Determination of a New Scale of Steric Substituent Constant E_s* by Means of Hydroboration Reaction

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Abstract: In the case of hydroboration of 2-alkyl-1-propenes, the influence of the alkyl groups on the reactivity is not correctly expressed by the Taft–Ingold relation, when these groups are tertiary. By means of a DARC topological system treatment, a new steric substituent constants E_s* scale is elaborated which seems suitable in reactions for which the transition state is analogous to that encountered in hydroboration.

The Ingold–Taft treatment of polar and steric effects has led Taft[1] to suggest that, in the absence of a noticeable $\rho^*\sigma^*$ polar effect the linear steric effect relationship

$$\log (k/k_0) = \delta E_s \qquad (1)$$

was a satisfactory approximation for the determination of the values of steric substituent constants E_s. The polar effect being small in the acid catalyzed ester hydrolysis, this reaction was selected by Taft as a standard ($\delta = 1$) for the measurement of the steric substituent constants E_s. More generally, in aliphatic chemistry the influence of environmental factors on the reactivity is given by the equation

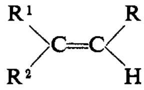
$$\log k = \rho^*\sigma^* + \delta E_s + \log k_0 \qquad (2)$$

provided that both $\rho^*\sigma^*$ and E_s separately fit in with a linear plot against $\log (k/k_0)$. This is true for reactions in which the steric effects involve "the same mechanism as in ester hydrolysis,"[2] *i.e.*, analogous structures in the transition state. Since the time of Taft's fundamental work, many reactions have been investigated, which agree in a quite satisfactory way with relation (2). Nevertheless, we should ask ourselves whether the ionic model of ester hydrolysis could be applicable to other transformation types, such as photochemical reactions, where the transition state seems to exhibit structures which are quite different from those encountered in ester hydrolysis.

The rapid progress in chemical knowledge led us to the idea that some reactions could now exist for which the polar effect would be of less importance than in ester hydrolysis. A detailed investigation of the addition of disiamylborane to 2-alkylpropenes showed us[3–5] that this reaction could be in some cases a more convenient standard for the study of reactions governed by the steric factor. This can already be foreseen by discussing some results[6,7] on hydroboration.

Using diborane and disiamylborane, Brown, *et al.*, carried out two series of experiments with aliphatic compounds (Table I). Whereas the orientation of the diborane addition seems to be influenced by polar substituents, especially when heteroatoms are present, such an effect is not observed in the case of disiamylborane. The discrepancy is particularly sensible in the case of 3-chloro-1-propene and of 3,3,3-trifluoro-2-methyl-1-propene. The quite exclusive orientation of the boron atom of disiamylborane toward the least substituted ethylenic carbon atom could be attributed to the important steric interaction between the two bulky groups of the disiamylborane and the alkyl groups of ethylene.

Table I

			Addition of B atom to the least substituted ethylenic C atom (in parts per 100 parts)	
R^1 =	R^2 =	R^3 =	B_2H_6	$(Sia)_2BH$
Alkyl	H	H	93–94[a]	99[b]
Benzyl	H	H	90[a]	98[b]
Phenyl	H	H	80[a]	98[b]
Ethyl or neopentyl	Methyl	H	99[a]	100[c]
Phenyl	Methyl	H	100[a]	100[c]
Methyl or *tert*-butyl	Methyl	Methyl	98[a]	98[b]
Methoxymethyl	H	H	90[d]	98[d]
Ethoxymethyl	H	H	84[e]	94[c]
Chloromethyl	H	H	60[f]	94[b]
Chloromethyl	Methyl	H	90[g]	100[g]
Trifluoromethyl	Methyl	H	70[h]	98[h]

[a] H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, **82,** 4708 (1960). [b] H. C. Brown and G. Zweifel, *ibid.*, **83,** 1241 (1961). [c] H. C. Brown, "Hydroboration," W. A. Benjamin, New York, N. Y., 1962, p 114. [d] H. C. Brown and M. K. Unni, *J. Amer. Chem. Soc.*, **90,** 2902 (1968). [e] H. C. Brown and O. J. Cope, *ibid.*, **86,** 1801 (1964). [f] H. C. Brown and K. Keblys, *ibid.*, **86,** 1795 (1964). [g] H. C. Brown and E. F. Knights, *Isr. J. Chem.*, **6,** 691 (1968). [h] Reference 3.

