Pergamon

Tetrahedron Letters 40 (1999) 5823–5826

TETRAHEDRON
LETTERS

SELECTED ELECTROPHILIC ADDITION REACTIONS OF REPRESENTATIVE ACYCLIC ALKENES

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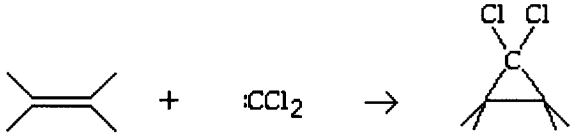
Received 17 May 1999; accepted 7 June 1999

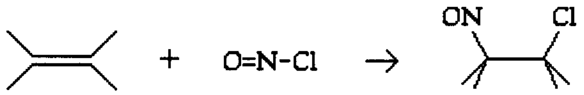
Abstract: In the reactions of dichlorocarbene, nitrosyl chloride, and osmium tetroxide with representative acyclic alkenes, alkene first ionization potentials (IP's) are correlated against log alkene relative reactivities (k_{rel}'s). Each reaction gives a single line of correlation, which includes all alkenes studied regardless of the degree of substitution.

We have reported a method of comparing steric and electronic effects in electrophilic addition reactions involving three-membered cyclic intermediates or products by correlating the ionization potentials (IP's) or highest occupied molecular orbital energies (HOMO's) versus the relative reactivities (k_{rel}'s) of representative acyclic alkenes.[1] In these studies, reactions having similar mechanisms gave similar correlation plots. In some reactions, the plot yields a single line of correlation which includes all alkenes studied,[1a,b] indicating that steric effects in the reactions of those alkenes are of a similar order of magnitude. In those cases, the rate-determining step leads to formation of a three-membered cyclic intermediate or product. In other reactions, the plots show correlations with IP's only among sterically similar alkenes, with a separate line of correlation for each group of sterically similar alkenes,[1a] indicating that steric effects of different groups are of different orders of magnitude, depending upon the steric requirements about the double bonds.

Most of our investigations pertained to reactions with three-membered intermediates or products,[1a,b] so it followed that the investigation of the addition of dichlorocarbene (eq. 1) should be included, since it is an example of a single-step kinetic reaction yielding a three-membered cyclic product with no intermediate.[2] However, it also seemed desirable to extend our investigations to additional and different types of mechanisms. The addition of nitrosyl chloride (eq. 2) is an example of a single-step reaction proceeding through a cyclic four-membered transition state.[3] The rate-determining step in the addition of osmium tetroxide (eq. 3) is also believed to proceed via a cyclic four-membered transition state.[4] Therefore, we have studied the reactions of dichlorocarbene, nitrosyl chloride, and osmium tetroxide with representative alkenes.



(1)



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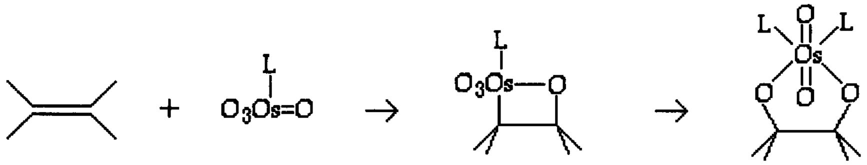

(3)

RESULTS AND DISCUSSION

Experimental first IP's for the alkenes, their HOMO's calculated using MNDO, and relative rates of the reactions listed above are given in Table I. Calculations were carried out by using the MNDO molecular orbital

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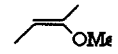
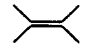
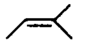
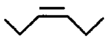
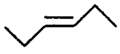
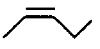
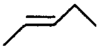
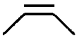
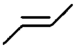
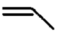
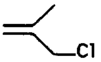
PII: S0040-4039(99)01149-1

Table I. Alkene IP's, HOMO's, and Relative Reactivities for Addition of CCl_2, of NOCl, and of OsO_4.

				relative reactivity		
no.	alkene	IP[a] (eV)	HOMO	$:CCl_2$[b]	NOCl[c]	OsO_4[d]
1		-8.25[e]	-9.52	2.04×10^4		
2		-8.27	-9.49	2.76×10^4	$>6.25 \times 10^4$[f]	2300[g]
3		-8.68	-9.63	1.098×10^4	3.33×10^5	470.0[h]
4		-8.95	-9.76		3.52×10^3	200.0[i]
5		-8.97	-9.76		6.67×10^3	420.0[j]
6		-9.04	-9.77		9.26×10^3	
7		-9.04	-9.76		1.630×10^4	
8		-9.08	-9.79		2.41×10^3	
9		-9.12	-9.79	1.150×10^3	7.78×10^3	
10		-9.12	-9.78		1.463×10^4	
11		-9.24	-9.80	3.364×10^3	4.44×10^3	130.0[k]
12		-9.45	-9.96		20.4	
13		-9.48	-9.97	100.0[l]	100.0	100.0[m]
14		-9.63	-9.94	104.9	94.4	
15		-9.74	-9.97	138.3		
16		-10.09[n]	-10.20		18.12[f]	

[a] Ref. 5a unless noted otherwise; IP's used in the plot for reaction with OsO_4 are given in the footnotes below.

