Bromination of Ethylenic Compounds. 38.[1a] Isoreactivity of Trisubstituted Geometrical Isomers

Daniel Grosjean, Gérard Mouvier, and Jacques-Emile Dubois*

Laboratoire de Chimie Organique Physique de l'Université Paris VII, associé au Centre National de la Recherche Scientifique, 1 rue Guy de la Brosse, 75005 Paris, France,[2] and Laboratoire de Physicochimie Instrumentale de l'Université Paris VII, 75005 Paris, France

Received June 10, 1974

The bromination rate constants of 30 trisubstituted alkenes (A_3) with various small or bulky alkyl substituents, measured in methanol, are high—between 48 and 1.26×10^5 M^{-1} s^{-1}. Comparisons with the reactivities of mono- and disubstituted alkenes show that in the A_3 series, the steric decelerating effect of an alkyl group becomes more important than its polar effect. This steric effect is observed in A_3 for small groups whereas in less substituted olefins it arises only when substituents are bulky. We conclude that the overall congestion of the molecule rather than the individual bulk of each substituent is the principal rate-determining factor in bromination of alkenes. Isoreactivity of *Z–E* isomeric pairs is also observed and is attributed to the preservation of ground state interactions in the bromonium-ion-like transition states. The increasing importance of steric effects with increase in the number of substituents is understood in terms of predominant bromine–substituent interactions in the rate-determining step.

The systematic study of the bromination of ethylenic compounds carried out in this laboratory has enabled us to account for the influence of several parameters on this reaction—structure, solvent, salts,[1] and reactant concentration[3]—and to deepen our knowledge of the mechanism by the discovery of a π complex as the first unstable intermediate whose ionization leads to the σ complex, the intermediate formed in the rate-determining step.[4]

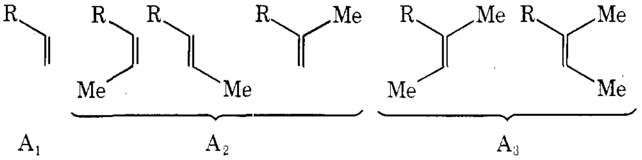
However, it is not easy to set up general and informative structure–reactivity relationships for alkene bromination, for essentially two reasons.[1a,b] Firstly, owing to the fact that the starting substrate is an olefin, there are two carbon atoms concerned by the ionization processes, whereas the empirical substituent parameters are generally defined by reactions involving one carbon atom. Secondly, bromination is influenced by both polar and steric substituent effects. Thus, the reactivity of only a limited number of compounds can be expressed in terms of classical free-energy relationships. Moreover, such relationships can account neither for the reactivity differences of cis and trans alkenes nor for the cumulative but not strictly additive effects of substituents, even when there are only two substituents to the carbon–carbon double bond.

We have therefore studied the reactivity of trisubstituted alkenes in order to determine whether the conclusions based on less substituted alkenes could be transposed to alkenes which are more crowded in the vicinity of the double bond.

Kinetic Results. To extend the data previously obtained[1b] for nine trisubstituted alkenes (A_3), we measured the bromination rate constants of 30 other A_3 in the same conditions—MeOH, 0.2 M NaBr, 25 °C—by the previously described couloamperometric method.[5] The results are given in Table I.

In methanol, in the presence of bromide ions, two brominating agents, Br_2 and Br_3^-, are in equilibrium, $Br_2 + Br^- \rightleftharpoons Br_3^-$, so that the measured rate constants k_{exp} are composite.[6] Elementary rate constants, k_{Br_2} and $k_{Br_3^-}$, were obtained by varying the bromide ion concentration for trimethyl-[7] and dimethyl-*tert*-butylethylenes.[6b] The rate constant[6c] ratios, $Q = 39.4$ and 18, respectively, for these compounds are higher than the limit, $Q = 16$, established for methanol[6b] and below which k_{exp} does not parallel k_{Br_2}. Moreover, the previously determined equation,[6a] $\log k_{Br_2} = \log k_{\text{exp}} + 1.13$, by which k_{Br_2} can be estimated from k_{exp} remains valid here. Consequently, the variations of the overall rate constants in Table I can be used to measure the variations of the elementary rate constants k_{Br_2}.