Results and Discussions

Brown and Zweifel[8] have shown that the reaction rate of disiamylborane addition to olefins is highly influenced by the number and the position of the ramifications of the alkyl substituents, *i.e.*, the use of this borohydride seems particularly interesting for kinetic studies. We should expect the complete absence of side reactions,

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(1) R. W. Taft, Jr., *J. Amer. Chem. Soc.*, **74,** 3120 (1952); **75,** 4538 (1953).

(2) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, p 229.

(3) R. Fellous, Dr. ès-Sciences Thesis, Nice, 1970; see CNRS registration No. AO 4487.

(4) R. Fellous and R. Luft, *Tetrahedron Lett.*, 1505 (1970).

(5) R. Fellous, R. Luft, and A. Puill, *Bull. Soc. Chim. Fr.*, 1801 (1972).

(6) H. C. Brown and R. L. Sharp, *J. Amer. Chem. Soc.*, **88,** 5851 (1966).

(7) D. J. Pasto and S. Z. Kang, *J. Amer. Chem. Soc.*, **90,** 3797 (1968).

(8) H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, **82,** 4708 (1960).

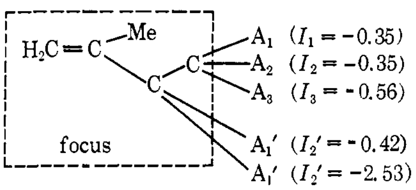

Figure 1.

and well-differentiated values for the rate constants, the disiamylborane being only able to transform into alkyldisiamylborane.

This situation has prompted us to select a series of 2-alkylpropenes for a kinetic study of the addition of disiamylborane. Our detailed working technique for the determination of the absolute rate constants has already been described,[5] and the values of the second-order rate constants are given elsewhere.[4]

An examination of these values reveals that the reactivity decreases by a nearly constant factor when passing from a C_n to a C_{n+1} alkyl group, the entering methylene group being attached to the carbon on the α or β position with respect to the nearest ethylenic carbon. We can express this in the diagram

$$\begin{tikzcd}
k_{\mathrm{et}} \arrow[r, "\times 0.6"] \arrow[d, "\times 0.5"] & k_{\mathrm{Pr}} \arrow[r, "\times 0.4"] \arrow[d, "\times 0.3"] & k_{i\text{-}\mathrm{Bu}} \arrow[r, "\times 0.3"] & k_{neo\text{-}\mathrm{pent}} \\
k_{i\text{-}\mathrm{Pr}} \arrow[r, "\times 0.3"] & k_{s\text{-}\mathrm{Bu}} & &
\end{tikzcd}$$

However, there is one exception: when going from $k_{i\text{-}\mathrm{Pr}}$ to $k_{t\text{-}\mathrm{Bu}}$ the multiplicative factor is only 0.006. This inhibiting "*tert*-butyl effect" is the consequence of a bulky overcrowding in the vicinity of the ethylenic bond and it is much more important than the overcrowding of the *neo*-pentyl group. This situation is not reflected by Taft's E_s scale.

After having discarded the values related to tertiary alkyl groups and introduced the classical values[9] of σ^* and E_s, associated with the corresponding log k values, in eq 2, we can determine the values of ρ^* and δ. The best parametric relation is given by

$$\log k = 0.01\sigma + 0.71E_s - 1.727 \qquad (3)$$

where the correlation coefficient is $r = 0.999$ and Exner test[10] is $\psi = 0.02$. The nearly zero value for ρ^* proves that polar effects have no importance in the transition state of the disiamylborane addition.

The fact that the kinetic results obtained with α-methylstyrene fit eq 3 indicates that even in the rate-determining step of α-methylstyrene hydroboration conjugative effects must be weak. In this context it is possible to simplify eq 3 and to replace it by

$$\log k = 0.72E_s - 1.737 \qquad (4)$$

where $r = 0.996$ and $\psi = 0.10$, when the E_s value for the phenyl group is taken into account for working out this simple regression. When the E_s values for primary and secondary alkyl groups are the only ones used, a much better linear extrathermodynamic relationship is obtained

$$\log k = 0.71E_s - 1.728 \qquad (5)$$

where $r = 0.999$ and $\psi = 0.02$.

Neither relationship 4 nor 5 satisfactorily fits the classical E_s values of tertiary alkyl groups. The best solution to account for this situation would be to work out a new steric substituent constants E_s^* scale, applicable in reactions where the transition state is similar to that encountered in hydroboration of alkenes. For the sake of simplicity, Taft's E_s scale and the new E_s^* scale should be given the same origin, if possible.

