J. Am. Chem. Soc. **1989**, *111*, 1414–1418

Simplified Method of Ascertaining Steric Effects in Electrophilic Addition Reactions. A Comparison of Bromination, Oxymercuration, and Hydroboration

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Abstract: Correlations of ionization potentials (IP's) versus relative reactivities of a variety of alkenes toward bromination, oxymercuration, and hydroboration show very good ($r = 0.83$) to excellent ($r = 0.98$) agreement. The use of alkenes having a broad range of steric requirements and electronic effects reveals that bromination is independent of steric effects while oxymercuration and hydroboration each exhibit a natural separation into sterically similar groups, within which alkene IP's correlate with relative reactivities. In hydroboration of allylic compounds, characteristics of the HOMO influence the regioselectivity as well as the relative reactivity. The data indicate that the transition states of the rate-determining steps of oxymercuration and hydroboration are similar, but both are different from that of bromination.

There has been much recent work[1–5] in the pursuit of mechanistic details of electrophilic additions to alkenes in order to advance regiochemical predictions and thereby to optimize the synthetic utility of these reactions. Considerable effort has been expended to gain such information via correlations of relative reactivities with vertical ionization potentials,[1a,2] π molecular orbital energy levels,[2,3] and relative rates of other reactions.[4] Among the most interesting investigations is that reported by Kochi et al.[4b] correlating the rates of bromination and oxymercurations with charge-transfer (CT) transition energies for the electron donor–acceptor (EDA) complexes. In this report, steric terms are developed for olefin–bromine and olefin–mercury (II) interactions. However, this is at odds with the previous report that the rate of bromination of an alkene is dependent upon alkene ionization potential (IP), with no steric effects.[1a] In both studies, the range of alkene steric requirements is nicely broad, while the range of electronic effects in the alkenes is rather narrow. An investigation employing alkenes with functionalities that exert pronounced electronic effects seemed appropriate, and our recent correlations prompted us to include hydroboration[2,4a] as well as oxymercuration[4b,5] and bromination.[4b,5]

Some similarities among these reactions should be mentioned: (1) In the Hammett and Taft plots, the ρ values obtained for oxymercuration ($\rho^* = -1.0$)[6] and hydroboration ($\rho^+ = -0.5$)[7] were lower than that for bromination ($\rho^* = -3.0$).[1a] This provides useful information concerning electronic effects in these reactions, but none for steric effects. (2) Generally, steric requirements of the alkene (specifically at the site of carbon–metal bond formation) preside over electronic effects in hydroboration[2a] and oxymercuration,[4a] in contrast to bromination.[1m] (3) The correlation of relative reactivities of a group of sterically dissimilar olefins with the π IP's[1a] is excellent for bromination, fair for oxymercuration, and poor for hydroboration. (4) In each of the three reactions, the possibility of a three-centered intermediate has been proposed.

Various efforts to separate electronic and steric effects, such as the Hammett and Taft correlations mentioned earlier and the inclusion of steric effects (quantified from EDA complexes) in correlation of the relative reactivities, have disadvantages. In the former, the remoteness of the functionality causes a lack of sensitivity to electronic effects in reactions that do not have significant charge buildup in the transition state, such as hydroboration.[7] In the latter, the derivation of steric terms must be done with great care, and the correlation with an intermediate makes inherent assumptions concerning the similarity between that intermediate and the transition-state structure of the rate-determining step.[4b] Therefore, we report correlations of bromination, oxymercuration, and hydroboration, using alkenes with functionalities that exert pronounced electronic effects and yielding an unambiguous separation of steric effects.

