Reactivity of Methyl-Substituted Ethylenebromonium Ions. Correlation between Charge Distribution and Regio- or Chemoselectivity

Jacques-Emile Dubois* and Jacques R. Chrétien

Contribution from the Laboratoire de Chimie Organique Physique, associé au CNRS, Université de Paris VII, 75005 Paris, France. *Received September 14, 1977*

Abstract: The rapid nucleophilic step of electrophilic bromination of alkenes is interpreted quantitatively for the first time. The opening of seven methyl-substituted ethylenebromonium ions $>C_\alpha-Br^+-C_\beta<$ from the ethylenebromonium ion itself to the tetramethylethylenebromonium ion, by a competitive nucleophilic attack between MeOH and Br^-, in a MeOH-0.2 M NaBr medium is studied. In each case, the dibromoalkane (DB) $>C_\alpha(Br)-C_\beta(Br)<$ and the bromomethoxyalkane (MB) $>C_\alpha(OMe)-C_\beta(Br)<$, labeled MeO-$C_\alpha$, with eventually its anti-Markownikoff isomer $>C_\alpha(Br)-C_\beta(OMe)<$, labeled MeO-$C_\beta$, are formed. Chemoselectivity, expressed here as MB %, varies from 38 to 84.7% but does not vary linearly with the number of methyl groups. This nonadditivity comes from the role played by bromine in the charge distribution on sites C_α and C_β in the ethylenebromonium ion. This charge distribution is evaluated from Olah's measurements of ^{13}C NMR chemical shifts of these ions, stabilized in a superacid medium. Chemoselectivity is correlated with the charge distribution on site C_α which is the most substituted carbon in dissymmetrical ions. This correlation underscores the determining influences of the increasing hardness of this site on the competitive attack, within the framework of the HSAB principle. The regioselectivity of this attack depends on the difference in free enthalpies of activation leading to MeO-C_α and MeO-C_β isomers and is well correlated with differences in charge distributions on C_α and C_β. Furthermore, this quantitative interpretation of the methoxylation of ethylenebromonium ions, in terms of charge distribution, shows that the nature of the bromonium ion is essentially the same in MeOH and in a superacid medium; it underlines the interest of ^{13}C NMR investigation of such intermediates in this latter medium.

Introduction

Recent results on electrophilic addition of halogens on olefins bring out the difficulties[1,2] encountered in a fine characterization of the transition states of this important reaction.[3,4] The study of this reaction's mechanism is made complex, aside from certain experimental difficulties, by the impossibility of handling the kinetic data and the product analysis results coherently.

Current kinetic data, generally used in an elaborate mechanistic manner,[5] in connection with spectrokinetic data on charge transfer complexes,[6] lead to quite satisfactory interpretations of the electrophilic stage per se which take into account structure effects,[5,7] the nature of electrophiles,[1] and the role of the solvent.[6,8] Stereochemical studies,[3] on the other hand, reveal the overall action of both successive stages, electrophilic and nucleophilic. It was, in fact, a judicious choice of structures that prompted the proposal of the overall Ad_E mechanism of the antielectrophilic addition on olefin.[3] Despite this success, stereochemical studies do not often make it possible to study the reactivity of the ionic intermediate with relation to nucleophilic entities, nor that ion's structure (often seen as close to α-halogenated carbenium ions, of a more or less free conformation, or close to more or less symmetrical bromonium ions). The nucleophilic stage has never been systematically and quantitatively studied both because of the difficult structural definition of the starting ion and because of lack of precision as to its concentration which hinders any direct kinetic investigation. We have, therefore, used new and different methods to study this nucleophilic stage of the Ad_EC1 electrophilic reaction of olefins. This stage follows, along the reaction path, the electrophilic transition state (TS_E) formed by a bromonium ion assisted ionization of the charge transfer complex with bromine. The nucleophilic attack may formally stem from the TS_E or from a nearby subsequent halonium ion intermediate.

We have used those characteristics of the starting halonium ion supplied by ^{13}C NMR spectroscopy, suggested by Olah's work on these ions when they are, however, stabilized in specific conditions.[9-11] Thanks to an analogy between reactive halonium ions in MeOH medium, on the one hand, and stabilized inert ions in superacid medium, on the other, we had at our disposal an ion model with more information than that which results from kinetic work carried out on the electrophilic stage, yielding an image of the TS_E anterior to the bromonium ion.

The nucleophilic reactivity of this ion is studied indirectly by observing the variations of chemoselectivity[12] (a) or of regioselectivity (b) factors which respectively translate the competitive attacks of a pair of nucleophiles (a) on the carbenium sites (b) of an ethylenehalonium. In a preliminary note,[14] we approached bromonium ion reactivity qualitatively by considering competitive dibromination and methoxybromination as resulting from the attack of the Br^- and MeOH bases on these bromonium ions, treated as more or less hard acids according to Pearson's theory. In this article, developing this interpretation, the reactivity of bromonium ions is approached in a general and more quantitative way thanks to the evaluation of charge distribution on hard and reactive carbenium sites of the ethylenebromonium ions studied.

Method and Results

1. Method. In the present work we rely on a simple model of reaction intermediates, the methyl-substituted ethylenebromonium ions used by Olah et al.[15] in a ^{13}C NMR study. We shall specify the reactivity of these ions in a MeOH-Br^- medium. In accordance with Bartlett and Tarbell's scheme,[16] the additions of the MeOH and Br^- nucleophiles are considered comparable.

The formation of dibromoalkanes (DB) is accompanied by that of bromomethoxyalkanes (MB) (Scheme I). In the case of dissymetrical intermediates we have conventionally used C_α to designate the more substituted carbon of the ethylenebromonium ion, and C_β the less substituted one. Obviously, in the case of symmetrical intermediates, sites C_α and C_β are equivalent. The bromomethoxyalkane positional isomers are designated by the position of the methoxyl groups, i.e., MeO-C_α or MeO-C_β.

