallacycle. A special case of this regularity is that heteroatoms more electronegative than carbon should preferentially go in α sites, donor substitutents on α carbons, acceptor substituents on β sites.

Metallacyclopentanes have been proposed or demonstrated to be key intermediates in numerous metal-catalyzed cycloadditions and cycloreversions of olefins. Stone,[1] Wilkinson,[2] and co-workers had already prepared the first such compounds, **1** and **2**, from perfluoroethylenes by 1961, and subsequently synthesized many others.[3] Substantial interest

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