Theoretical Procedure

The HOMO energy level calculations were carried out with the MNDO molecular orbital approximation for several reasons: (1) The programs have been parametrized for a wide variety of

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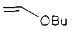
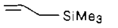
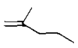
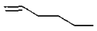
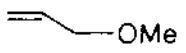
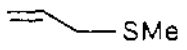
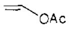
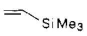
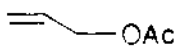
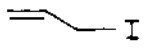
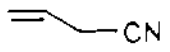
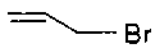
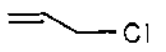
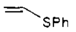
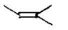
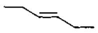
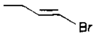
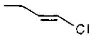
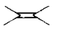
Table I. Ionization Potentials and Relative Rates of Reaction of Alkenes

			HOMO	relative reactivity		
no.	alkene	IP,[a] eV	energy level	hydroboration (9-BBN)	oxymercuration ($Hg(OAc)_2$)	bromination[b] (Br_2)
1		−9.07	−9.92	1615		
2		−8.85	−9.61	300		
3		−9.08	−9.79	196[c]	1000[d]	895
4		−9.48	−9.97	100	100	100
5		−9.44	−10.17	32.5	31.8	7.20[e]
6		−9.95[f]	−10.10[g]	26.1		
7		−9.85	−10.03	22.8		
8		−9.82	−10.04	22.8	25.4	
9		−10.09[h]	−10.34	21.9		0.72
10		−9.75[f]	−10.17	7.1[i]		
11		−10.18[h]	−10.53	5.9		0.7
12		−10.18	−10.32	4.5[i]		
13		−10.34	−10.48	4.0[i]	2.36	0.06
14		−10.5[k]	−10.39[g]	2.71		
15		−8.68	−9.63	1.13[i]	25.8[d]	1.40 × 10^5
16		−8.95	−9.76	0.68[i]	11.7[d,j]	9.76 × 10^3
17		−8.97	−9.76	0.32[i]	3.54[d,j]	3.57 × 10^3
18		−9.12		0.95[c]		4.05 × 10^3
19		−9.82	−10.05	0.011[i]		
20		−10.00	−10.16	0.003[i]		
21		−8.3	−9.49	0.006[i]	1.27[d]	1.40 × 10^6

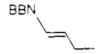
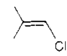
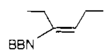
[a] First IP, ref 2. (IP's are given as negative numbers in order to facilitate comparison with HOMO's.) [b] Reference 4c. [c] Reference 8. [d] Reference 9. [e] For the corresponding ethyl ether. [f] Second IP. [g] For NHMO. [h] Reference 10. [i] Reference 11. [j] For the corresponding 2-pentenes.

Table II. Demonstration of the effect of HOMO AO Coefficient upon the Regiochemistry of Hydroboration Using 9-BBN of Allylic Compounds $H_2C{=}CHCH_2X$

	AO coefficients			regiochemistry
X	C_1	C_2	Δ	of C_1:C_2
$SiMe_3$	0.645	0.582	0.063	>99:<1[a]
BMe_2	0.674	0.627	0.047	>99:<1[b]
Pr	0.686	0.664	0.022	>99:<1[c]
I	0.653	0.635	0.018	>99:<1[d]
NMe_2	0.673	0.662	0.011	70:30[e]
SMe[f]	0.667	0.661	0.006	97.6:2.4[g]
Br	0.666	0.668	−0.002	99:1[d]
OMe	0.688	0.698	−0.010	98.4:1.6[h]
CN	0.684	0.698	−0.014	98:2[i]
Cl	0.671	0.687	−0.016	98.9:1.1[h]
OAc	0.680	0.703	−0.023	97.6:2.4[h]

[a] Reference 11b. [b] Reference 11c. [c] Reference 11d. [d] Reference 11a. [e] Reference 17. [f] NHMO. [g] This work and reference 14. [h] Reference 15. [i] Reference 16.

Table III. Calculated HOMO Energy Levels and Relative Rates of Hydroboration of Additional Alkenes

no.	alkene[a]	rel react.[b]	HOMO energy level, eV
22		7.97	−9.60
23		2.98	−9.58
24		0.0045	−10.02
25		0.00332	−9.76

[a] BBN = borabicyclo[3.3.1]nonyl. [b] Reference 11.

elements.[18b,21-22] (2) MNDO can easily accommodate relatively large molecules; this was helpful, since we wanted to use models as close to the actual reactants as possible. (3) The program was conveniently obtained through QCPE,[23] equipped with additional parameters,[22] converted to VS FORTRAN 77, and adapted to run on an IBM 3081 computer.

