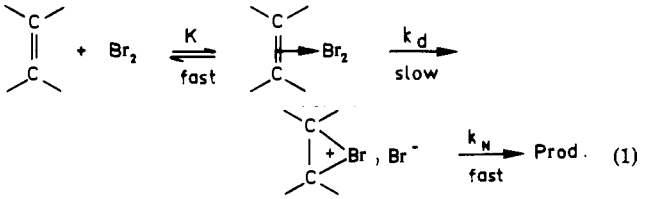
Solvation and Steric Effects on Electrophilic Reactivity of Ethylenic Compounds. 2. Kinetic Criteria for Nucleophilic Assistance and Return in Bromination[1]

Marie-Françoise Ruasse,* Shahrokh Motallebi, and Bernard Galland

Contribution from the Institut de Topologie et de Dynamique des Systèmes de l'Université Paris 7, Associé au CNRS, URA 34, 1, Rue Guy de la Brosse, 75005 Paris, France.
Received June 12, 1990. Revised Manuscript Received December 12, 1990

Abstract: Three kinetic criteria, m_{Br}, R $(k_{aqEtOH}/k_{AcOH})_Y$, and KSIE (kinetic solvent isotope effect), are used to estimate the magnitude of the electrophilic and nucleophilic involvement of protic solvents and the occurrence of return in the bromination of alkenes. m_{Br} are obtained from $m_{Br}Y_{Br}$ correlations using only water, methanol, ethanol, and their aqueous mixtures, whose nucleophilicities are almost identical. R are the deviations from the Winstein-Grunwald plots of the less nucleophilic acetic acid and occasionally of trifluoroethanol. KSIE in MeOD or EtOD are compared with the factors ϕ_{Br}- corresponding to their maximum values for fully developed bromide ions. The values of these criteria are measured for methylideneadamantane and allylbenzene, which are brominated via Ad_ECl and Ad_EC2-intermediate mechanisms, respectively. The first mechanism, involving only electrophilic solvent assistance to the rate-limiting ionization, is characterized by an m_{Br} value of 1.1, associated with R close to unity and high KSIE (1.3). For the second, in which the solvent also assists nucleophilically, m_{Br} (0.8) is significantly smaller than unity and R (8.0) is markedly greater; the KSIE is still high. The reaction of adamantylidenealkanes, Ad=CH*t*-Bu, Ad=CMe_2, and Ad=CM*e*i-Pr, is also investigated; R are close to unity but m_{Br} are only ~0.8 and significantly smaller KSIE (1.13 for Ad=CH*t*-Bu) are found. This set of values is consistent with reversible formation of highly congested bromonium ions in protic solvents. The results are compared with those obtained in halogenated solvents and in acetic acid, where return has been observed. The different magnitudes of return in protic and nonprotic media are discussed in terms of substituent dependence of solvent involvement.

Jencks-More O'Ferrall diagrams have widely popularized the idea that reaction mechanisms can be significantly altered by changing the substituents and/or the medium.[2] This concept has been extensively applied to nucleophilic additions or substitutions[3] but apparently never to electrophilic reactions. For example, electrophilic bromination of ethylenic compounds, a well-known basic reaction of organic chemistry,[4] is still believed to follow uniformly the long-established Ad_ECl mechanism.[5] According to this mechanism, three successive steps are involved in olefin bromination: (i) fast-equilibrated formation of an olefin-bromine charge-transfer complex, (ii) rate-limiting ionization of this π complex into a σ complex, the so-called bromonium ion, and finally, (iii) fast product formation by nucleophilic trapping of the ionic intermediate. A recent modification of this scheme concerns the magnitude of bromine bridging in the σ complex. Bromine bridging depends markedly on the double-bond substituents,[6] and a spectrum of intermediates from bridged to open cations, rather than an exclusive bromonium ion, is now well-established. Moreover, examples of reversible bromonium ion formation have been reported.[7]



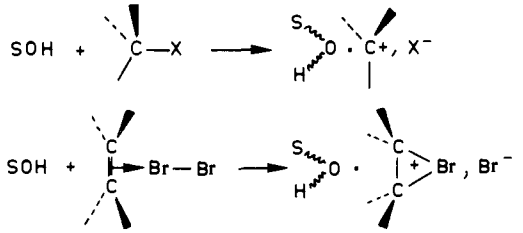
(1)

The Ad_ECl mechanism is supported by kinetic substituent and solvent effects, which show high charge development in the rate-limiting transition states. The bromination ρ and m values have been interpreted by comparison with analogous data on solvolytic reactions leading to similarly ionic intermediates.[8] Insofar as in both reactions neutral reagents undergo ionization to a cation-anion pair, there is an analogy between bromination and solvolysis. However, it is now known that the solvolysis mechanism is not uniformly S_N1 or S_N2. In particular, depending on the substituents and the media, heterolysis can involve return and nucleophilic assistance to the ionization. Return has been shown to occur, in particular in the solvolysis of adamantyl derivatives,[9] while nucleophilic solvent involvement in the cation-forming step via an S_N2-intermediate mechanism is also well-documented.[10]

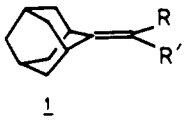
If there is an analogy between bromination and solvolysis, it is surprising that these two latter mechanistic features of solvolytic reactions are not found in the electrophilic additions. In fact, two series of results suggest that they do occur in bromination. Return from bromonium-bromide ion pairs is implied by two experiments,[7] which show that either bromine or alkene can be obtained from bromonium ions prepared by heterolysis of β-bromo derivatives under particular conditions. Nucleophilic solvent assistance is invoked to interpret the dependence of the solvent effect, k_{MeOH}/k_{AcOH}, on the double-bond crowding.[11] In addition to the usual Ad_ECl mechanism, there could be an Ad_EC2 intermediate, analogous to the S_N2 intermediate in solvolysis, that involves nucleophilic solvent assistance to the rate-limiting ionization.