[b] Ref. 2a.

[c] Ref. 3a.

[d] Ref. 4a, relative to 1-undecene.

[e] Ref. 5b.

[f] Ref. 4b

[g] Data for 2,3-dimethyl-2-octene, IP = -8.13 eV.

[h] Data for citronellyl benzoate, HOMO = -9.65 eV, interpolated IP = -8.70 eV.

[i] Data for Z-5-decene, IP = -8.77 eV.

[j] Data for E-5-decene, IP = -8.76 eV.

[k] Data for 2-methyl-1-tridecene, HOMO = -9.74 eV, interpolated IP = -9.18 eV.

[l] Data for 1-pentene, IP = -9.52 eV.

[m] Data for 1-undecene, HOMO = -9.94 eV, interpolated IP = -9.45.

[n] Ref. 5c.

approximation for reasons and with procedures which have been discussed previously.[1] The alkenes are listed in order of increasing IP's, which places the alkenes generally in the order of decreasing HOMO energy levels and decreasing relative reactivities. In order to demonstrate more clearly the correlations, the alkene IP's are plotted versus the log k_{rel}'s, and the correlation coefficient r is given for each group (Fig. 1). A variety of substitution about the double bond in each study, from mono- to tetrasubstituted, explores steric requirements about the double bond. Comparison of alkene relative reactivities against IP's in order to explore steric effects is appropriate, because IP's are not themselves sensitive to steric effects.

A. Reactions with three-membered transition state structures.

The correlation of IP with log k_{rel} for dichlorocarbene addition to alkenes (Fig. 1a) is very strong (r = 0.94). The single line of correlation indicates that steric effects are of the same order of magnitude for all alkenes studied, regardless of steric requirements. The positive slope is appropriate for a reaction which is considered to be an electrophilic addition. Similar results were obtained in the studies of other electrophilic additions to alkenes in which the rate-determining step leads to formation of a cyclic three-membered intermediate or product: (1)bromine addition,[1a] (2)arylsulfenyl chloride addition,[1b] and (3)oxidation via peracetic acid.[1b]

A factor common to all four of the above reactions is the nature of the reaction pathway in the rate-determining