Attenuation of the Polar Contribution of the Substituents and Enhancement of Their Steric Effects in A_3 Relative to A_2 and A_1 Alkenes. *The contribution of an alkyl group R* to the reactivity of the A_3 population can be compared to that of the same group R in the corresponding mono- and disubstituted alkenes: $CH_2{=}CHR$, $MeCH{=}CHR$, and $MeCH{=}CMeR$ with R = Me, Et, *n*-Pr, *i*-Pr, *sec*-Bu, and *t*-Bu.



The reactivity ratios, $I = k_{\text{exp}}(R)/k_{\text{exp}}(Me)$, which represent the effect of R relative to the methyl, depend markedly on the number of substituents. These ratios shown in Figure 1 reveal an attenuation of the accelerating polar effect of a substituent and a considerable enhancement of its decelerating steric effect when the number of substituents increases from two to three. Thus, the replacement of a methyl by an ethyl group increases the reactivity by a factor of 1.58 for A_1 alkenes, 1.60 for *cis*-A_2, and by only 1.19 for *Z*-A_3. In the same way, the introduction of a *tert*-butyl in the place of a methyl decreases the reactivity by a factor of 2.3 for A_1, 2.0 for *cis*-A_2, and 18.4 for *Z*- or *E*-A_3.

Similar analysis of the reactivity of the *gem-trisubstituted alkenes,* $(R_1)_2C{=}CHR$, reveals a comparable variation of the contribution of an alkyl group. Data on A_1 and A_2 showed that the replacement of a methyl group by an ethyl enhances the reactivity by a factor of approximately 1.5. This factor can legitimately be attributed[1b] to the enhancement of polar effects on passing from methyl to ethyl. This increase in reactivity does not remain valid for the trisubstituted alkenes. For example, the replacement of the two *gem*-methyl groups in 2-methyl-2-pentene by two ethyls diminishes the reactivity. If we calculate the expected increase in reactivity by enhancement of polar effects, the decrease which can be attributed to enhancement of steric effects is a factor of 3.25.

$$\begin{tikzcd}
& 2.25 \times 10^5 \arrow[dr, "\text{steric effects}\ \times 1/3.25"] & \\
\begin{matrix}\text{Me}_2\text{C}{=}\text{CHEt}\\ 1 \times 10^5\end{matrix} \arrow[ur, "\text{polar effects}\ \times 1.5 \times 1.5"] & & \begin{matrix}\text{Et}_2\text{C}{=}\text{CHEt}\\ 7.31 \times 10^4\end{matrix}
\end{tikzcd}$$

Table I. Bromination Rate Constants of Trisubstituted Alkenes

Registry no.	No.	Alkene	k_{exp}, M^{-1} $s^{-1\,a}$
627-97-4	1	$Me_2C{=}CH$-*n*-Bu	7.23×10^4
16993-86-5	2	$Me_2C{=}CH$-*n*-Pe	7.16×10^4
16789-51-8	3	$Et_2C{=}CH$-Et	7.31×10^4
19781-31-8	4	$Et_2C{=}CH$-*n*-Bu	5.76×10^4
4485-13-6	5	*n*-$Pr_2C{=}CH$-Et	2.83×10^4
59643-66-2	6	*t*-$Bu_2C{=}CH$-Et	4.80×10
10574-36-4	7	*Z*-Me-*n*-PrC=CH-Me	4.85×10^4
20710-38-7	8	*E*-Me-*n*-PrC=CH-Me	4.73×10^4
4914-89-0	9	*Z*-Et-MeC=CH-Et	1.26×10^5
3899-36-3	10	*E*-Et-MeC=CH-Et	1.10×10^5
4914-91-4	11	*Z*-*i*-Pr-MeC=CH-Me	2.16×10^4
4914-92-5	12	*E*-*i*-Pr-MeC=CH-Me	2.03×10^4
19550-81-3	13	*Z*-*sec*-Bu-MeC=CH-Me	1.05×10^4
19550-82-4	14	*E*-*sec*-Bu-MeC=CH-Me	1.05×10^4
39761-64-3	15	*Z*-*t*-Bu-MeC=CH-Me	3.63×10^3
39761-57-4	16	*E*-*t*-Bu-MeC=CH-Me	3.60×10^3
42067-48-1	17	*Z*-*i*-Pr-EtC=CH-Me	3.88×10^4
42067-49-2	18	*E*-*i*-Pr-EtC=CH-Me	9.50×10^3
14255-24-4	19	*Z*-*n*-Pr-MeC=CH-Et	5.98×10^4
13714-85-7	20	*E*-*n*-Pr-MeC=CH-Et	5.95×10^4
59643-67-3	21	*Z*-Me-EtC=CH-*sec*-Bu	8.06×10^3
59643-68-4	22	*E*-Me-EtC=CH-*sec*-Bu	8.06×10^3
59643-69-5	23	*Z*-Et_2CH-EtC=CH-Me	5.36×10^2
59643-70-8	24	*E*-Et_2CH-EtC=CH-Me	5.36×10^2
59643-71-9	25	*Z*-Et-MeC=CH-*t*-Bu	1.90×10^4
59643-72-0	26	*E*-Et-MeC=CH-*t*-Bu	1.90×10^4
59643-73-1	27	*Z*-*i*-Pr-MeC=CH-*n*-Pr	1.98×10^4
59643-74-2	28	*E*-*i*-Pr-MeC=CH-*n*-Pr	1.98×10^4
59643-75-3	29	*Z*-*i*-Pr-MeC=CH-Et	3.03×10^4
27656-50-4[b] 27656-49-1[c]	30	*Z*- + *E*-*neo*-Pe-MeC=CH-*t*-Bu	1.80×10^2