The reactivity of the ethylenebromonium intermediates is

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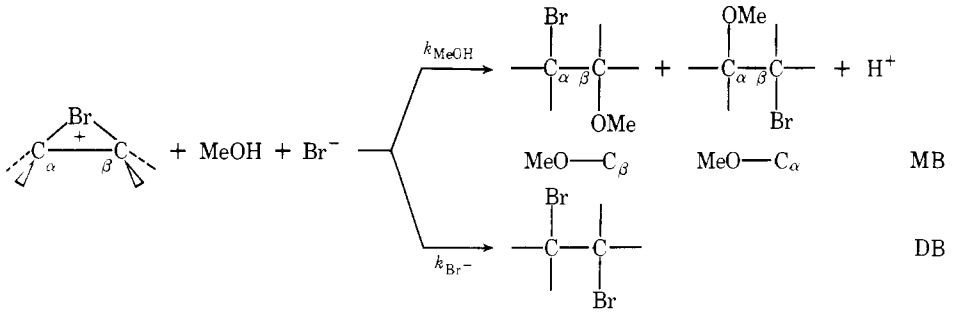
Scheme I



not directly measurable by kinetics because of their weak concentration governed by the stationary state principle. However, we avoided this difficulty by considering a competitive reaction. This reaction is defined not with respect to a reference reaction, but to the ratio of the rates of attack of an intermediate (i) by the two nucleophilic agents MeOH and Br^-. The ratio Q_i of the final products, MB and DB, expresses the relative rate of attack by the two nucleophiles:

$$Q_i = \mathrm{MB/DB} = k^i_{\mathrm{MeOH}}(\mathrm{i})(\mathrm{MeOH})/k^i_{\mathrm{Br}^-}(\mathrm{i})(\mathrm{Br}^-)$$

For $(Br^-) \gg$ (alkene), the ratio $(MeOH)/(Br^-)$ remains quasi-constant during the reaction, thus:

$$Q_i = k^i_{\mathrm{MeOH}}/k^i_{\mathrm{Br}^-} \times \text{constant}$$

The ratio of the products, MB and DB, depends on the olefin structures[17-19] and, consequently, on the ethylenebromonium ion structures arising from these olefins.

The different variations in the ratio of the rate constants result from the structural effects on these intermediates. In order to interpret them, the observed chemoselectivity and regioselectivity, which can be analyzed in terms of hardness and softness according to Pearson's HSAB theory, are correlated with the charge distribution on these intermediates. The charge distributions are calculated on the basis of the ^{13}C NMR chemical shifts of their carbenium sites C_α and C_β in a superacid medium.

2. Experimental Conditions. The systematic kinetic study of the electrophilic stage of the bromination of various populations of ethylenic compounds was carried out in our laboratory in order to specify the influence of structure,[20-22] solvent,[6,8,23] salt,[24] and reagent concentration[25] effects. The studies on structural effects are based on the processing of bromination rate constants, determined in a MeOH-0.2 M NaBr medium at 25 °C. These standard experimental conditions, used to study electrophilic attack, remain valid for nucleophilic attack based on analysis of bromination products, according to a method developed elsewhere.[26] The bromine concentration is held at 10^{-5} M, but it still has no influence on the ratio of bromination products. The alkene concentration alone was increased to 10^{-3} M in order to allow a direct gas chromatography analysis of the products in the reaction medium. This direct analysis avoids an extraction which would favor an elimination reaction with the most unstable bromomethoxyalkanes. The ratio of concentration $(MeOH)/(Br^-) \simeq 120$ is very high, but the bromide ion has a nucleophilic constant which is much greater than that of methanol. The bromide nucleophilic constant equals 5.79, when MeOH is taken as the reference nucleophile and CH_3I as the standard substrate.[27,28] This gives an acceptable relative reactivity ratio $k_{\mathrm{MeOH}}/k_{\mathrm{Br}^-}$ for this competitive method and for all alkenes studied. Here the alkenes are limited to those methyl-substituted ethylenes whose bromonium ions were studied by ^{13}C NMR.[15]

3. Results. The products formed during bromination in MeOH-0.2 M NaBr of the seven methyl-substituted alkenes ranging from ethylene to tetramethylethylene are indicated in Table I. We notice that chemoselectivity (expressed here as MB %) is about 40% for the intermediate from ethylene (a), and about 60% for the intermediates from propene (b), (*Z*)-2-butene (d), (*E*)-2-butene (e), and 2,3-dimethyl-2-butene (g); it reaches about 80% for the intermediates from 2-methylpropene (c) and from 2-methyl-2-butene (f). We verified that the antiaddition was stereospecific (100%) on the (*Z*)- and (*E*)-2-butenes. We have supposed this to be valid for the other cases which cannot be studied stereochemically. The chemoselectivity of the competitive nucleophilic attack depends on the overall degree of substitution, which varies from 0 to 4 when going from (a) to (g), and on the symmetry of the substitution. This substitution can be symmetrical for intermediates (a), (d), (e), and (g), or dissymmetrical for intermediates (b), (c), and (f). The attack by MeOH is regioselective for intermediate (b) and C_α regiospecific for (c) and (f).

Discussion

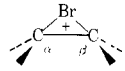
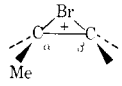
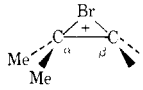
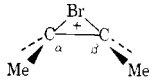
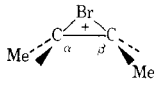
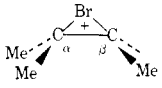
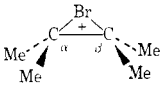
1. Structure Effects on Chemoselectivity and Regioselectivity. In studying the first step of the electrophilic addition of bromine under identical experimental conditions,[21] the absolute rate constants, k_{Br_2}, for the bromination of the seven alkenes in Table I vary by 10^6 and the function $\log k_{\mathrm{Br}_2} = f$ (degree of substitution) is almost linear. This indicates good additivity of the effect of the methyl groups. In contrast, the variation of the ratio $Q = \mathrm{MB/DB}$, shown in Table I, is not a linear function of the degree of substitution of the methyl-substituted ethylenebromonium ions. This nonadditivity of the effect of the methyl groups on the distribution of the products formed underscores the complexity of the effects which govern the nucleophilic step. It accounts for the relatively few and nonquantitative studies in this field.

Among the factors governing this second step, we can a priori anticipate the degree of substitution, the type of substitution (symmetrical or not), the carbenium character of the intermediate, the solvation possibilities of each carbenium site C_α and C_β, possible steric effects, etc. In order to methodically set apart the influence of both the degree and the type of substitution on product distribution, we have grouped the seven bridged bromonium intermediates into three series: series I, containing the intermediates (a, b, c); the substitution increases from 0 to 2 on site C_α, and site C_β is unsubstituted; series II, containing the intermediates (c, f, g); C_α is disubstituted, and the substitution increases from 0 to 2 on site C_β; series III, containing the intermediates (a, d, e, g); the substitution simultaneously increases from 0 to 2 on sites C_α and C_β.

Series I and II correspond to a progressive dissymetric substitution, and series III to a progressive symmetric one. The variation of the chemoselectivity (MB %) with the overall degree of substitution appears in Figure 1 for these three sequences.

