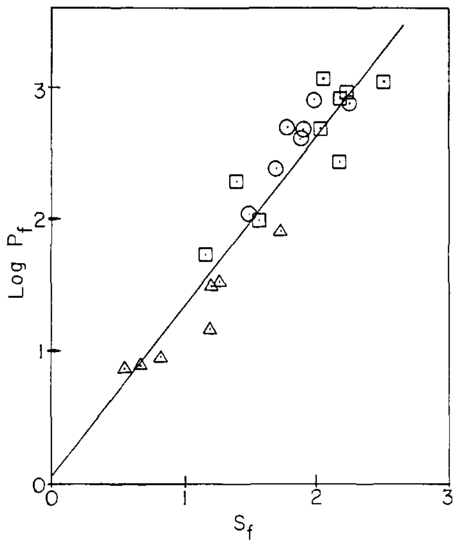

Figure 1. Relationship between log p_f and selectivity factor, S_f, for acylation and sulfonylation reactions: acetylation (○), ref 2, Table I; benzoylation (□), ref 2, Table II; sulfonylation (△), ref 3, Table I.[11]

one standard deviation (±0.10). *Clearly, this sulfonylation and acylation data is in excellent agreement with the Brown selectivity relationship and therefore is strongly supportive of a σ-complex mechanism.*

Rys, Skrabal, and Zollinger[4] have applied regression analysis to Olah's nitration data and have found the correlation to π-complex stabilities is really no better than the correlation to σ-complex stabilities required by Brown's theory. Neither correlation is satisfactory.

Although Olah's argument for the π-complex mechanism has been weakened considerably by the results of these regression analyses, we decided to study the benzoylation reaction using our improved vacuum line techniques and thoroughly dried solvents. This approach in both ethylation[5] and benzylation[6] studies yielded reproducible results substantially different from that previously reported.

We now report noncompetitive kinetic results for the $AlCl_3$ catalyzed reaction between the strong electrophile 2,4-dichlorobenzoyl chloride and benzene or toluene in nitromethane at 20 °C. Thoroughly dried Spectrograde CH_3NO_2 gave inconsistent kinetic data for low $AlCl_3$ concentrations.[7] When the CH_3NO_2 was purified by low temperature recrystallization,[8] the 2-nitropropane impurity was reduced to <0.03%. Consistent and reproducible kinetic data were then obtained for all reactions, including $AlCl_3$ concentrations as low as 0.02 M. For both toluene and benzene, third-order kinetics were found, i.e., first order in $AlCl_3$, 2,4-dichlorobenzoyl chloride, and aromatic hydrocarbon. The third-order rate constant however did show a tendency to decrease as the initial $AlCl_3$ concentration was increased in a manner very similar to that observed by Brown and Young.[9] A rate constant ratio k_T/k_B of 480 ± 120 was calculated using the k_3 values for benzene, $(5.4 \pm 0.4) \times 10^{-3}$ $M^{-2}\,s^{-1}$, and toluene, 2.6 ± 0.5 $M^{-2}\,s^{-1}$, at 0.03 M $AlCl_3$ concentration. For toluene, the isomeric distribution is 8.4 ± 0.3% ortho, 0.4 ± 0.1% meta, and 91.2 ± 0.9% para.

Not surprisingly, these results fit the selectivity relationship. What is surprising, however, is the marked substrate and positional selectivity of 2,4-dichlorobenzoyl chloride. In systematically varying the ring substituents in benzoyl chloride, Olah found k_T/k_B values ranging from 16 to 233.[2] As expected, his highest ratios occurred with electron-donating groups: p-CH_3, p-F, 2,4,6-trimethyl, and p-CH_3O. With the much stronger electrophile, 2,4-dichlorobenzoyl chloride,[10] we obtain a k_T/k_B value along with product isomer percentages expected of a very weak electrophile. At present we are unable to explain this unusual result.

Acknowledgment. We are indebted to the National Science Foundation (Grant CHE 77-07604), the Research Corporation, and the National Science Foundation Undergraduate Research Participation Program for financial support.

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(10) R. Verbeerst and P. J. Slootmaekers, *Bull. Soc. Chim. Belg.*, **77,** 287 (1968), have found 2,4-dichlorobenzoyl chloride to be 69.6 times more reactive than benzoyl chloride in the $AlCl_3$ catalyzed acylation of toluene, thus establishing the 2,4-dichloro compound as a strong electrophile.