The calculations were carried out with the recommended procedure.[24] Thus, the geometries of stable species were found by minimizing the total energy by the standard Davidon–Fletcher–Powell[25,26] optimization procedure. The minimum energy geometry of each compound was used for our studies. To ascertain that we had located the true minimum energy geometry rather than a local minimum, for each compound we carried out a series of geometry optimizations using starting geometries with dihedral angles of 0°, 30°, 60°, 90°, 120°, 150°, and 180°. For each alkene, all optimized geometries were compared, and data from the one with the lowest heat of formation are reported.

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(23) *QCPE 353*.

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(25) Davidon, W. C. *Comput. J.* **1968**, *10*, 406–10.

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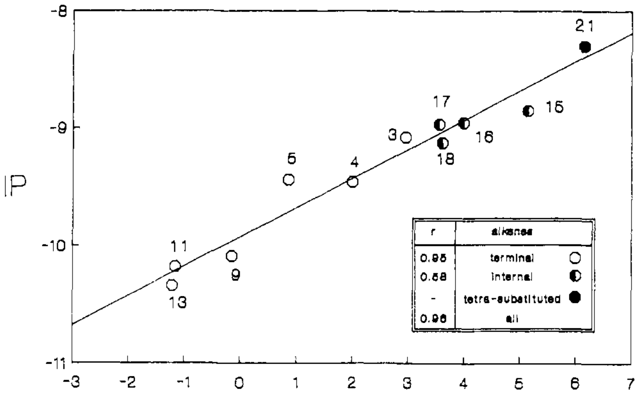


Figure 1. Plot of log *k*(rel) for bromination of alkenes using Br_2 versus alkene IP. Numbers next to data points refer to alkenes in Table I. All alkenes, Regardless of steric requirements, lie on one line, which has an excellent correlation constant; this indicates that the reaction is independent of steric effects. Legend for octagon type versus site of Br–C bond formation: open, H_2C; half-filled, HRC; filled, R_2C.

Results and Discussion

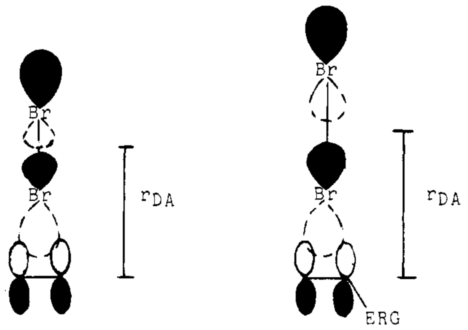
Relative reaction rates of bromination using Br_2, oxymercuration using $Hg(OAc)_2$, and hydroboration using 9-BBN, of a variety of alkenes having substituents that differ widely in steric and electronic effects are tabulated along with their IP's in Table I. The functionalized alkenes chosen undergo reaction with high regioselectivity ≥97% to place boron or mercury at one carbon of the double bond (the left carbon as drawn in Tables I and III). The alkenes are grouped according to the degree of substitution: terminal and di- and trisubstituted alkenes. For each of the three reactions, within each group of sterically similar alkenes, a dependence of relative reactivity upon IP is apparent: as the IP is increased, the rate of reaction decreases. In the allylic position, electron-withdrawing substituents, such as halo, methoxy, and acetoxy, reduce the rate of reaction, while electron-donating ones, such as trimethylsilyl, increase the rate, probably mainly through hyperconjugation. In the vinylic position, substituents that withdraw electron density through induction or conjugation, such as halo, or through hyperconjugation, such as trimethylsilyl, reduce the rate; those that donate electron density conjugatively, such as butoxy, increase the rate. However, comparing the general relative rates of the sterically similar groups themselves, as a means of gaining information upon the steric effects, leads to different results and conclusions, which are discussed below.