We recently proposed extending Pearson's HSAB concept[29] to the competitive nucleophilic attack of these bridged reaction intermediates.[14] Indeed, the two carbenium sites C_α and C_β of the ethylenebromonium ions can be considered as two acid centers which undergo a competitive attack by two bases

Table I. Structure Effects on Chemoselectivity and Regioselectivity of the Nucleophilic Competitive Attack of Methyl-Substituted Ethylenebromonium Ions

Alkene		Intermediate	Chemoselectivity, % MB	DB	Q = MB/DB	Regioselectivity, % Isomers[a] MeO-C_α	MeO-C_β	R(MeO-C_α)[c]
Ethylene	a		38	62	0.61		*b*	0.5
Propene	b		60.7	39.3	1.54	49.4	11.3	0.8
2-Methylpropene	c		84.7	15.3	5.53	84.7	0	1
(*Z*)-2-Butene	d		63.0 T[d]	37.0 T[d]	1.70		*b*	0.5
			59.4 E[d]	40.7 E[d]	1.46		*b*	0.5
2-Methyl 2-butene	f		81.4	18.6	4.38	81.4	0	1
2,3-Dimethyl-2-butene	g		56.2	43.8	1.28		*b*	0.5

[a] Isomeric bromomethoxyalkanes: MeO-C_α = C_β-bromo-C_α-methoxyalkane; MeO-C_β = C_α-bromo-C_β-methoxyalkane. [b] Attack is equally probable on sites C_α and C_β for these symmetric intermediates. [c] Regioselectivity factor: R(MeO-C_α) = MeO-C_α/(MeO-C_α + MeO-C_β). A regioselectivity factor R(MeO-C_α) = R(MeO-C_β) = 0.5 accounts for a lack of regioselectivity in the case of symmetric intermediates; a value R(MeO-C_α) = 1 accounts for a (MeO-C_α) regiospecificity. The average relative error is 3%. [d] Diastereoisomers: E = erythro, T = threo.

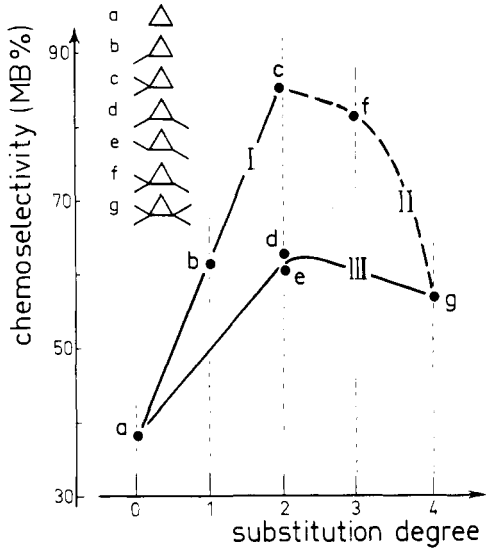


Figure 1. The structure effects on the chemoselectivity of MeOH and Br^- nucleophilic competitive attacks on methyl-substituted ethylenebromonium ions underscore the nonadditivity of methyl substitutions. I. Dissymmetrical substitution: increasing on C_α, equal to zero on C_β. II. Dissymmetrical substitution: dimethyl substituted on C_α, increasing on C_β. III. Symmetrical substitution: increasing on C_α and C_β (chemoselectivity is expressed here as bromomethoxyalkane percentage, MB %, with respect to the sum of bromination products; see note 12b).

MeOH and Br^-. The MeOH base is considered to be hard, and the Br^- base moderately hard.[27]

The hardness of carbenium centers C_α and C_β can either be analogous or different, depending on the substituents of these sites. The thermodynamic data deduced from the reaction of the alcohols with hydrogen sulfide[27] show that the hardness of the carbenium ions increases in the following order: $CH_3^+ < C_2H_5^+ < (CH_3)_2CH^+ < (CH_3)_3C^+$. This classification is not restricted to free cations. Indeed, Ho has specified that "the more carbenium character a center attains during a reaction, the harder it will be".[30] According to the HSAB principle we have assumed that *any increase in hardness of a carbenium center would favor its attack by methanol molecules which are relatively harder than the bromide ions.* This would increase the chemoselectivity (MB %) and also the regioselectivity associated with dissymmetrical structural effects.

Indeed, this is what we observe in series I, for the ethylenebromonium ion (a) the attack is not regioselective, R(MeO-C_α) = 0.5, and chemoselectivity is relatively low (MB = 38%); for methylethylenebromonium ion (b), the regioselectivity factor increases, R(MeO-C_α) = 0.8, and MB does too, 60.7%; for the 1,1-dimethylethylenebromonium ion the attack becomes regiospecific and MB reaches 84.7%. The substitution of the C_α site of this latter intermediate by two Me groups would harden it enough to provoke a regiospecific attack at the same time as a strong chemoselectivity. Series I thus indicates a good additivity of the effect of the methyl group on the C_α site which is expressed by a 20% increase in the amount of bromomethoxyalkane when going from (a) to (b) or from (b) to (c).

In contrast, in series II (c, f, g) where site C_α is already disubstituted, but where the degree of substitution of site C_β increases from 0 to 2, the chemoselectivity shows a marked decrease. This decrease is greatest when the overall degree of substitution reaches 4, i.e., for intermediate (g). It is noteworthy that for the trimethylethylenebromonium ion (f) the attack on site C_α (the most highly substituted site) is still regiospecific[31] and is accompanied by a high chemoselectivity (MB = 81.4%). This seems to indicate that despite substitution

by a methyl group on site C_β the disubstitution of site C_α gives it a relatively strong carbenium ion character and hardness. Furthermore, in series I and II, Figure 2 shows a *linear correlation between the regioselectivity (MeO–C_α) and the chemoselectivity (MB %) for intermediates (a), (b), (c), and (f).*

In series III (a, d, e, g), the simultaneous symmetric substitution on C_α and C_β (d and e) by a methyl group provokes an increase in the chemoselectivity which is about the same as that observed for (b) which is substituted on C_α by a methyl group only. This suggests relatively similar carbenium ion characters of the C_α sites in the three intermediates (b), (d), and (e). Moreover, passage from a symmetric situation to one with more substitution, i.e., the transition from unsubstituted (a) to disubstituted (d, e) and tetrasubstituted (g) intermediates, is marked by an increase followed by a decrease in chemoselectivity (for (g) MB = 56.2%).

In series III, is this nonadditivity of the methyl effect on the variation of the chemoselectivity due primarily to a steric inhibition of the antiattack by the methanol molecules on intermediate (g) or to a relatively weak carbenium ion character of intermediate (g)?

To clarify the dependence between a strong chemoselectivity (MB %) and a strong regioselectivity or a regiospecificity (MeO–C_α), a quantitative evaluation of the relative carbenium character of sites C_α and C_β seemed to us highly relevant.