(11) Reactions with percent meta product isomer percentages listed as ~0 and ~1 were not included in the statistical analysis.

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On "Anomalous" Selectivities in Electrophilic Aromatic Substitutions

Sir:

The selectivity relationship[1] for electrophilic aromatic substitutions (EAS) quantitatively accounts for the relationship between substrate and positional selectivites in a large number of EAS.[2] According to this principle, and its interpretation through the Hammond postulate, as the reactivity of an electrophile decreases, both the substrate and positional selectivities increase. However, Olah and co-workers have reported a class of reactions which appear to give high positional but low substrate selectivity. They suggested that these reactions do not follow the selectivity relationship because they involve, first, as rate-determining step—that determining substrate selectivity—the formation of a π complex, followed by a second faster step, which determines positional selectivity.[3] These "anomalous" cases have been given several theoretical rationales.[4-7] However, we report here that few of these reactions show "anomalous selectivities", and, for that reason, some previous rationales of such selectivities do not correctly identify the factors influencing selectivities in "early" transition states of EAS.

Brown and co-workers established that the vast majority of

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EAS fit the selectivity relationship.[2] The substrate selectivity, measured by the difference between the free energies of attack of a reagent at the para position of toluene and at one position of benzene (log p_f^{Me}), is found to be proportional to the positional selectivity, measured by the difference between the free energies of activation for attack at the para and meta positions of toluene (log (p_f^{Me}/m_f^{Me})). For a series of 47 EAS, Brown and Stock found the selectivity relationship log $p_f^{Me} = 0.0071 + 1.31$ log (p_f^{Me}/m_f^{Me}), which has a correlation coefficient of 0.999.[2b] This line (—) and 47 points from which it is derived (points 1-47) are shown in Figure 1, along with additional experimental data to be discussed below.

Olah and co-workers reported a "new and important, quite general" type of EAS,[3a] in which high positional selectivity is observed in spite of low substrate selectivity. For nitration with nitronium salts, the substrate selectivity is low ($k_t/k_b \simeq 1$-2), even though only small amounts of meta products are formed from toluene. However, these reactions have been shown to involve mixing control,[8] so that they do not represent anomalies in selectivity. Nitration of reactive aromatics does show low substrate selectivity and high positional selectivity, which has been attributed to an electron-transfer mechanism with high intramolecular selectivity resulting from spin density distributions in the aromatic radical cation.[9]

However, Olah and co-workers have studied several cases in which mixing control or electron transfer does not appear to occur.[3a,c] In the $TiCl_4$ catalyzed benzylation of benzene and toluene with a series of benzyl halides,[3a,c] Olah found that (1) very little meta product is observed in any of the cases, even when k_t/k_b is very low (thus, high positional and low substrate selectivity is observed); (2) as the k_t/k_b ratio increases, so does the para/ortho ratio. Similar data have been observed for a variety of EAS, particularly with very reactive reagents.[3]

Olah suggested that high k_t/k_b and para/ortho ratios occur in reactions of relatively unreactive electrophiles, because transition states resembling σ complexes (benzenium ions or Wheland intermediates) are involved. Low k_t/k_b and para/ortho ratios are postulated to occur in reactions of highly reactive electrophiles, because these reactions involve transition states resembling π complexes. Olah proposed that the latter involve two transition states; the first, or π-complex-like transition state is rate determining and leads to low substrate selectivity, while the second is σ-complex-like, and leads to relatively high positional selectivity.[3]

Zollinger and co-workers have critized Olah's interpretation, since the rates of attack of very reactive electrophiles upon a series of aromatics correlate no better with π-complex stabilities than with σ-complex stabilities.[10] Similary, Modro, Schmid, and Yates have concluded that solvent effects on rates of bromination of alkenes do not show anomalous selectivities, and do not require a transition state resembling a π complex.[11]