[a] k_{exp} measured in methanol, 0.2 M NaBr at 25 °C. Standard deviation: ±4–7% from five to six runs. [b] *Z*. [c] *E*.

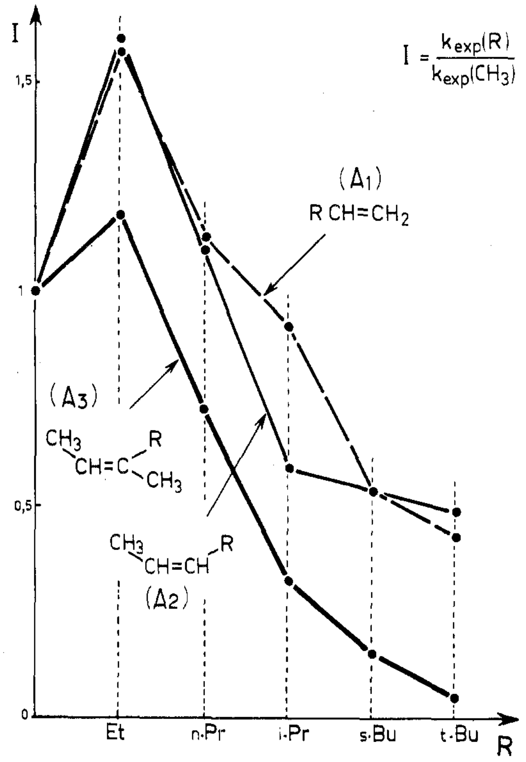


Figure 1. Increase of the decelerating effect of an alkyl group R from A_1 to A_3 alkenes.

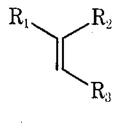
Table II. Decelerating Steric Effects of Two *gem*-Alkyl Groups on the Reactivity of Di- and Trisubstituted Alkenes

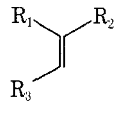
R_1	k_{rel}, $(R_1)_2C{=}CH_2$	Registry no.	k_{rel}, $(R_1)_2C{=}CHEt$	Registry no.
Me	1.00	115-11-7	1.00	625-27-4
Et	1.65	760-21-4	0.73	16789-51-8
t-Bu	4.65×10^{-3}	5857-68-1	0.48×10^{-3}	

Analogous decreases are observed for the two other trisubstituted alkene pairs for which the reactivity of the *gem*-diethylalkene is always less than that of the *gem*-dimethyl. The observed steric decelerating factors in $Et_2C{=}CHR$ relative to $Me_2C{=}CHR$, calculated after taking into account the polar factor of 1.5 × 1.5, are 2.73 and 2.82 for R = Me and *n*-Bu, respectively. Thus, with the introduction of two ethyl groups, and although the individual steric contribution of ethyl groups is generally considered to be small, the enhancement of the steric effects compensates the increase in the inductive effects and the *gem*-diethyl trisubstituted alkenes are less reactive than the corresponding *gem*-dimethyl alkenes. When this comparison is carried out for two bulky groups in geminate position, the relative decrease in reactivity is still higher (Table II). The decrease observed in A_2 series for bulky groups only appears in A_3 even when the geminate substituents are ethyl groups.