2. The Carbenium Character of Ethylenebromonium Ions. The ab initio calculations of the charge distribution on the ethylenebromonium ion remain limited.[32] At present, only the $\delta^{13}C$ chemical shifts are available for calculating the C_α and C_β charge distribution on these intermediates.[15,33]

(a) Downfield Chemical Shifts and Growing Carbenium Character. The tetramethylchloronium ion has a $\delta^{13}C$ downfield chemical shift of 26.9 ppm more than its iodonium ion homologue.[15] Olah bases the interpretation of his observation on the relative electronegativity of halogens: the greater electronegativity of chlorine as compared to iodine confers a greater carbenium character to sites C_α and C_β.

The $\delta^{13}C$ chemical shift of sites C_α and C_β of the tetramethylethylenehalonium ion is four times more sensitive to the nature of the halogen than that of the C_α and C_β sites of the unsubstituted ethylenehalonium ions. This is apparent when comparing the differences in slope in the correlations expressing the variation of C_α and C_β chemical shifts with the electronegativity of the Cl, Br, and I halogens. It enhances the idea of a stronger carbenium character of sites C_α and C_β in the tetramethylhalonium ion than in the unsubstituted ethylenehalonium ion.

The sp^2 carbons of carbenium ions[39] have downfield chemical shifts greater by about 180–210 ppm than the corresponding sp^2 carbons of alkenes.[40] These downfield chemical shifts are in reasonable agreement with the 160–190 ppm/charge unit often admitted in correlation between the ^{13}C NMR chemical shift and the positive charge density.[38] By extending this reasoning to ethylenebromonium ions, the relative carbenium character of sites C_α and C_β can be calculated. In a first approximation we admit proportionality between the chemical shift and the charge density, which we justify in ref 33.

In order to define the role played by the bromine in the charge distribution of our bridged bromonium ions, we first studied, via the same spectroscopic approach, the charge distribution occurring on sites C_α and C_β of the parent alkenes.

(b) Charge Distribution on Sites C_α and C_β in Methyl-Substituted Ethylene Compounds. The structure effects on the $\Delta\delta^{13}C$ chemical shifts of the sp^2 carbons C_α and C_β of the alkenes in question appear in Figure 3a. In a first approximation we have, as before, admitted the proportionality between the chemical shift and the π charge variations.

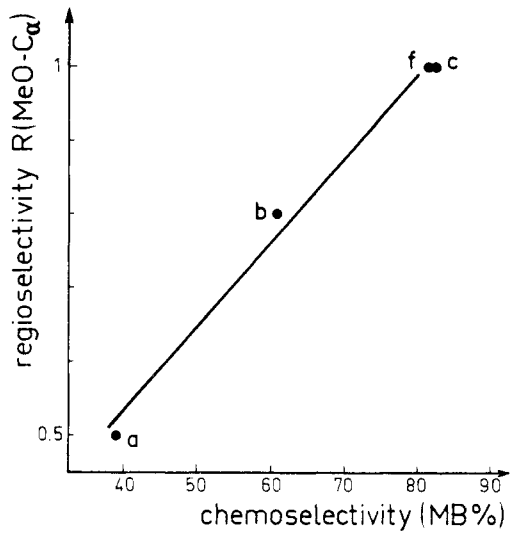


Figure 2. Increasing regioselectivity (MeO–C_α) is accompanied by a corresponding increase in chemoselectivity (MB %) for intermediates a, b, c, f.

The ^{13}C chemical shifts of sites C_α and C_β of the methyl-substituted ethylene are distributed over a range of only 30 ppm.[40] The strongest dissymmetry is observed for 2-methylpropene (c). The substitution by a Me group on site C_β, in alkene (f), partially compensates for the influence of two methyl groups on site C_α. For symmetrical alkenes, in series III_0, compensations between identical substitutions on sites C_α and C_β are almost total. The expected symmetry of Figure 3a based on experimental spectroscopic data should be stressed.

(c) Carbenium Character of Sites C_α and C_β in the Ethylenebromonium Ions. As opposed to Figure 3a, it is shown in Figure 3b that the carbenium character of sites C_α and C_β of the corresponding ethylenebromonium ions lead to a dissymmetrical correlation. The $\delta^{13}C$ chemical shifts of sites C_α and C_β of the dissymmetrical methyl-substituted ethylenebromonium ions are distributed over a range of 150 ppm. This variation range is twice as large as that of the symmetrical ethylenebromonium ions and five times as large as that of their parent alkene. The skeleton structural effects, then, simultaneously modify the charge distribution between each of the two carbenium sites C_α and C_β, and also between bromine and these two carbenium sites. Such overall charge distribution variations can be specified for each series.

In series I (a, b, c) when the degree of substitution on site C_α goes from 0 to 2 with no change on site C_β, a strong C_α positive charge increase is observed. Simultaneously, one notices a positive charge decrease on site C_β, which remains relatively small in comparison to the variation on C_α. These observations support the idea that *for sequence (a), (b), (c) the increase in positive charge on site C_α occurs mainly at the expense of the charge carried by the bromine.*

In series II (c, f, g) where the substitution on C_α remains constant and equal to 2, the increase in the degree of substitution (0, 1, 2) on site C_β is accompanied by a strong reduction of the positive charge on C_α in favor of a strong increase in the C_β positive charge. For these intermediates, according to the sum of the relative deviations of the chemical shifts ($\Sigma\Delta\delta = \Delta\delta C_\alpha + \Delta\delta C_\beta$), the total charge carried by the two carbenium sites remains relatively constant. This implies a constant charge for the bromine atom and suggests that *for sequence (c), (f), (g) the positive charge increase on site C_β occurs at the expense of the positive charge carried by site C_α.*

In series III, shown in Figure 3b, the equivalent sites C_α and C_β of these symmetrical ethylenebromonium ions (e, d, e, and g) have $\delta^{13}C$ chemical shifts which are distributed over 70 ppm,