A. **Bromination.** A general trend is observed by comparing the sterically similar groups to one another: more highly substituted alkenes react more rapidly. This seems to indicate the lack of a steric effect. However, a more rigorous evaluation can be made from a plot and correlation coefficient. The correlation becomes obvious by plotting the IP versus log *k*(rel) (Figure 1). This yields a linear relationship for all alkenes, regardless of steric requirements. An excellent correlation is demonstrated by the correlation constant (0.96).[12] Such correlations indicate that experimental IP's of alkenes not yet investigated can be used to predict relative rates of bromination. The correlation between the relative reactivities and a characteristic (the IP's) of the alkenes is in keeping with the generally accepted designation of formation of the complex, which is reactant-like, as the rate-determining step.[1c–f,j,k] The lack of steric effects in the transition-state structure of this step seems logical because the bromine atoms are rather remote from the alkyls attached to C=C. It might be argued that the same conclusion could have been reached from the data compiled in Freeman's review.[1a] However, the clustering in his plot of IP versus relative reactivity, due to a lack of functionalized alkenes, raised some doubts and prompted our examination.

The conclusion that there is a total lack of steric effects in bromination of alkenes is at odds with an earlier investigation.[4b] In that study, steric terms were derived for bromination and oxymercuration and included in order to obtain a set of identical log *k*(rel) for the reactions. However, the discrepancy may be due to the manner of derivation of the steric terms; the assumption was made that the steric terms were proportional to the interaction energy ω, the largest contributor of which is the electrostatic work term $(-e^2/r_{DA})$.[13]

$$\epsilon = \Delta E/2.3RT = (\omega - \omega_0)/2.3RT = -e^2/\Delta r_{DA}$$

It is true that increasing the degree of substitution of the double bond could increase r_{DA} due to steric interactions, giving a positive ϵ. This would result from a greater separation of Br_2 from the alkene. However, increasing the degree of substitution of the double bond could also increase r_{DA} due to electronic effects. Increasing the substitution, and thereby the π electron density, not only would cause tighter complex formation, but it would also lead to a greater donation of electron density into the σ^* on Br_2. This increases the Br–Br bond length and moves the anionic center of the EDA complex farther out (ERG = electron releasing group). In light of our results that the steric effects are negligible, it is likely that the ϵ values reported earlier are to some degree due to these electronic effects.



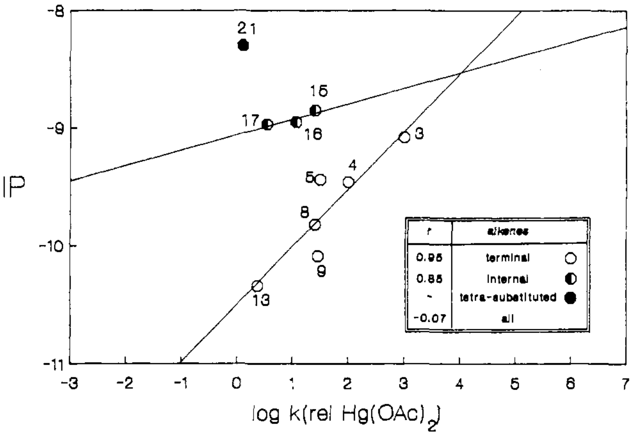


Figure 2. Plot of log *k*(rel) for oxymercuration of alkenes using $Hg(OAc)_2$ versus alkene IP. Numbers next to data points designate alkenes in Table I. There is a natural separation of sterically similar alkenes. However, within sterically similar groups, there is a very good correlation between log *k*(rel) and IP. Legend for octagon type versus site of Hg–C bond formation: open, H_2C; half-filled, HRC; filled, R_2C.

B. **Oxymercuration.** When the sterically similar groups are compared, a general trend in relative reactivities is again observed: less highly substituted alkenes react more rapidly. This trend is opposite to that observed for bromination. This suggests an overriding steric effect, which is confirmed by plotting the data (Figure 2). The correlations of IP's versus relative reactivities for the terminal (r = 0.95) and internal di- or trisubstituted (r = 0.85) alkenes are very good.