In conclusion, although the reactivity of the trisubstituted ethylenes is higher than that of mono- and disubstituted ethylenes, the reactivity enhancement caused by increasing the degree of substitution is substantially lower than that expected from polar substituent effects estimated in less substituted olefins.[8] The accumulation of alkyl substituents on the double bond results in an increasingly important contribution from total steric effects.

Isoreactivity of the *Z* and *E* Isomers. From Table I, it appears that the *Z* and *E* isomers have very similar reactivities with bromine, excluding only the isolated case[10] of the couple 17–18. The position of the R_3 substituent, relative to R_1 or R_2, the geminate substituents, is unimportant whatever the size of R_3. This can be understood in part by considering the differences in reactivity between disubstituted cis and trans alkenes. The higher reactivity of the cis isomer has been attributed[1b,11] to easier approach of the bromine: in the cis isomer, whose substituents are in the same part of the olefinic plane, steric repulsions between bromine and substituents can be avoided if the bromine attacks off the perpendicular and approaches from the side opposite the substituents. For the trans isomer, bromine approach must be perpendicular without possible minimization of repulsions. In *Z* and *E* isomers, there are always two substituents in the trans configuration so that minimization of repulsions by off perpendicular attack is impossible. Thus, it is not surprising that these A_3 isomers exhibit similar reactivities. However, the reactivity differences between cis and trans isomers depend on the size of the substituents and similar differences might be expected for A_3 when one bulky group is cis or trans to another small one. In particular, for compounds where R_2 is bulky and R_1, R_3 are small, the *Z* compound could react slightly more rapidly than the *E* isomer. This is not, however, confirmed by the isomeric couples 15–16, 23–24, or 27–28.





Furthermore, complementary thermodynamic and conformational reasons can be advanced to explain the similar reactivities of the *Z* and *E* isomers.

No conformational studies of trisubstituted alkenes are at present available. However these A_3 alkenes have pairs of substituents in geminate, cis, and trans configurations at the same time. Recent calculations and experimental data[12] indicate that, in cis olefins, repulsions between nonbonded atoms are minimized by opening of the C–C=C angle[13] rather than by twisting the molecule or deformation of the double bond. For the simplest *gem*-disubstituted olefin, isobutene,[14] this angle is not significantly deformed but for more bulky substituents one would expect it to be somewhat closed. With three alkyl groups on the double bond, supplementary steric constraints must exist. Therefore, in addition to the C–C=C angle deformation, the occurrence of some twist about the sp^2–sp^2 bond, apparently absent in A_2 alkenes, is not impossible. Isoreactivity of *Z–E* isomers suggests a similar crowding of the two sides of the double bond. Until detailed structural data on these crowded olefins are available, it is difficult to state with certainty how the *Z* and *E* isomers become sterically equivalent toward bromine attack.

Thermodynamic data on A_3 alkenes[15,16] show that the enthalpies of formation of *Z* and *E* isomers differ very little, whereas between cis and trans alkenes[15–19] these differences can amount to several kcal M^{-1} (Table III). In bromination, it has been shown[19] that the reactivity differences of A_2 alkenes are very small compared to the large stability differences between their ground states, which means that these differences are retained in the transition states. It is, therefore, reasonable to expect an even smaller difference in reactivity for the *Z–E* isomers whose ground states are energetically very similar.

Interactions in the Bromonium-Ion-Like Transition States. The overall crowding of the olefin influences the reactivity more than the steric effects of individual alkyl groups, so that steric effects of substituents increase and become more important than their polar effects, as the number of substituents increases. Moreover, the fact that steric tensions in the ground state are preserved in the transition state might suggest that the latter are bromonium-ion-like. It was thought that steric repulsions between nonbonded atoms increase on passing from the alkene to the bromonium ion,[20] whereas in an α-bromocarbonium ion these interactions can be minimized since the hybridization of one carbon atom changes from sp^2 to sp^3.[21] In fact, this hypothesis is not valid: Yates et al.[19] have shown that transition state tensions are similar to those of ground states, regardless of the carbonium or bromonium nature of the intermediates.