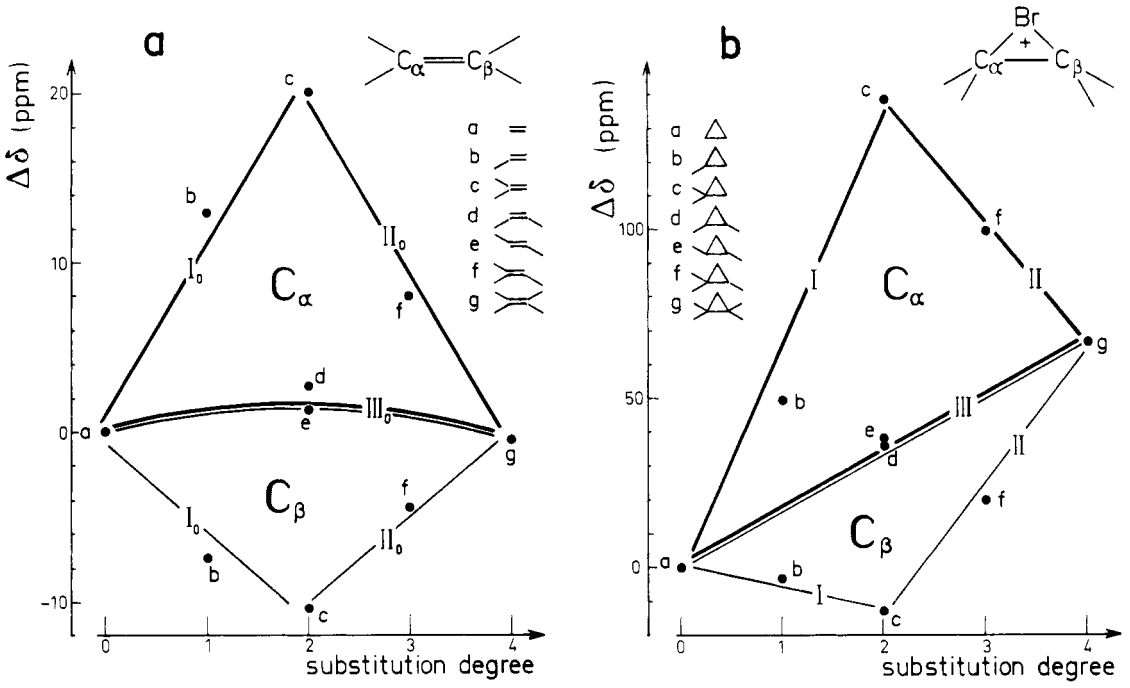


Figure 3. Structure effects on relative chemical shifts $\Delta\delta$ in ^{13}C NMR for the C_α and C_β sites of methyl-substituted ethylenes (a) and for their corresponding ethylenebromonium ions (b). Chemical shift is related to charge distribution. A downfield chemical shift, $\Delta\delta > 0$, accounts for a decrease in net π charge with respect to ethylene in Figure 3a; it accounts for an increase in carbenium character of sites C_α and C_β, with respect to the ethylenebromonium ion (a) in Figure 3b. The upper part of these figures corresponds to site C_α, the lower to site C_β. The symmetry in Figure 3a shows the compensation on the net π charge distribution contributed by the substitution on C_α with respect to the substitution on C_α only. On the contrary the dissymmetry in Figure 3b underscores variations in bromine participation in the positive charge distribution.

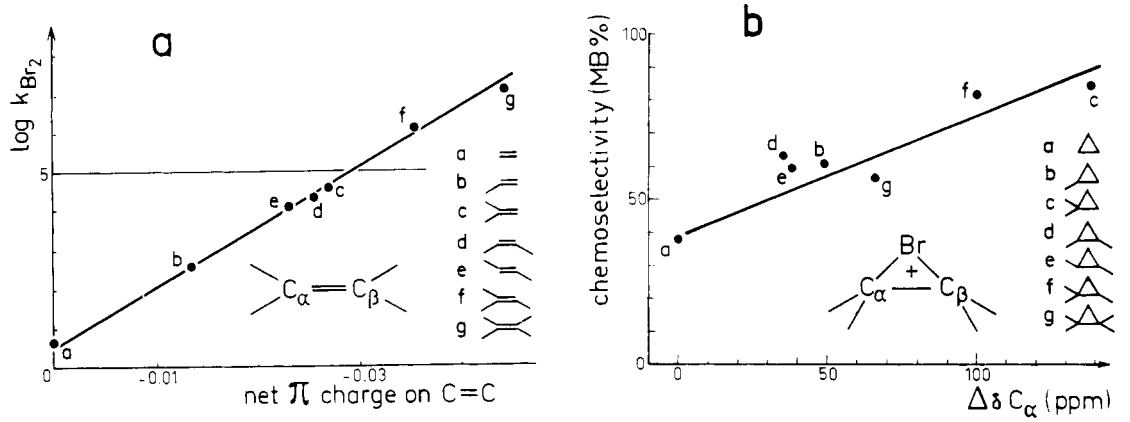


Figure 4. Coherent interpretation of the reactivity of methyl-substituted ethylene in the electrophilic (a) and nucleophilic (b) steps of the bromination reaction in accordance with charge distribution. (a) Correlation of log k_{Br_2} of these ethylenes with the net π charge distribution calculated by CNDO/2 (in electron). (b) Correlation of the chemoselectivity, MB %, with the carbenium character of sites C_α of their ethylenebromonium ions. This correlation points out the preponderance of the hardness of C_α on this nucleophilic competitive attack.

whereas for their parent alkenes the chemical shifts are almost identical. The increases in the substitution and in the C_α and C_β positive charges initiate both the slope of series III and an overall strong dissymmetry in Figure 3b. Here, and in contrast to the parent series III_0 (Figure 3a), the symmetrical substitution on C_β only partially compensates for the influence of the substitutions on C_α. Furthermore, the slope for series III is one-half that of the slope for series I (C_α), although the site C_α substitutions are comparable. *These points suggest that in series III the charge increase on C_α and C_β associated with substitution occurs at the expense of the positive charge carried by the bromine.*

To summarize, the dissymmetry of Figure 3b expresses a double charge transfer occurring on these ethylenebromonium ions: firstly, a charge transfer between each of the two carbenium centers; secondly, a charge transfer between bromine and the two carbenium centers. This latter charge transfer is all the greater when the dissymmetry of the charge distribution between C_α and C_β is large. *In a first approximation, Figure 3b provides a scale of the carbenium character of sites C_α and C_β of the methyl-substituted ethylenebromonium ions* and permits the establishment of correlations between the carbenium character and chemoselectivity or regioselectivity.

3. Correlation between Carbenium Character and Chemoselectivity. By assuming that the chemoselectivity (MB %) is a function of the carbenium character of site C_α we obtain the correlation shown in Figure 4b. Although this chemoselectivity (MB %) varies widely, *Figure 4b shows that, in a first approximation, the chemoselectivity of all seven intermediates is well expressed by the charge distribution on site C_α.*

It is to be noticed that the order of the compounds in this correlation does not correspond to that usually obtained for the series of corresponding methyl-substituted ethylenebromonium ions. Indeed, by using the heat formations of these entities

calculated from the vicinal dihalide precursors, in SbF_5-SO_2 at −60 °C,[41] the following sequence of energy levels is established for these ions.

$$(a) < (b) < (c) < (f) < (g)$$

This is also the sequence relative to the corresponding alkenes' reactivity.[20,21]

The linear correlation of Figure 4b with a *more complex relative order of structures* underscores the special role played by the hardness of site C_α on the nucleophilic competitive attack of ethylenebromonium ions. It proves that the reduction of the chemoselectivity in series II (c, f, g) results primarily from a decrease in the carbenium character of site C_α. Moreover, our interpretation minimizes the steric hindrance factor in the antinucleophilic approach, contrary to what might have been supposed beforehand. In view of these results, it is not surprising that the chemoselectivity, insofar as it is controlled by the differential term $\Delta\delta C_\alpha$, has not been approached quantitatively by simple structural considerations before this work.