This suggestion of an overriding steric effect contrasts with that obtained from the plot of IP's versus relative reactivities for compiled data previously reported.[1a] However, the use of a small number of alkenes without functionalities that introduce adequate electronic effects is probably the problem here. The presence of such a steric effect agrees with findings in the earlier study by Kochi et al.[4b] The effect upon Δr_{DA} due to electronic effects and electron donation into the LUMO should be less here than in

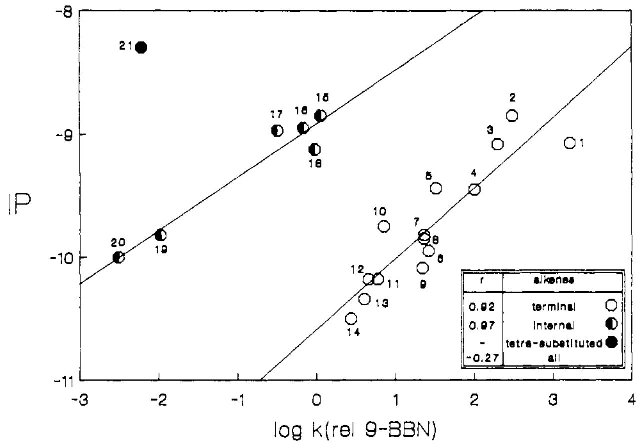


Figure 3. Plot of log k(rel) for hydroboration of alkenes using 9-BBN versus alkene IP. Numbers next to data points refer to alkenes in Tables I and III. The natural separation of sterically similar alkenes is more pronounced here than in oxymercuration, indicating a greater influence by steric requirements here. Within sterically similar groups, there is an excellent correlation between log k(rel) and IP. Legend for octagon type versus site of B–C bond formation: open, H_2C; half-filled, HRC; filled, R_2C.

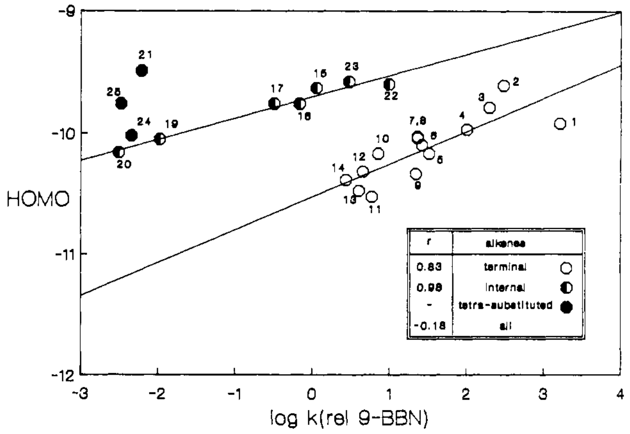


Figure 4. Plot of log k(rel) for hydroboration with alkene π MO (usually HOMO), displaying almost as good a correlation as with IP's. Legend for octagon type versus site of B–C bond formation: open, H_2C; half-filled, HRC; filled, R_2C.

bromination since the Hg–O bonds are at a rather large angle to r_{DA}.

It is surprising that a characteristic of the reactants (the IP's) or of the EDA complexes (the $h\nu_{CT}$'s) shows a good correlation with the relative rates of oxymercuration, if the rate-determining step is indeed nucleophilic attack upon the mercuronium ion.[27] An explanation might be that the mercuronium ion is sufficiently similar in structure to the alkene for the correlation to hold. However, if the rate expression for oxymercuration is of the form rate $K_{eq}k_2$ [A][B],[28] it is possible that the trend in rates could reflect a diminution in K_{eq} and not in k_2.

C. Hydroboration. Comparison of relative reactivities of sterically similar groups yields the same trend as was observed in oxymercuration: less highly substituted alkenes react more rapidly. A plot (Figure 3) of log k(rel) versus alkene IP confirms the separation of reactivities due to differing steric requirements of the groups of alkenes. Correlation coefficients for terminal (r = 0.92) and internal di- or trisubstituted (r = 0.97) alkenes are excellent. The natural separation of sterically similar alkenes is more pronounced than in oxymercuration, indicating a greater influence by steric requirements here. This is logical since the length of the partially formed boron–carbon bond is shorter than that of the mercury–carbon bond.