While the idea that anomalous selectivities may parallel large variations in transition-state structure seems attractive, the necessity for a new mechanism of EAS requires that the anomalous cases deviate from the selectivity relationship. In order to verify this, we have plotted lot p_f^{Me} vs. log (p_f^{Me}/m_f^{Me}) for data used or measured by Olah on benzylations,[3a,c] benzoylations,[3d] formylations,[3b] acylations,[3d] halogenations,[3a] and nitrations,[3a,e] as well as recent data on gas phase and "unsolvated" (electrophile generated by radioactive decay of neutral species) solution EAS.[12] The 108 independent points on the graph shown in Figure 1 provide the somewhat altered selectivity relationship, log $p_f^{Me} = -0.17 + 1.38$ log (p_f^{Me}/m_f^{Me}) (r = 0.91). This line (- - -) is also shown in Figure 1. The correlation is poorer than that of Brown and Stock, but, even with the inclusion of reactive electrophiles, the positional selectivity approaches zero when the substrate selectivity vanishes. Since the intercept is slightly, but significantly, negative (standard deviation of intercept = 0.046), there is a deviation in the direction expected if reactive electrophiles show anomalous substitutions. However, there are very few reactions which deviate substantially from the selectivity relationship and there are many more points for highly reactive, and unselective, electrophiles on the line than off! For example, of the 108 reactions, only a single acylation, △-11 (CO/HF-SbF_5, SO_2ClF), two halogenations, ◇-48 (Br_2, $FeCl_3$, CH_3NO_2) and ◇-52 (I^+ generated electrochemically in MeCN), two of the benzylations, □-36 (m-Me) and □-27 (p-NO_2), and the three previously mentioned nitrations with nitronium salts (53-55) deviate substantially enough from the cluster of points about the line to suggest anomalous behavior.[13] If these eight points are omitted from the least-squares correlation, the relationship, log $p_f^{Me} = -0.08 + 1.37$ log (p_f^{Me}/m_f^{Me}) with r = 0.95 is obtained. Most remarkably, four (○-62, -63, -64, and -67) of the seven gas phase or unsolvated electrophile examples fit the selectivity relationship adequately. If the 21 points for which $k_T/k_B < 20$ are treated separately, log $p_f^{Me} = 0.70 + 0.38$ log (p_f^{Me}/m_f^{Me}), which has a correlation coefficient of only 0.15!