For a closer analysis of the chemoselectivity we established a parallel between the electrophilic reactivity step and the subsequent nucleophilic reactivity, both interpreted as controlled by the estimated charge densities of their reactive carbons. The reactivity of methyl-substituted ethylenes, measured by one of us,[20,21] correlates very well (Figure 4a) with the net π charge distribution on C=C calculated by CNDO/2 by Clark.[42] It accounts for the increasing reactivity of the dimethyl-substituted ethylene according to the following sequence:

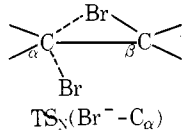
(*E*)-2-butene < (*Z*)-2-butene < 2-methyl-2-propene

This excellent correlation (Figure 4a) constitutes a major improvement over the Hammett-Taft treatment.[43]

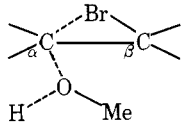
Although the chemoselectivity correlation (Figure 4b) is not as good as the electrophilic one (Figure 4a), the two together give a valid and coherent explanation of the reactivity of methyl-substituted ethylenes in the electrophilic attack of the parent alkenes and of the nucleophilic attack of their associated ethylenebromonium ions. The correlation of Figure 4a shows that, in the electrophilic attack, the free enthalpy of activation $\Delta G^\ddagger$ decreases directly with increasing π net charge on C=C. It is to be noted that in the chemoselectivity correlation (Figure 4b), the competitive nucleophilic attack, also monitored by charge distribution, is not directly controlled by a free activation enthalpy but by the difference between the free activation enthalpies related to (Br^-) and (MeOH) attack.

$$\delta\Delta G^\ddagger_{(Br^-)-(MeOH)} = \Delta G^\ddagger_{(Br^--C_\alpha)} - \Delta G^\ddagger_{(MeOH-C_\alpha)}$$

More information can be derived from those correlations (Figures 4a, 4b) by further consideration on the nature of the TS_E and TS_N of the two reactions. The nucleophilic transition state (TS_N), i.e., carbon-pentacoordinated transition state, labeled TS_N (Br^--C_α) or TS_N (MeOH-C_α), is more crowded

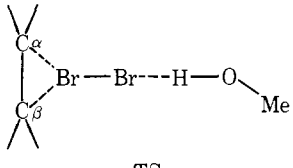


$TS_N(Br^-$-$C_\alpha)$



TS_N(MeOH-C_α)

than the electrophilic transition state (TS_E) which is a car-



TS_E

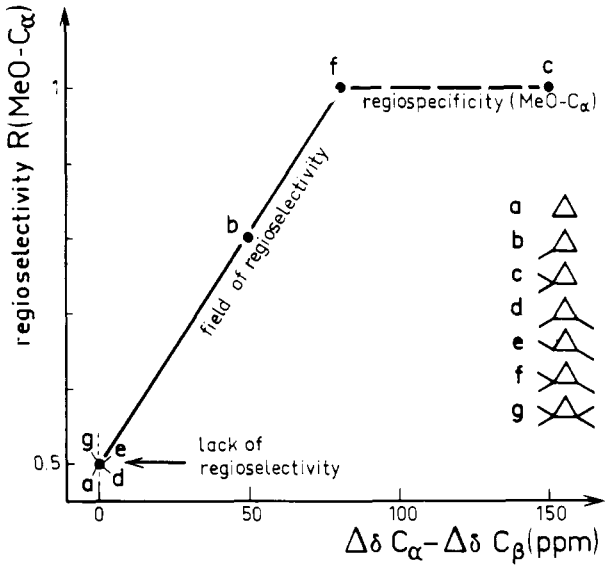


Figure 5. Variation of regioselectivity MeO-C_α with the difference in carbenium character of site C_α and C_β. This difference is related to that in ^{13}C NMR chemical shifts. Above a threshold of 80 ppm the reaction becomes MeO-C_α regiospecific.

bon-tetracoordinated transition state. Therefore, steric effects could easily be more important for the TS_N than for TS_E.

For the nucleophilic transition state TS_N, the slight deviations from the linearity of the correlation might reflect the influence of different steric inhibitions to solvation. These perturbations play a second role with respect to charge distribution in this case of methyl-substituted ethylenebromonium ion.

4. Correlation between Carbenium Character and Regioselectivity. The regioselectivity corresponds to the difference in the probability of the MeOH attack at C_α and C_β and this competition is expressed by the difference of free enthalpies of activation:

$$\delta\Delta G^\ddagger_{\alpha-\beta} = \Delta G^\ddagger_{(MeOH-C_\alpha)} - \Delta G^\ddagger_{(MeOH-C_\beta)}$$

Evidently this difference is zero for the symmetrical intermediates (a, d, e, g). Examination of the relative dissymmetry of the C_α and C_β sites of intermediates (a), (b), (c), and (f) makes it reasonable to assume that $\delta\Delta G^\ddagger_{\alpha-\beta}$ increases in the order (a) < (b) < (f) < (c). We have related this difference in free enthalpies of activation to the variation in the carbenium characters of site C_α and C_β. *The regioselectivity (MeO-C_α) is thus expressed as a function of the difference in charge distribution between sites C_α and C_β expressed in parts per million units* (Figure 5).

It should be noted that the attack by MeOH becomes regiospecific for a large difference in charge distribution which is expressed by a change in chemical shift of 80 ppm. *This threshold* corresponds to the trimethylethylenebromonium (f) and is largely surpassed by the dimethyl-1,1-ethylenebromonium ion intermediate (c) where the difference $\delta C_\alpha - \delta C_\beta$ equals 150 ppm. The representative point of this latter intermediate (c) lies so much beyond this threshold that the range (f, c) looks surprisingly wide. It is reasonable to assume that other dialkyl-1,1-ethylenebromonium ions are located on the straight line f-c and that other monoalkylethylenebromonium ions, whose attack by MeOH is only regioselective, might be located on the straight line a-b-f.

As we have seen, differences in chemoselectivity between intermediates (a), (b), and (f) are great but the one between intermediates (c) and (f) is very small despite their dissimilarity in charge distribution. This leveling effect on selectivity

above a given reactivity would seem to indicate that the differences of activation free enthalpies of formation

$$\delta\Delta G^{\ddagger}_{(Br^-)-(MeOH)}$$

of the methoxybromide compound and that of the dibromide one originating from intermediates (c) or (f) are very similar. According to the reactivity-selectivity principle[44-46] this would suggest that for intermediates (c) and (f) the transition states, TS_N, leading to methoxybromide occur early along the reaction coordinate and would be more reactant-like than for other halonium intermediates.