The similar plot of IP versus relative reactivity reported earlier[1a] did not reveal the separation due to steric requirements of the alkenes probably because of the limited number and substitution of alkenes included. The steric effects at the site of carbon–metal bond formation preside over the IP's and, more importantly, over the steric effects at the other terminus of the original C=C bond (e.g., the rate increase for 2-methyl-1-pentene compared to that for 1-hexene). This implies that, in the transition state of the rate-determining step, the metal is not bound equally to both carbons of the C=C bond. While these results do not identify the rate-determining step of either of these reactions, they do rule out such steps in which the metal is oriented symmetrically with respect to the π bond throughout (such as rate-determining π-complex formation).

The correlation of relative rates with the MNDO values for alkene HOMO's (Table I and Figure 4) is almost as good as with IP's. This would be expected, since the value for the first IP is usually the energy required to remove an electron from the π MO, and the correlation between the experimental IP's and our MNDO π MO energy levels is excellent (r = 0.94). From a practical standpoint, these excellent correlations indicate that such MNDO values could be used to predict relative π IP's or relative rates of hydroboration. In a few cases, the π MO is not the HOMO but the next highest molecular orbital; in these cases, values for the latter are given and designated in the tables by NHMO.

The π MO's also appear to affect the regiochemistry. The π MO atomic orbital coefficients for C_1 and C_2 are given for several allylic compounds in Table III. The differences ($C_1 - C_2$) and the regiochemistry for hydroboration of each alkene are also tabulated. In general, as the $C_1 - C_2$ difference diminishes, the regiochemistry favors C_1 less. There is one glaring exception, allyldimethylamine, in which the reduced regioselectivity is probably due to complexation of 9-BBN with nitrogen, which delivers boron to the nearer end of the double bond.[27] Recently, it was shown that the regioselectivity in this reaction can be shifted to favor C_1 more by employing a complex of the amine.[17c] Thus, the characteristics of the π MO influence the regioselectivity as well as the rate of hydroboration. This also indicates an unsymmetrical transition state in the rate-determining step. Such a transition state could be a four-centered or an unsymmetrical three-centered structure.[18] However, our results give no indication of whether such a transition state would be preceded by a π complex intermediate.[18c–e]

Conclusion

Excellent correlations of the alkene π IP's with the relative rates of hydroboration, oxymercuration, and bromination of alkenes are demonstrated. The linearity of these correlations using many more data points is obviously much improved over previous such correlations. In hydroboration, characteristics of the alkene π MO's correlate not only with the relative rates of reaction but also with the regioselectivities. This indicates an unsymmetrical reactant-like transition state in the rate-determining step for hydroboration. The correlation of relative rates of bromination versus IP's seems effectively independent of steric effects. Conversely, there is a natural separation of groups of alkenes differing sterically at the site of carbon–metal bond formation in oxymercuration and hydroboration. This pronounced separation demonstrates the importance of steric effects at that site in the transition state of the rate-determining step in each of those reactions.

Experimental Section

General Data. The general procedures for manipulation of boron reagents are given elsewhere.[11d] The preparation of 9-BBN[19] and the distillation of THF[11d] have been previously described. The alkenes were purchased from Aldrich Chemical Co., except for the following: 3-(trimethylsilyl)propene, Fluka Chemical Corp.; vinyltrimethylsilane and 3-methoxypropene, Columbia Organic Chemicals, Co.; 3-(dimethylamino)propene, Pfaltz and Bauer Research Chemicals. The alkenes were distilled under nitrogen from a small amount of calcium hydride and then stored under nitrogen. Some functionalized alkenes, which were not

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[27] (a) Kitching, W. *Organomet. Chem. Rev.* **1968**, *3*, 61. (b) Bach, R. D.; Richter, R. F. *Tetrahedron Lett.* **1973**, 4099.