To determine the nature of the intermediate of A_3 bromination we measured the stereoselectivity of the reaction in chloroform of the *Z* and *E* 3-methyl-2-pentene.[23] The dibromides obtained result from an anti addition with a stereospecificity of at least 99%, as observed for disubstituted alkenes. Moreover, detailed analysis of reactivity–structure correlations,[24] including the least crowded A_3 alkenes, shows that bromonium ion intermediates account for the substituent effects better than carbonium ions. Thus, there is at present no evidence for carbonium ion intermediates in A_3 bromination and it is reasonable to assume that the intermediate remains a bromonium ion, even for the most heavily substituted olefins.

The type of interaction which controls the rate-determining step is that between bromine and substituents[26] and not the modifications of the interactions between nonbonded substituents as was advanced for nitration.[25]

This is clearly evidenced by the retention of the ground state tensions in the transition states.[19] Thus, the interactions controlling the rate can only be those between bromine and substituents. The high sensitivity of the reactivity of alkenes to total steric crowding, which determines the ease of approach of the bromine toward the olefinic carbon atoms, is consistent with this view.

Table III. Differences of Enthalpies of Formation between Isomeric Alkenes

Registry no.				
Cis	Trans	Alkene pair	$\Delta\Delta H_f°$ [a]	Ref
624-64-6	590-18-1	*cis–trans*- MeCH=CH-Me	1.0	15
627-20-3	646-04-8	*cis–trans*- MeCH=CH-Et	0.88	15
7688-21-3	4050-45-7	*cis–trans*- MeCH=CH-*n*-Pr	0.37	15
691-38-3	674-76-0	*cis–trans*- MeCH=CH-*i*-Pr	0.96	15
762-63-0	690-08-4	*cis–trans*- MeCH=CH-*t*-Bu	4.90	18
15840-60-5	692-24-0	*cis–trans*- EtCH=CH-*i*-Pr	1.0	15
690-92-6	690-93-7	*cis–trans*- EtCH=CH-*t*-Bu	5.12	19
10557-44-5	692-70-6	*cis–trans*- *i*-PrCH=CH-*i*-Pr	1.96	19
692-47-7	692-48-8	*cis–trans*- *t*-BuCH=CH-*t*-Bu	10.5	16
922-62-3 (*Z*)	616-12-6 (*E*)	*Z–E*- Me-EtC=CH-Me	0.22	15
		Z–E- Me-*n*-PrC=CH-Me	0	15
		Z–E- Me-*i*-PrC=CH-Me	0	15
		Z–E- Et-MeC=CH-Et	0.62	16

[a] $\Delta\Delta H_f° = \Delta H_f°$ (cis) − $\Delta H_f°$ (trans) or $\Delta H_f°$ (*Z*) − $\Delta H_f°$ (*E*) in kcal M^{-1}.

Experimental Section

Starting Materials. The alkenes are commercial products (Chemical Samples) with the exception of 2,2-dimethyl-3-*tert*-butyl-3-hexene, which was synthesized in the laboratory.[27] All the compounds were purified by GLC. The structures and geometries (*Z* and *E*) of all alkenes were checked by NMR, ir, and mass spectroscopy. NaBr (Prolabo RP) was used after drying for 24 h at 120 °C. Absolute methanol was freed of impurities likely to be brominated by two distillations over bromine and its water content was less than 0.03% (w/w).

Kinetic measurements were performed by the method of couloamperometry developed in this laboratory.[4] The concentration–time data (second-order kinetics) were handled by a computer. In the particular case of a *Z–E* mixture where the alkenes 30 (mixture ca. 50/50) could not be separated by GLC, the measurements were performed on the purified GLC mixture. The logarithmic plot obtained from the kinetic data is a straight line up to 95% of the reaction. If there is any reactivity difference between the *Z* and *E* isomers, it is less than the experimental error (5%) and we have therefore attributed to the two isomers the same reactivity.

Acknowledgment. The authors thank Drs. J. S. Lomas and M. F. Ruasse for helpful discussions; we thank also Miss I. Lim, who purified all the olefins by GLC.

References and Notes

(1) (a) Preceding paper: E. Bienvenue-Goëtz and J. E. Dubois, *J. Org. Chem.*, **40**, 221 (1975). (b) J. E. Dubois and G. Mouvier, *Bull. Soc. Chim. Fr.*, 1426 (1968). (c) M. F. Ruasse and J. E. Dubois, *J. Am. Chem. Soc.*, **97**, 1977 (1975). (d) X. Q. Huynh and J. E. Dubois, *J. Chim. Phys.*, 1482, 1488 (1972).
(2) Address to which correspondence should be sent.
(3) D. Grosjean, G. Mouvier, and J. E. Dubois, *Bull. Soc. Chim. Fr.*, 1735 (1973).
(4) F. Garnier and J. E. Dubois, *Bull. Soc. Chim. Fr.*, 3797 (1968).
(5) J. E. Dubois, P. Alcais, and G. Barbier, *J. Electroanal. Chem.*, **8**, 359 (1964).