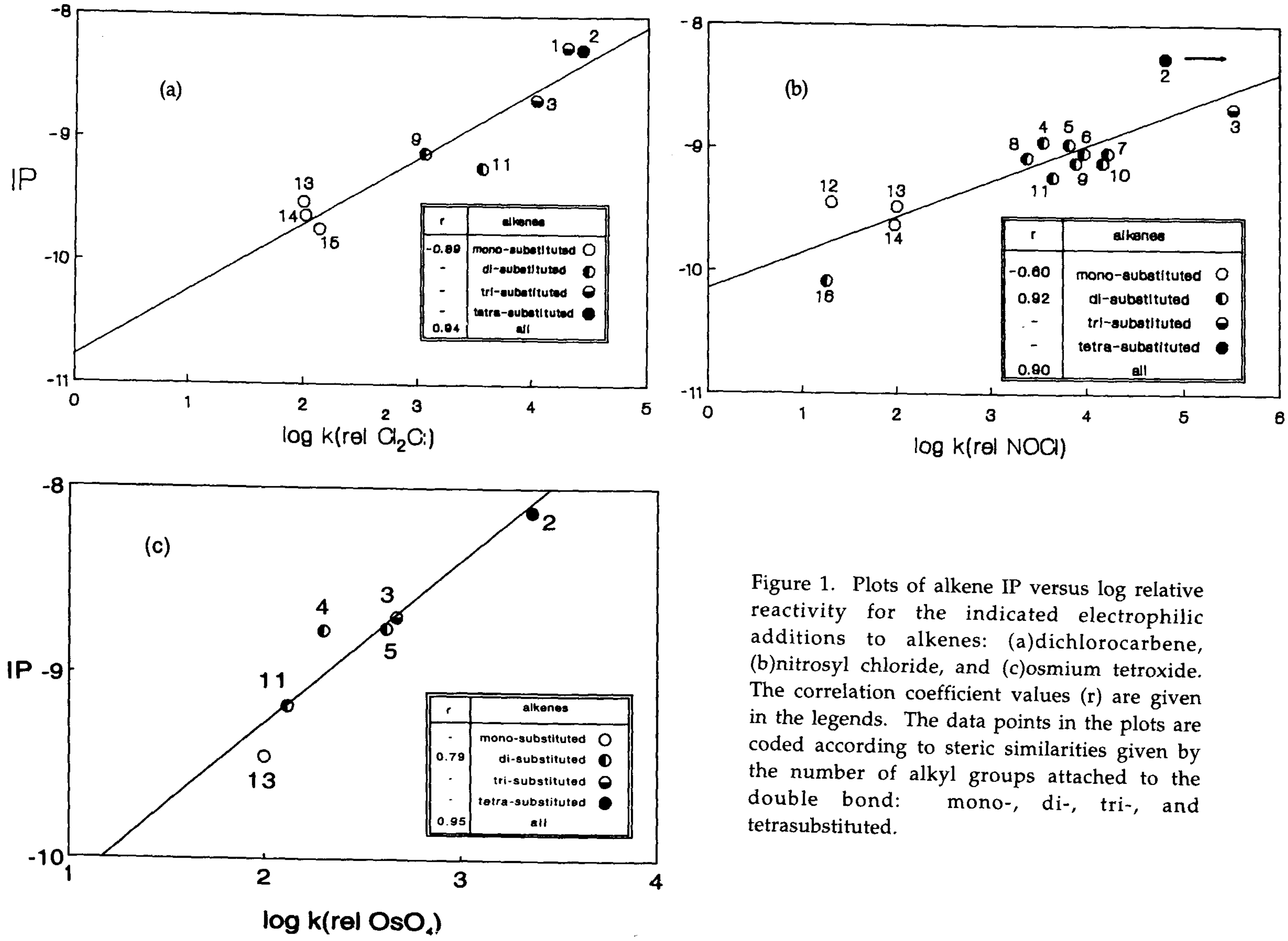


Figure 1. Plots of alkene IP versus log relative reactivity for the indicated electrophilic additions to alkenes: (a)dichlorocarbene, (b)nitrosyl chloride, and (c)osmium tetroxide. The correlation coefficient values (r) are given in the legends. The data points in the plots are coded according to steric similarities given by the number of alkyl groups attached to the double bond: mono-, di-, tri-, and tetrasubstituted.

step. A symmetrical three-centered geometry is maintained throughout the rate-determining step in each. Apparently, for the alkenes studied, steric effects in their reaction with CCl_2 are of the same order of magnitude regardless of steric requirements about the double bond.

B. Reactions with four-membered transition state structures

Plots and correlations with a single line of correlation for all alkenes studied, similar to those above, are observed for NOCl addition (Figure 1b, r = 0.90) and oxidation with OsO_4 (Figure 1c, r = 0.96). This indicates that steric effects are of the same order of magnitude regardless of steric requirements about the double bond in both of these addition reactions.

The addition of nitrosyl chloride is reported to be a single-step reaction proceeding through a four-membered transition state.[3] The fact that the application of this technique gives different results for nitrosyl chloride addition (a single line of correlation) than for hydroboration[1a] (multiple lines of correlation) is in accord with different mechanisms for these two reactions. This comparison further supports the previous rationale[1a,b] favoring the rate-determining step in hydroboration to be leading from a π-complex through a four-center transition state to the product, rather than a simple concerted four-center reaction.

It is now generally accepted that oxidation with OsO_4 proceeds through a four-centered transition state.[4] Since NOCl addition also is reported[3] to have a four-centered transition state structure, similar plots for the two reactions might be expected. However, π-complex formation leading to the oxaosmetane, which has been isolated and studied,[4e] has also been proposed.[4c,f] The single line of correlation for addition of OsO_4 is also consistent with such rate-determining formation of a π-complex, as has been obtained in other systems.[1a] However, a single line would not be expected if the rate-determining step leads from the π-complex to the oxaosmetane; instead, the results would be expected to be similar to those for oxymercuration and for hydroboration,[1a,b] in each of which the rate-determining step leads from a π-complex to products.[1a,b] The plots for the hydroboration and the oxidation reactions display multiple lines, each line corresponding to a group of alkenes having steric requirements which are similar at the carbon which becomes bonded to the metal. Thus, in OsO_4 addition, this technique can be used to counter the mechanism having a rate-determining step following π-complex formation, but not to differentiate between the concerted four-centered mechanism versus rate-determining π-complex formation.

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