[28] Lewis, A. *J. Org. Chem.* **1987**, *52*, 3099.

stable to the hydride/distillation, were stirred over 4-Å molecular sieves, sparged with nitrogen, and stored under nitrogen. The alkanes used as internal standards were obtained from the Humphrey Chemical Co. and were used as received. A solution of 9-BBN in THF was made and standardized prior to use according to the literature procedure.[11d]

Instruments. The GC analyses were carried out on a Hewlett-Packard 5790A gas chromatograph equipped with a flame ionization detector and 3.2-mm-o.d. columns. The chromatograph was connected to a Hewlett-Packard 3390A integrator for determining peak areas. The following GC columns were used: 4 m of 10% SE-30 on 100/120-mesh Chromosorb W; 6 m of 10% Carbowax 20M on 100/120-mesh Chromosorb W; 2 m of OV-17 on 100/120-mesh Chromosorb W. The GC/MS spectra were obtained on a Hewlett-Packard 5985 gas chromatograph/mass spectrometer/data system equipped with 2 m of a 3.2-mm-o.d. column packed with 3% SE-30 on 100/120-mesh Chromosorb W.

Oxymercuration. Reversibility of Oxymercuration. Since oxymercuration can be reversible under the conditions employed here, it was necessary to ascertain the irreversiblity of a reaction before it could be used in a competitive study. Irreversiblity had been established for the nonfunctionalized alkenes,[9] 3-chloropropene,[5f] vinyltrimethylsilane,[5d] and 3-methoxypropene.[5e]

The relative reactivities of the alkenes were determined by competitive reactions, using the following typical procedure:[9] 10 mmol each of two olefins was introduced into 50 mL of 80% aqueous THF. The solution was cooled to 0 °C. Then, 10 mmol of mercuric acetate was added to the stirred solution. After the solution was stirred for a sufficient time to ensure complete reaction, 10 mL of 0.5 M sodium hydroxide was added followed by 10 mL of 0.5 M sodium borohydride in 3 N sodium hydroxide. A suitable internal standard was added. After the precipitated mercury had coagulated, the aqueous phase was saturated with sodium chloride and potassium carbonate, and the organic layer was analyzed for residual alkenes. In all cases, the total equivalents of alkenes consumed was consistent with the equivalents of $Hg(OAc)_2$ used. The alkene pairs studied by competitive oxymercuration include the following: 3-chloropropene/2-methyl-1-pentene, 3-chloropropene/3,3-dimethyl-1-butene, vinyltrimethylsilane/cyclohexene, 3-methoxypropene/cyclohexene.

Hydroboration. Irreversibility of Hydroboration. The irreversibility of hydroboration under the conditions employed here has been established.[11]

Competitive Reactions. The relative reactivities of the alkenes were determined by competitive reactions, which were carried out as follows:[8] A total of 10 mL of THF was injected into a flask, which had been baked at 140 °C for 24 h, cooled under a flow of nitrogen, and equipped with an adapter and a magnetic stirring bar. A total of 1 equiv (5 mmol) of each of the two alkenes to be compared was added via syringe. Then 0.5 equiv (2.5 mmol) of an *n*-alkane was added as an internal standard. After a small amount of the solution (1 μL) was removed for analysis, 1 equiv of 9-BBN (5 mmol) in THF solution was injected. The temperature was maintained at 25 °C, and the solution, stirred for 24 h. The contents of the flask were then analyzed by GC to determine the amounts of the residual alkenes. In all cases, the total equivalents of alkenes consumed were consistent with the equivalents of 9-BBN employed. The alkene pairs thus studied include the following: 1-hexene/3-(trimethylsilyl)propene, 1-hexene/2-propenylethanoate, 3,3-dimethyl-1-butene/2-propenylethanoate, 1-hexene/3-(methylthio)propene, 3,3-dimethyl-1-butene/3-(methylthio)propene, 1-hexene/3-methoxypropene, 3,3-dimethyl-2-butene/3-methoxypropene, 1-hexene/3-butenenitrile, 2-methyl-2-butene/3-butenenitrile, cyclopentene/3-butenenitrile, 3,3-dimethyl-1-butene/3-butenenitrile, 1-octene/vinyl acetate, 1-octene/vinyltrimethylsilane, 1-hexene/vinyl phenyl sulfide, 2-methyl-2-butene/vinyl phenyl sulfide, 1-octene/vinyl butyl ether, 2-methyl-1-pentene/vinyl butyl ether, 2,3-dimethyl-1-butene/*trans*-1-bromo-1-butene, cyclohexene/*trans*-1-bromo-1-butene, 1-chloro-2-methylpropene/2,3-dimethyl-2-butene.