A good estimation of the steric substituent effects of a population of chemical substances could be reached by means of the DARC topological system (Documentation-Acquisition-Restitution-Correlation).[11,12] This theory allows the establishment of constitutive relationships associating increments with structural units. To this end the molecules of the populations under examination are hypothetically broken down into two parts: the "focus" or common part of all the molecules of the population and the "environment" of the focus, varying from substance to substance. The focus and the environment are identified unambiguously and associated with the magnitude of physical and chemical properties or comportments of the molecules underlaying the examination by means of a multiple regression analysis.[13]

In the present work on 2-alkylpropenes the focus corresponds to 2-methyl-1-butene (*i.e.*, 2-ethylpropene),[14] and we must retain five structural development directions A_1, A_2,... for each of which the incremental contribution I_1, I_2,... of the first carbon atom to the reactivity against disiamylborane is indicated in Figure 1.

In the reaction of disiamylborane with 2-alkylpropenes the correlation between the logarithm of the rate constants k and the topology of the alkyl groups is given by the linear relationship

$$\log k = \Sigma I_i A_i + \log k_{\mathrm{Et}} \qquad (6)$$

where k_{Et} is the rate constant of the first term of the population. On the other side, log k is related to E_s^*

$$\log k = \delta E_s^* + \log k_{\mathrm{Me}} \qquad (7)$$

(the E_s^* values include the steric parameters of tertiary groups) and the E_s^* values are expressed by

$$E_s^* = [\Sigma I_i A_i + \log (k_{\mathrm{Et}}/k_{\mathrm{Me}})]/\delta \qquad (8)$$

In order to give Taft's E_s scale and the E_s^* scale the same origin, we must take the value 0.71 for δ. Then relationship (8) becomes

$$E_s^* = (\Sigma I_i A_i/0.71) - 0.07 \qquad (9)$$

and the E_s^* values of Table II can be determined.

The differences between the values of the two scales are very important only when tertiary alkyl groups are concerned. This can be explained appropriately by an examination of molecular models taking van der Waals

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(9) See ref 2, p 222 for σ^* and p 228 for E_s.

(10) The Exner test is a measurement of the quality of a correlation. It simultaneously takes into account the correlation coefficient, *r*, the number, *f*, of parameters, and the number, *n*, of experimental points.

(11) J. E. Dubois and H. Viellard, *Bull. Soc. Chim. Fr.*, 900, 905, 913 (1968).

(12) J. E. Dubois, D. Laurent, and H. Viellard, *C. R. Acad. Sci., Ser. C*, **264**, 1019 (1967); *C. R. Acad. Sci., Ser. A*, **268**, 405 (1969).

(13) For an abridgement of the DARC theory see J. E. Dubois, *J. Chromatogr. Sci.*, 9, 220 (1971).

(14) As isobutene (*i.e.*, 2-methylpropene) is gaseous under our working conditions, no kinetic measurement was possible in this case, and the value of the rate constant *k* was extrapolated. For this reason we have selected the following higher term of the series as the focus.

Table II

Alkyl groups	DARC descriptor[a]					$-E_s$ by ester hydrolysis	$-E_s^*$ by hydroboration with $(Sia)_2BH$	$\Delta(E_s^* - E_s)$
	A_1'	A_2'	A_1	A_2	A_3			
CH_3						0	0	
CH_2CH_3	0	0	0	0	0	0.07[b]	0.07	
$CH_2CH_2CH_3$	0	0	1	0	0	0.36[b]	0.56	0.20
$CH(CH_3)_2$	1	0	0	0	0	0.47[b]	0.66	0.19
$CH_2CH(CH_3)_2$	0	0	1	1	0	0.93[b]	1.06	0.13
$CH(CH_3)CH_2CH_3$	1	0	1	0	0	1.13[b]	1.15	0.02
$CH(CH_3)CH(CH_3)_2$	1	0	1	1	0		1.65	
$CH_2C(CH_3)_3$	0	0	1	1	1	1.74[b]	1.84	0.10
$CH(CH_3)C(CH_3)_3$	1	0	1	1	1	3.33[b]	2.43	0.90
$C(CH_3)_3$	1	1	0	0	0	1.54[b]	4.22	2.68
$C(CH_3)_2CH_2CH_3$	1	1	1	0	0	2.17[c]	4.72	2.55
$C(CH_3)_2CH(CH_3)_2$	1	1	1	1	0		5.21	
$C(CH_3)_2C(CH_3)_3$	1	1	1	1	1	3.90[b]	6.00	2.10

[a] When the A_i position is occupied by a C atom we note 1; when this position is not occupied or occupied by a H atom we note 0. [b] See ref 9. [c] See N. B. Chapman, J. R. Lee, and J. Shorter, *J. Chem. Soc. B*, 778 (1969).

radii into account. These clearly show that, in order to reach the transition state between the hydroboration reagent[15] and the 2-alkyl-1-propene, the shapes of tertiary alkyl substituents would be the only strong factor of hindrance. Whatever the real structure[5,17–19] of this transition state could be, it implicates simultaneously the two carbon atoms of the ethylenic linkage.