(6) (a) E. Bienvenue-Goëtz and J. E. Dubois, *Bull. Soc. Chim. Fr.*, 2086 (1968). (b) J. E. Dubois and X. Q. Huynh, *ibid.*, 1436 (1968). (c) For trimethyl- and dimethyl-*tert*-butylethylenes, the rate constants k_{Br_2} experimentally measured are 1.29×10^6 and 1.67×10^5 M^{-1} s^{-1}, respectively.

(7) M. Marie de Ficquelmont, Doctoral Thesis, CNRS AO 8355, Paris, 1973.

(8) A referee has pointed out that the values for the k_{Br_2} process could be close to the diffusion controlled limit for bimolecular reactions. The bromination rate constants for enols limited by reagent diffusion has been evaluated as 10^9 M^{-1} s^{-1}.[9] The rate constants measured for the trialkyl- and tetraalkylethylenes are below this limit by at least two powers of ten. It seems unlikely that the structural effects of alkenes could lower the diffusion controlled limit to such an extent. Therefore we can reasonably assume that the measured substituent effects are the effects on the bromination reaction.

(9) J. E. Dubois and J. Toullec, *Tetrahedron*, **29**, 2859 (1973).

(10) The exception of this couple to the general isoreactivity of the *Z-E* isomers is not easily understood. The presence of an *i*-Pr group could explain this deviation: Figure 1 shows that this group has an abnormal effect on the relative reactivities in the A_2 series. However, this interpretation is not satisfactory since the couples 11–12 and 27–28 do not exhibit the same deviation.

(11) C. L. Dean, D. G. Garratt, T. T. Tidwell, and G. H. Schmidt, *J. Am. Chem. Soc.*, **96**, 4958 (1974).

(12) N. L. Allinger and J. T. Sprague, *J. Am. Chem. Soc.*, **94**, 5734 (1972); E. W. Garbisch, Jr., S. M. Schildcrout, D. P. Patterson, and C. M. Sprecher, *ibid.*, **87**, 2932 (1965).

(13) O. Ermer and S. Lifson, *J. Am. Chem. Soc.*, **95**, 4121 (1973).

(14) V. W. Laurie, *J. Chem. Phys.*, **34**, 1516 (1961); L. H. Scharpen and V. W. Laurie, *ibid.*, **39**, 1732 (1963).

(15) D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds", Wiley, New York, N.Y., 1969, Chapter 14.

(16) (a) J. D. Rockenfeller and F. D. Rossini, *J. Phys. Chem.*, **65**, 267 (1961); (b) H. F. Bartolo and F. D. Rossini, *ibid.*, **64**, 1685 (1960).

(17) K. W. Egger, *J. Am. Chem. Soc.*, **89**, 504 (1967).

(18) R. B. Turner, D. E. Nettelton, Jr., and M. Perelman, *J. Am. Chem. Soc.*, **80**, 1430 (1958); R. B. Turner, A. D. Jarrett, P. Goebel, and B. J. Mallon, *ibid.*, **95**, 790 (1973).

(19) (a) K. Yates and R. S. MacDonald, *J. Am. Chem. Soc.*, **93**, 6297 (1971); (b) *J. Org. Chem.*, **38**, 2465 (1973).

(20) (a) P. B. D. De La Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems", American Elsevier, New York, N.Y., 1966; (b) T. G. Taylor, *Acc. Chem. Res.*, **2**, 152 (1969); (c) I. Roberts and G. E. Kimball, *J. Am. Chem. Soc.*, **59**, 947 (1937).

(21) Bach et al.[22] attribute a bond index ρC-Br of 0.34 to the symmetrical bromonium ion, close to that of the covalent bond in CH_3Br ($\rho = 0.57$). This index would be only 0.068 in an α-bromocarbonium ion whose stability is about 25 kcal M^{-1} less than that of the bromonium ion.

(22) R. D. Bach and H. F. Henneike, *J. Am. Chem. Soc.*, **92**, 5589 (1970).