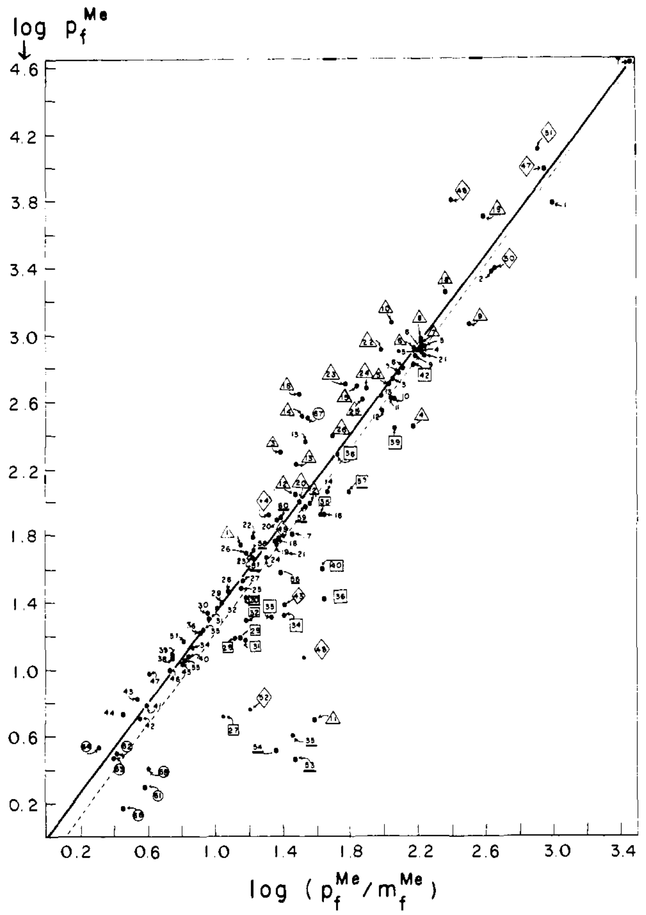

Figure 1. — is the Brown-Stock correlation between log p_f^{Me} and log (p_f^{Me}/m_f^{Me}) for 47 EAS. The 47 Brown-Stock points are labeled with the unadorned numbers, which correspond to the numbering in the original reference.[2b] △: containing numbers 1-10 are benzoylations from ref 3d; 11-19 are formylations from ref 3b; 20-26 are acylations from ref 3d. □: 27-42 are benzylations with $XPhCH_2Cl/TiCl_4$, where X's = p-NO_2 (27), o-F (28), m-F (29), p-F (30), o-Cl (31), m-Cl (32), p-Cl (33), H (34), o-Me (35), m-Me (36), p-Me (37), 2,4,6-Me_3 (38), o-MeO (39), m-MeO (40), p-MeO (41), and 2,4,6-$(MeO)_3$ (42) from ref 3a. ◇: 43-52 are halogenations from ref 3a. 53-60 are nitrations (53-55 are with nitronium salts in polar aprotic solvents) from ref 3a. ○: 61-67 are reactions in the gas phase or with "unsolvated" electrophiles from ref 12. - - - is the least-squares correlation for all 108 independent points. (Points 44, 45, 49, 50, 57, and 58 are also included in Olah's tabulations.[3]) In the text, symbols containing numbers will be designated as symbol-number.

Figure 1 also shows point T, from the experimental proton affinities of benzene and toluene,[14] which fix the maximum

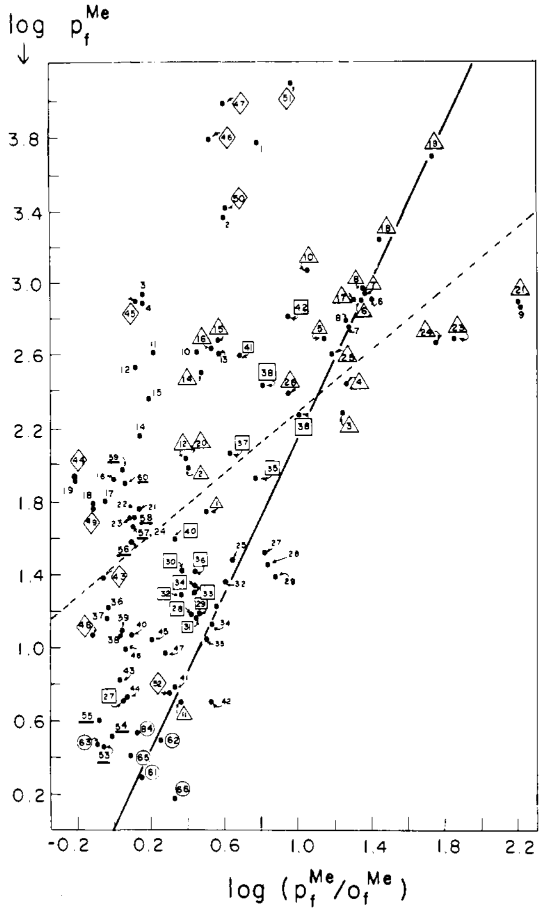

Figure 2. Plot of log p_f^{Me} vs. log (p_f^{Me}/o_f^{Me}) for electrophilic aromatic substitutions. Symbols are the same as those in Figure 1. The dashed line represents the least-squares treatment of the data, while the full line is the hypothetical "normal" selectivity line discussed in the text.

p_f^{Me} and p_f^{Me}/m_f^{Me} expected for very selective reagents. Since there are no patterns of anomaly discernible in Figure 1, from most selective to least selective reactions, we conclude that there is no experimental basis for the necessity of two transition states, the first of which is rate determining and the second of which is product determining.

The further suggestion that highly reactive electrophiles give anomalously high ortho/para ratios[3] is tested in Figure 2, which is a plot of log p_f^{Me} vs. log (p_f^{Me}/o_f^{Me}). The least-squares line (- - -), log p_f^{Me} = 1.39 + 0.88 log (p_f^{Me}/o_f^{Me}), has a correlation coefficient of only 0.57, so that no statistically valid conclusions can be made. A line through the origin and point Δ-19 (—) is sheerly arbitrary but probably the most reasonable for "normal" behavior, but, as with Figure 1, no clear patterns of anomaly can be discerned here. In fact, the eight clearly anomalous points cited earlier in Figure 1 all fall very close to a hypothetical line through the origin and Δ-19 ((log p_f^{Me} = 1.49 log (p_f^{Me}/o_f^{Me}), which, using log p_f^{Me} = 4.62 from the experimental proton affinities of benzene and toluene, gives log (p_f^{Me}/o_f^{Me}) = 3.11 for maximum selectivity)), while the many points lying above this line are mainly "normal" EAS. The considerable scatter in Figure 2, far greater than in Figure 1, suggests that steric effects are of variable importance in determining para/ortho ratios. It is interesting that the vast majority of reactions seem to give too much ortho product! As noted before,[2,3d] para/ortho ratios are not suitable for testing the relationship between substrate and positional selectivity.