In conclusion, our hypotheses as to the nature as well as the importance of the correlations between charge densities on reactive carbons and the selectivities which express their relative capacity to react account for the ratios of the products. The success of this interpretation of the nucleophilic step also confirms the proposed analogy between transient bromonium ions as they exist in MeOH and as they appear, in a stable form, in superacid medium. This confirmation underlines the interest of further ^{13}C NMR investigation of such intermediates for kinetic studies in other solvents. Moreover, our results point out the similarity or proximity of the nucleophilic transition states TS_N with ethylenebromonium ions. This paper's approach, by quantitative product analysis and ^{13}C NMR correlations, enabled us to isolate information belonging solely to the nucleophilic step. Greater insight is thus gained into the total reaction path of the complex electrophilic Ad_EC1 addition. The experimental conditions being those of the electrophilic kinetic studies, our results and their interpretation make it possible to compare the structures of the two transition states TS_E and TS_N with those of bromonium ions as physical transient intermediates located between them.

Conversely, the simultaneous use of these chemo- and regioselectivities should make it possible to estimate the charge distribution on given halonium intermediates insofar as there is no prevailing steric effect unrevealed.

Experimental Section

Product Ratios in Analytical Conditions. The product analysis method of olefin bromination in methanol has been described previously.[26] Bromine was produced in the medium by electrolysis of NaBr. Reactant concentrations are specified in the Method and Results section. The great dilution of products in MeOH was favorable to their stability: it avoided HBr elimination and prevented HBr autocatalytic action. Product ratios were determined by direct gas phase chromatography analysis of the solution.

Product Identification. Ethylene, 2-methylpropene, (*E*)-2-butene, and (*Z*)-2-butene products were prepared classically. Approximately 0.1 mol of alkene was brominated in 500 mL of MeOH. Optimal conditions to favor MB formation at the expense of DB formation were used.[26] Products were extracted with pentane and dried. MB was separated from DB by spinning band distillation. In the case of propene bromination, MB products, i.e., MeO-C_α and MeO-C_β isomers, are unstable when submitted to necessary heating for distillation. Thus, this mixture of MB and DB was separated directly by preparative gas phase chromatography.

Bromination of 2-methyl-2-butene and, chiefly, of 2,3-dimethyl-2-butene gave very unstable products (HBr elimination reactions, tar formation). Great dilution in MeOH or in N_2 during gas-phase chromatographic analysis avoided secondary reactions. Products were not isolated from MeOH here and were analyzed directly by MS-GC coupling.

Distillation was carried out on a NFT 50 Nester and Faust spinning band column. Elemental analysis was done by the CNRS Microanalysis Center in Thiais. Product ratios were determined on an 1200-1 Aerograph gas chromatograph equipped with a flame ionization detector. The column most often used was stainless steel, 20 ft × 1/8 in., 15% Carbowax 600 on Chromosorb W 60-80, N_2, flow rate 25 mL/mn. Preparative gas phase chromatography was carried out on an A-700 Autoprep Aerograph chromatograph equipped with a flame ionization detector; Carbowax 600 was also used as stationary phase with a 20 ft × 3/8 in. aluminum column. Infrared spectra were carried out on a 457 Perkin-Elmer spectrograph on pure liquid in a KBr cell with a 0.02 mm cell path. Mass spectra were carried out on a 208 Thomson spectrograph at 70 eV or on a JMS D 100 JEOL spectrograph at 20 eV. The ^1H NMR spectra were carried out on a 90-MHz Bruker spectrograph, with Me_4Si as internal reference, in 10% by weight carbon tetrachloride solutions.

A. Ethylene Bromination. Ethylene (Naphta-Chimie, purity ≥95%). 1-Methoxy-2-bromoethane: bp 58.5 °C (118 mm) [lit.[47] bp 40.6 °C (66 mm)], n^{20}_D 1.4472 [lit.[47] n^{20}_D 1.4417). Anal. (C_3H_7OBr) C, H, O, Br. IR C-O-C 1096 (m), 1125 (s), 2833 cm^{-1} (vw). 1-2-Dibromoethane: bp 74.5 °C (118 mm) [lit.[48] bp 52.1 °C (50.8 mm); n^{20}_D 1.5358 (lit.[48] n^{20}_D 1.5379). Anal. ($C_2H_4Br_2$) C, H, Br. IR C-Br 571.4 cm^{-1} (vs).

B. Propene Bromination. Propene (Air-Liquide, purity >99%). Mixture of 1-bromo-2-methoxypropane (MeO-C_α) and of 2-bromo-1-methoxypropane (MeO-C_β): bp 44.5 °C (42 mm), n^{20}_D 1.4458 (lit.[48] (MeO-C_α) bp 72.5-73.5 °C (145 mm)). Anal. (C_4H_8OBr) C, H, O, Br. Mass spectrum (70 eV) (MeO-C_α) *m/e* 137-139, 59 (base peak); (MeO-C_β) *m/e* 45 (base peak). 1-2-Dibromopropane: bp 60.5 °C (47 mm) [lit.[48] bp 52.3 °C (30 mm)]; n^{20}_D 1.5173 (lit.[48] n^{20}_D 1.5192). Anal. ($C_3H_6Br_2$) C, H, Br.

C. 2-Methylpropene Bromination. 2-Methylpropene (Philipps, purity >99%). 1-Bromo-2-methoxy-2-methylpropane: bp 54 °C (30 mm) [lit.[49] bp 72.5-73.5 °C (145 mm)], n^{20}_D 1.4532. Anal. ($C_5H_{11}OBr$) C, H, Br. Mass spectrum (70 eV) *m/e* (fragment, rel intensity) 73 (M − (CH_2Br), 100)), 151-153 (M − (CH_3), 7); IR 670 (m), 740 (m), 1070 (s), 1100 (s), 2830 cm^{-1} (w); NMR δ 1.26 (6 H, CH_3), 3.18 (3 H, OMe), 3.29 (2 H, CH_2Br). 1,2-Dibromo-2-methylpropane: bp 58 °C (34 mm) [lit.[48] 60-61 °C (36 mm)], n^{20}_D 1.5059 (lit.[48] n^{20}_D 1.5118). Anal. ($C_4H_8Br_2$) C, H, Br. NMR δ 3.94 (2 H, CH_2Br).