(23) J. E. Dubois and J. Chretien, to be published.

(24) E. Bienvenue-Goetz and J. E. Dubois, to be published.

(25) E. G. Bordwell and J. B. Biranowsky, *J. Org. Chem.*, **32**, 629 (1967).

(26) J. E. Dubois and G. Mouvier, *Tetrahedron Lett.*, 1629 (1965).

(27) J. S. Lomas, D. S. Sagatys, and J. E. Dubois, *Tetrahedron Lett.*, 1349 (1971); 165 (1972).

Bromination of Ethylenic Compounds. 39. Predominance of Steric Effects on the Reactivity of Tetrasubstituted Alkenes[1]

Daniel Grosjean, Gérard Mouvier, and Jacques-Emile Dubois*

Laboratoire de Chimie Organique Physique de l'Université Paris VII, associé au Centre National de la Recherche Scientifique, 1 rue Guy de la Brosse, 75005 Paris, France, and Laboratoire de Physicochimie Instrumentale de l'Université Paris VII, 75005 Paris, France

Received June 10, 1974

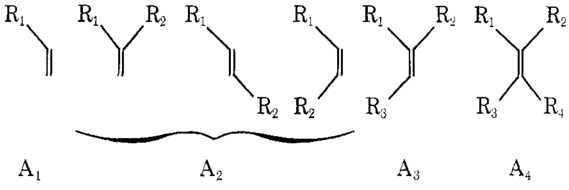
The bromination rate constants of 15 tetrasubstituted A_4 alkenes have been measured in methanol. Comparison of the effect of R in the trimethylalkylethylenes $Me_2C{=}CMeR$ with that of the same R in less substituted alkenes, $RCH{=}CH_2$, $RCH{=}CHMe$, or $Me_2C{=}CHR$, shows that the rate-diminishing steric effect is enhanced as the number of methyl on the double bond increases. Furthermore, the reactivity diminishes progressively when the methyls of tetramethylethylene are successively replaced by ethyl groups. Thus, substituent steric effects become more important than polar ones for the tetrasubstituted alkenes. Whereas for less substituted alkenes reactivity–structure correlations in terms of σ^* are obtained, a correlation with ΣE_s^c only accounts for the reactivity of tetrasubstituted alkenes. The importance of steric effects is further underlined by the absence of any relationship between the reactivity and the ionization potentials in the A_4 series and by the similarity of the substituent effects on bromination and on the addition reactions of bulky electrophiles whose rates are controlled by steric effects.

The systematic study of the bromination of ethylenic compounds has focused on several olefin populations: alkenes,[1,2] arylalkenes (styrenes and diphenylethylenes),[3] and cycloalkenes.[4] In order to complete previous studies on mono-, di-, and trisubstituted alkenes, we measured the reactivity of tetrasubstituted alkenes for which only the simplest structures, tetramethyl- and trimethylethylethylenes, have so far been studied.[2,9]

On the basis of early data of Dubois and Mouvier, the kinetic effect of different alkyl groups, their number, and their relative positions were evaluated.[2] Polar and steric effects, expressed in terms of linear free energy relationship, are additive for only a limited number of alkenes. The polar reaction constant has been determined from monoalkenes where it has been shown that steric effects are weak and negligible. The study of tetraalkylethylenes should allow us to determine the role of steric effects on their reactivity.

Results

We shall use the abbreviation A_4 for the tetrasubstituted alkenes and A_1, A_2, and A_3 for the mono-, di-, and trisubstituted ones, respectively.



For our study of the A_4 series, we have chosen 15 alkenes, either commercial or synthetized in the laboratory,[5] with substituents ranging from methyl to neopentyl. The rate constants, measured competitively[6] or directly[7] in our usual medium (methanol with 0.2 M NaBr at 25 °C), are given in Table I. In addition, we measured under the same conditions the rate constants of two *gem*-A_2 alkenes whose values were useful in the discussion which follows:

$$n\text{-Bu-MeC}{=}CH_2\ k_{exp} = 2.27 \times 10^3\ M^{-1}\,s^{-1}$$

$$n\text{-Pe-MeC}{=}CH_2\ k_{exp} = 1.98 \times 10^3\ M^{-1}\,s^{-1}$$

Table I shows distinct series in the A_4 population. The first group contains the trimethylalkylethylenes, $Me_2C{=}CMeR$, with variable R (compounds no. 1–8). The second one contains