The present E_s^* scale could be a valuable tool in all the reactions in which the transition state is similar to that encountered in hydroboration of 2-alkyl-1-propenes. Moreover, we have checked[5] that in the reaction of tetrasiamyldiborane with methyl ketones, the E_s^* scale is a suitable expression of the reactivity, in spite of a noticeable polar effect.

Acknowledgments. The authors wish to thank the Centre National de la Recherche Scientifique (France) for financial support (RCP No. 100 Grant) and Professor J. E. Dubois, Laboratoire de chimie organique physique, Université de Paris VII, for fruitful discussions.

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(15) We used THF as solvent in our kinetic studies on the hydroboration of 2-alkyl-1-propenes. In this medium the disiamylborane is present in its dimeric form only.[16]

(16) H. C. Brown and G. J. Klender, *Inorg. Chem.*, 1, 204 (1962).

(17) H. C. Brown and A. W. Moerikofer, *J. Amer. Chem. Soc.*, **83**, 3417 (1961).

(18) T. P. Fehlner, *J. Amer. Chem. Soc.*, 93, 6366 (1971).

(19) P. R. Jones, *J. Org. Chem.*, 37, 1886 (1972).

Aprotic Solvent Effects on Substituent Fluorine Nuclear Magnetic Resonance Shifts. III. *p*-Fluorophenyl-*p*′-substituted-phenyl Systems[1]

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Abstract: Studies of aprotic solvent effects on substituent fluorine nuclear magnetic resonance (F nmr) shifts of *p*-fluorophenyl labeled systems have provided evidence of general significance regarding the nature of solvation of molecules. The correlation of the aprotic polar solvent F nmr shifts with the σ_I parameter of the substituent and the E_T solvent polarity parameter is shown to be highly general. It is concluded that local fields of aprotic polar solvents enhance the electron-withdrawing effects of substituents principally by supporting greater separation of charge in polar σ bonds. In contrast, the π-electronic distribution in a neutral molecule is generally represented by a poorly solvated multipole of centers of relatively small charge spread over an extensive π-electron framework. Consequently, aprotic polar solvents effects show little or no dependence upon the σ_R parameter of the substituent. While the magnitudes of aprotic polar solvent effects on F nmr substituent shifts in a wide variety of systems have been found to be directly related (approximately) to the substituent σ_I value, the direction of the solvent effect in the systems considered depends upon whether shift components due to solvation of polar σ bonds or to the effective dielectric constant are predominant. For para-substituted fluorobenzenes and 10-substituted-9-fluoroanthracenes, the former components are thought to control the shift, accounting for the increasing *downfield* shifts which are observed with increasing substituent σ_I parameter and increasing polarity of the aprotic solvent. A similar result appears to hold for the para ^{13}C nmr substituent shifts for monosubstituted benzenes. In diphenyl systems of the structure I type (data reported herein), the effective dielectric constant component is believed to control the shift direction. As a consequence, the shifts for substituents, *e.g.*, *p*-NO_2, *p*-CN, *p*-CF_3, and *p*-halogen, are expected (as observed) to be increasingly shifted *upfield* with increasing solvent polarity. Although field effects apparently control the aprotic solvent effects on the F nmr substituent shifts for structure I systems, inductive transmission of substituent σ_I effects through the π-electron framework is found to be the dominant factor in the substituent shifts. Further aspects of results and interpretation are discussed.

Recent investigations of structural and medium effects on F nmr substituent shifts have prompted this further study. Relatively effective transmission of the effects of substituents, X, through a variety of neutral and charged cavities for structure I has been found.[2] These F nmr substituent shifts were usefully

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(1) This work was supported in part by the National Science Foundation. We also gratefully acknowledge their support in making available the nmr spectrometer of the University of California, Irvine, Chemistry Department.

(2) S. K. Dayal, S. Ehrenson, and R. W. Taft, *J. Amer. Chem. Soc.*, 94, 9113 (1972).