Regioselectivity in Hydroboration of 3-(Methylthio)propene. Hydroboration of 3-(methylthio)propene (5 mmol) with 9-BBN was performed as above, and after it was stirred overnight, the contents were oxidized with 1.83 mL of 3 N sodium hydroxide and 1.63 mL of H_2O_2 (31%) solution. After the solution was stirred for 1 h, the aqueous layer was saturated with sodium chloride and the THF layer separated and dried over anhydrous $MgSO_4$. The GC/MS of the solution was run, and the peaks were identified and weighed. The ratio of 3-(methylthio)propan-1-ol to 3-(methylthio)propan-2-ol was found to be 97.6 to 2.4.

Calculation of Relative Reactivities. For maximum precision, the relative reactivity of alkenes in each pair compared should be less than 7. If it is greater, the residual amounts of the two alkenes differ greatly, and there will be an undesirably high error in the measurement of the alkene present in lower concentration. Therefore, an initial value of the reactivity of each functionalized alkene was determined through a competitive reaction with 1-hexene. If this number was greater than 7, it was refined by carrying out a competitive reaction of the functionalized alkene with another alkene having a similar, previously determined reactivity. In these cases, internal consistency of the relative reactivities was expected and observed. The relative rates were calculated according to the Ingold–Shaw equation.[20] Each reaction was run in triplicate, and the average is reported.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research. We also appreciate the support of the Research Corp. and the National Science Foundation.

Registry No. 1, 111-34-2; **2**, 762-72-1; **3**, 763-29-1; **4**, 592-41-6; **5**, 627-40-7; **6**, 10152-76-8; **7**, 108-05-4; **8**, 754-05-2; **9**, 591-87-7; **10**, 556-56-9; **11**, 109-75-1; **12**, 106-95-6; **13**, 107-05-1; **14**, 1822-73-7; **15**, 513-35-9; **16**, 7642-09-3; **17**, 13269-52-8; **18**, 590-18-1; **19**, 32620-08-9; **20**, 7611-87-2; **21**, 563-79-1; **22**, 116504-05-3; **23**, 116504-06-4; **24**, 513-37-1; **25**, 69322-51-6; 9-BBN, 280-64-8; $Hg(OAc)_2$, 1600-27-7; $H_2C{=}CHCH_2BMe_2$, 44389-67-5; $H_2C{=}CHCH_2NMe_2$, 2155-94-4.

Reactivity of Polycyclic Aromatic Aryl Radicals

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Abstract: Results of experimental and theoretical studies of the properties and reactions of polycyclic aromatic aryl radicals are reported. Reactions of phenyl, 1- and 2-naphthalenyl, and 9-anthracenyl radicals with toluene and naphthalene were examined in the gas phase at 400 and 450 °C. Arylation rates for each radical were measured relative to hydrogen abstraction from toluene (k_{ar}/k_{abs}). For reactions with toluene of both phenyl and 2-naphthalenyl radicals, this ratio was 0.20–0.25. For the 1-naphthalenyl and 9-anthracenyl radicals, these ratios were signficantly lower (0.05 and 0.01, respectively). Relative rates for arylating the different available positions in toluene and naphthalene, however, were not nearly as different. Differences in arylation/abstraction rates of the different radicals are explained in terms of differing degrees of reversibility for the initial addition step. Results are consistent with literature dissociation rate constants measured by Ladaki and Szwarc for aryl bromides. MNDO calculations on a range of arene–aryl radical pairs suggest that these differences originate primarily from differences in radical stabilities. Calculations also suggest that, on the basis of bond strengths, aryl radicals can be roughly divided into three groups, which depend on the nature of the two neighboring aromatic carbon atoms and are independent of the size of the aromatic cluster.

A wealth of information on the reactivity of phenyl and substituted phenyl radicals is available.[1-8] Their ubiquity, relative ease of generation, and high reactivity are responsible for the large number of studies in this area. However, there exist little data