D. (*Z*)-2-Butene Bromination. (*Z*)-2-Butene (Philipps, purity >99%). *threo*-2-Bromo-3-methoxybutane: bp 37 °C (15 mm) [lit.[50] bp 55.6 °C (40 mm)], n^{20}_D 1.4465 (lit.[50] n^{25}_D 1.4478). Anal. ($C_5H_{11}OBr$) C, H, O, Br. ^1H NMR $J(H_\alpha H_\beta)$ 4.0 Hz; δ 1.53 (3 H, CH_3CHBr-), 1.14 (3 H, CH_3(CHOMe)), 3.32 (3 H, OMe); IR 642 (m), 1095 (s), 1122 (s), 2820 cm^{-1} (w). *threo*-2,3-Dibromobutane: bp 49 °C (13 mm) [lit.[51] bp 51 °C (16 mm)], n^{20}_D 1.5110 (lit.[51] n^{20}_D 1.5147). Anal. ($C_4H_8Br_2$) C, H, Br. ^1H NMR $J(H_\alpha H_\beta)$ = 3.15 Hz; IR 445 (w), 500 (w), 540 (s), 560 (s), 635 (m), 650 cm^{-1} (m).

E. (*E*)-2-Butene Bromination. (*E*)-2-Butene (Philipps, purity ≥99%). *erythro*-2-Bromo-3-methoxybutane: bp 34.5 °C (14 mm) [lit.[50] bp 55.7 °C (40 mm)], n^{20}_D 1.4549 (lit.[50] n^{25}_D 1.4483). Anal. ($C_5H_{11}OBr$) C, H, Br. NMR $J(H_\alpha H_\beta)$ = 5.6 Hz, δ 1.16 (3 H, CH_3(CHOMe-)), 1.59 (3 H, CH_3(CHBr-)), 3.32 (3 H, OMe); IR 1095 (m), 1110 (m), 2820 cm^{-1} (m). *erythro*-2,3-Dibromobutane: bp 47.2 °C (14.5 mm) [lit.[51] bp 51 °C (19 mm)], n^{20}_D 1.5100 (lit.[51] n^{20}_D 1.5116). Anal. ($C_4H_8Br_2$) C, H, Br. NMR $J(H_\alpha H_\beta)$ = 8.35 Hz; IR 465 (w), 550 (s), 600 (w), 640 cm^{-1} (m).

F. 2-Methyl-2-butene Bromination. 2-Methyl-2-butene (Philipps, purity ≥99%). 3-Bromo-2-methoxy-2-methylbutane: mass spectrum (20 eV) *m/e* (rel intensity, characteristic fragmentation) 41 (119), 43 (89), 45 (33), 55 (48), 69 (101), 73 (1000, M − (CHBr − CH_3)), 74 (48), 85 (32, M − (BrH, CH_3)), 86 (57, M − (Br, CH_3)), 165-167 (31, M − (CH_3)). 2,3-Dibromo-2-methylbutane: mass spectrum (20 eV) *m/e* (rel intensity, characteristic fragmentation) 41 (1000, M − (CH_3CHBr, Br, H), 42 (115), 43 (204), 53 (120), 55 (262, M − (BrH, Br, CH_3)), 59 (67), 67 (48), 69 (868, M − (BrH, Br)), 70 (150), 83 (39), 97 (39), 107 (43), 109 (39), 121 (68), 123 (65), 149-151 (770-761, M − (Br)), 150 (51), 152 (46).

G. 2,3-Dimethyl-2-butene Bromination. 2,3-Dimethyl-2-butene (Fluka, purity ≥99%). 2-Bromo-3-methoxy-2,2-dimethylbutane: mass spectrum (20 eV) *m/e* (rel intensity, characteristic fragmentation) 41 (142), 43 (82), 45 (31), 55 (121), 56 (31), 57 (97), 67 (50), 69 (52), 73 (1000, M − (($CH_3)_2CBr$)), 74 (52), 83 (117), 84 (31), 85 (55), 99 (72, M − (CH_3, Br, H)), 100 (78, M − (CH_3, Br)), 115 (81, M − (Br)), 179-181 (29-27, M − (CH_3)). 2,3-Dibromo-2,3-dimethylbutane: mass spectrum (20 eV) *m/e* (rel intensity, characteristic fragmentation) 41 (1000, M − (($CH_3)_2CBr$, BrH)), 42 (102), 43 (419), 53 (109), 55 (679, M − CH_3, CH_2, 2Br), 56 (91), 57 (84), 67 (190), 69 (517, M − (2Br, CH_3)), 80 (102), 81 (109), 83 (630, M − (2Br, H)), 84 (295), 121-123 (179-169, M − (($CH_3)_2CBr$)), 163-165 (911-904, M − (Br)), 164 (10).

Identification of the MB and DB compounds is coherent with their relative retention data or with their Kovats indexes which we determined on Squalane and Carbowax 1500 and published elsewhere.[52]

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(12) (a) The term chemoselectivity has been used particularly by Negishi.[13] It interprets the possible variations in the product distribution, here solvent incorporated products and dihalides. This term has the advantage of coherence in view of the various selectivities observed in product studies of olefin halogenation: stereo-, regio-, and chemoselectivity. (b) In this paper, chemoselectivity has been identified to the MB % experimental values. It could have been defined as log Q = log (MB/DB) which is directly related to (k'_{MeOH}/k'_{Br^-}); corresponding values which vary from −0.2 to 0.7 would have been less evident for the reader. Nevertheless, with both definitions Figures 1 and 4b remain very similar.
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(31) It is noteworthy that intermediates (c) and (f) which have a dimethyl-substituted C_α site both undergo a MeO–C_α regiospecific attack which in all likelihood is also (Br^-–C_α) regiospecific. Indeed we have observed that the attack on ethylenebromonium intermediates by Cl^- ions follows the same regiospecificity as the attack by MeOH.
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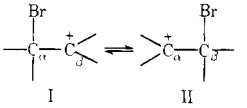
(33) The validity of this is based on three points: (1) Our study only deals with first-order variations distributed over a large interval of 150 ppm. The controversies concerning the validity of ^{13}C chemical shift–charge density correlations deal with second-order variations in a reduced interval. These controversies center around phenyl- or cyclopropyl-substituted carbocations which are likely to offer large possibilities of charge delocalization.[34–37] (2) Instead of using the chemical shift we use its relative variation $\Delta\delta$ with respect to the ethylenebromonium ion. These $\Delta\delta$ variations allow us to overcome the usual objections made by Farnum for the establishment of chemical shift–charge density correlations.[38] They also help to avoid the drawback of a possible systematic difference in the charge distributions between superacid and MeOH media. (3) By taking the $\delta^{13}C$ chemical shifts of sites C_α and C_β of the methyl-substituted and symmetrical ethylenebromonium ions as a function of Pauling's electronegativity of Cl, Br, and I halogens, we obtain good correlations. This indicates that the deshielding of the carbon atom by these halogens occurs inductively.[39] This can be interpreted in favor of the lack of back-donation due mostly to the chlorine. It stresses a fortiori the very slight probability of an α-bromoethylenecarbenium ion structure (I, II) being able to yield the following equilibrium:



I II

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