Since there is no experimental basis for two separate transition states in EAS (other than nitration of reactive aromatics), it is of interest to explore the possibility that the selectivity relationships shown in Figure 1 might be interpreted in terms of a single transition state, whose character varies from π complex-like, or "early", for reactive electrophiles, to σ-complex-like, or "late", for selective electrophiles. Qualitatively, it certainly follows from the Hammond postulate that both positional and substrate selectivity ought to diminish as the transition state becomes earlier.

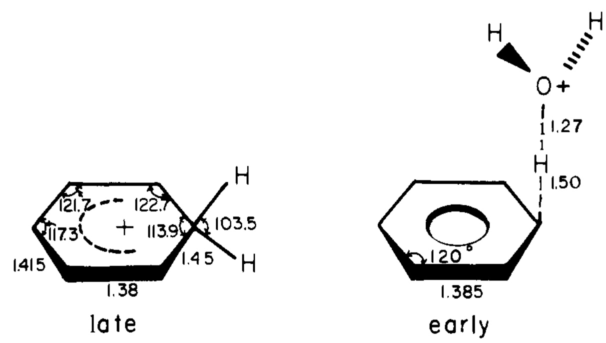

Figure. 3. Geometries used for model calculations on "late" and "early" transition states for EAS.

Table I. STO-3G Energies of "Late" and "Early" Transition States of EAS on Benzene and Toluene[a]

transition state	late	early
benzene + E^+	≡0.0[b]	≡0.0[c]
toluene + E^+, para	−9.5	−2.9
toluene + E^+, meta	−1.3	−1.1
toluene + E^+, ortho	−6.3	−2.2
toluene + E^+, ipso	+1.4	+4.2

[a] In kilocalories/mole. [b] Calculated interaction energy, relative to benzene + H^+, is −227.1 kcal/mol. [c] Calculated interaction energy, relative to benzene + H_3O^+, is −45.2 kcal/mol.

Ab initio STO-3G calculations of the relative energies of "late" and "early" transition-state models for attack of a proton on benzene and the various positions of toluene are shown in Table I. The models for the "late" or σ-complex transition states were the cyclohexadienyl cation and various methyl-substituted derivatives, with the geometries shown in Figure 3. As shown by McKelvey et al., calculations give excellent predictions of relative energies of the cyclohexadienyl cations.[15] The models for the "early" or π-complex transition state were undistorted benzene and toluene coordinated to a distorted hydronium ion (Figure 3).[16] Table I shows that the relative energies of the five species are para < ortho < meta < H < ipso, for both late and early transition states. These values verify the qualitative expectation that both positional and substrate selectivity diminish as the transition state becomes earlier. In particular, early transition states show no anomalous selectivity. Indeed, with this model of an early transition state, any anomaly is in the opposite direction to that claimed, since positional selectivity decreases less than substrate selectivity. Moreover, this model suggests that the ipso position is deactivated toward formation of an early transition state, whereas nitration leads to unusually high proportions of ipso attack.[9]

These observations indicate that several previous qualitative theoretical interpretations of positional selectivity in EAS have explained a phantom phenomenon. Klopman and Hudson[4] suggested that low para/ortho ratios arise from electrostatic (Coulombic) control in early transition states, while higher para/ortho ratios arise from frontier MO control, owing to the large coefficient at the para carbon in the HOMO. Olah[3] made a similar suggestion, involving the charge distribution in the aromatic, while Fukui[5] and Epiotis[6] cite only frontier MO interactions to explain product ratios. Chalvet and co-workers[7] attempted to explain the varying selectivities of the benzylations in terms of a perturbation model. However, this treatment required the unreasonable assumption that solvation reverses the order of electron affinities of benzyl cations, even though such reversal does not occur with trityl cations.[17] Rate-determining formation of the benzyl cations undoubtedly explains the reactivity orders in the reactions investigated by Chalvet.[13]

A theoretical study,[18] which will be reported at a later date, will consider in more detail the origins of selectivity in "early" transition states.

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Influence of Molecular Distortions upon Reactivity and Stereochemistry in Nucleophilic Additions to Acetylenes

Sir:

We report here ab initio molecular orbital studies which show that the changes in frontier molecular orbital energies and shapes upon bending distortions of acetylene and ethylene explain several preplexing, but general, phenomena: (1) alkynes are much more reactive than alkenes toward nucleophiles;[1-4] (2) nucleophilic additions to alkynes generally proceed with anti stereochemistry,[1] although some highly activated alkynes give syn adducts with amines;[1,5] (3) nucleophiles, N, are predicted to attack acetylenes, RCCR, with an RCN angle of 120°,[6] even though this would seem to require an unreasonable NCC angle of 60°.

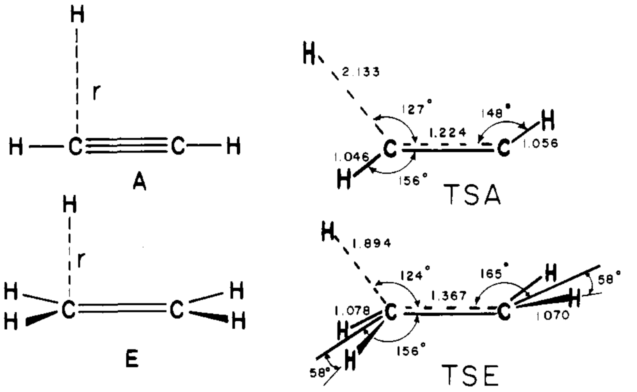

Figure 1. Geometries of complexes between hydride and acetylene (A) or ethylene (E) used in calculations reported in Table I. TSA and TSE are the 4-31G transition states for addition of hydride to acetylene and ethylene, respectively.

Frontier molecular orbital theory adequately accounts for the greater reactivity of electrophiles toward alkenes than toward similarly substituted alkynes:[1,7] the HOMO of ethylene (IP = 10.5eV) is higher in energy than that of acetylene (IP = 11.4 eV) and provides more charge-transfer stabilization upon interaction with the LUMO of an electrophile. However, the LUMO of acetylene (EA = −2.6 eV)[8] is higher in energy than that of ethylene (EA = −1.8 eV),[9] suggesting that acetylene is less capable of charge-transfer (CT) stabilization upon interaction with the HOMO of a nucleophile. This implication gains numerical support from an energy decomposition analysis[10] of the ab initio SCF 4-31G calculations[11] (Table I) for the interaction of hydride (at 2 Å) with the equilibrium geometries of acetylene and ethylene (Figure 1, structures A and E, r = 2 Å). The stabilizing CT interaction is smaller upon interaction of hydride with undistorted acetylene than with undistorted ethylene. The exchange repulsions (EX) are largely reponsible for the overall enormously repulsive interaction energies, but differences in CT control the relative interaction energies. This simple picture changes dramatically as molecular distortions occur along the reaction pathway.

The transition states (TS) for hydride addition to acetylene and ethylene calculated here with the 4-31G basis set are shown in Figure 1 (TSA and TSE, respectively).[12] Using 4-31G optimized geometries of reactants and transition states, and 4-31G plus 3 × 3 configuration interaction (CI) calculations, activation energies of 16.7 and 16.6 kcal/mol are predicted for the additions of hydride to acetylene and ethylene, respectively. Overall reaction energies compare favorably with those calculated by others.[12-15] Even for these relatively early transition states, the attack of hydride on acetylene is essentially as easy as attack on ethylene, and preferential attack on acetylene should become pronounced for a less reactive nucleophile.

Bending of the hydrogens out of linearity or planarity is the most significant distortion occurring in these transition states, along with a change of attack angle away from 90°; CC stretching is of minor importance. The "driving force" for bending of acetylene or ethylene upon attack by nucleophiles can be deduced from Figure 2, which shows that the LUMOs of both species are lowered in energy[17] and change shape appreciably upon bending to the transition-state geometries. Calculations on cis bending or one-end bending of these molecules reveal the same trends shown in Figure 2: for compa-