(1) Part 1: Ruasse, M. F.; Motallebi, S.; Galland, B.; Lomas, J. S. *J. Org. Chem.* **1990**, *55*, 2298.
(2) More O'Ferrall, R. A. *J. Chem. Soc. B* **1970**, 274. Grunwald, E. *J. Am. Chem. Soc.* **1985**, *107*, 125. Jencks, W. P. *Chem. Rev.* **1985**, *85*, 511.
(3) (a) Albery, W. J.; Kreevoy, M. M. *Adv. Phys. Org. Chem.* **1978**, *16*, 87. Richard, J. P.; Jencks, W. P. *J. Am. Chem. Soc.* **1984**, *106*, 1383. Bordwell, F. G.; Hughes, D. L. *J. Org. Chem.* **1980**, *45*, 3320. (b) Grunwald, E. *J. Am. Chem. Soc.* **1985**, *107*, 4710, 4715. (c) Gandler, J. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1982**, *104*, 1937.
(4) (a) De la Mare, P. B. D.; Bolton, R. *Electrophilic Additions to Unsaturated Systems*, 2nd ed.; Elsevier: Oxford, 1982. (b) V'yunov, K. A.; Ginak, A. I. *Russ. Chem. Rev. (Engl. Transl.)* **1981**, *50*, 151.
(5) (a) Garnier, F.; Dubois, J. E. *Bull. Soc. Chim. Fr.* **1968**, 3797. (b) Olah, G. A. *Halonium Ions*; Wiley: New York, 1975. (c) Olah, G. A.; Hockswender, T. R., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 3574.
(6) Ruasse, M. F. *Acc. Chem. Res.* **1990**, *23*, 87.
(7) (a) Brown, R. S.; Gedye, R.; Slebocka-Tilk, H.; Buschek, J. M.; Kopecky, K. R. *J. Am. Chem. Soc.* **1984**, *106*, 4515. (b) Bellucci, G.; Chiappe, C.; Marioni, F. *J. Am. Chem. Soc.* **1987**, *109*, 515.
(8) (a) Rolston, J. H.; Yates, K. *J. Am. Chem. Soc.* **1969**, *91*, 1483. (b) Ruasse, M. F.; Argile, A.; Dubois, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 7645. (c) Ruasse, M. F.; Dubois, J. E. *J. Am. Chem. Soc.* **1975**, *97*, 1977.
(9) Paradisi, C.; Bunnett, J. F. *J. Am. Chem. Soc.* **1985**, *107*, 8223.
(10) Bentley, T. W.; Schleyer, P. v. R. *Adv. Phys. Org. Chem.* **1976**, *14*, 1. Bentley, T. W.; Bowen, C. T.; Morten, D. H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5466.
(11) Ruasse, M. F.; Zhang, B. L. *J. Org. Chem.* **1984**, *49*, 3207. Ruasse, M. F.; Lefebvre, E. *J. Org. Chem.* **1984**, *49*, 3210.

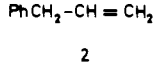
0002-7863/91/1513-3440$02.50/0



Kinetic solvent effects are obviously the appropriate tool for investigating the second mechanism. Although a number of relevant data on a large variety of ethylenic compounds are available,[5,8,12-15] it is difficult to interpret them in terms of mechanistic changes because they have not been obtained with this objective in mind. Consequently, we shall attempt to establish criteria for distinguishing whether bromonium ion formation is nucleophilically assisted or not and is reversible or irreversible. We recently showed[16] that methylideneadamantane (**1**) probably



1



2

1: R = R′ = H

3a: R = *t*-Bu, R′ = H

3b: R = R′ = Me

3c: R = *i*-Pr, R′ = Me

reacts with free bromine via a pure Ad_ECl mechanism; we take this, therefore, as a model of this first mechanism. As a model of Ad_EC2–intermediate bromination, we choose allylbenzene (**2**), a relatively unreactive noncongested alkene whose reaction could be readily assisted. Finally, we also investigate bromine addition to highly congested adamantylidenealkanes[1] **3a–c**, for which return should be enforced by strong inhibition of nucleophilic attack on their bromonium ions. In this paper, we show that return and assistance can be demonstrated by associating three kinetic criteria, m coefficients, R ratios $(k_{aqEtOH}/k_{AcOH})_Y$, and solvent isotope effects, that depend significantly on the occurrence of these mechanistic features.

Results

Kinetic Solvent Effects. The rate constants of free bromine addition to alkenes **1–3** were measured in ethanol, methanol, and several water–alcohol mixtures by following bromine uptake spectrophotometrically[17] or amperometrically.[18] The highest bromination constants accessible are $\sim 5 \times 10^7$ M^{-1} s^{-1}. For each alkene, in order to obtain significant m values, the solvents were chosen to cover a reactivity range as wide as possible. The rate constants shown in Table I were obtained[19] from kinetic experiments carried out in the presence of several bromide ion concentrations by extrapolation to $[Br^-] = 0$. This procedure separates the kinetic term for free bromine addition from those related to tribromide ion addition and/or to bromide-assisted bromine addition, according to the usual equation (eq 2), where α is the

$$k_{exp}(1 + K[Br^-]) = \alpha + \beta[Br^-] \qquad (2)$$

relevant rate constant, β the salt effect coefficient, and K the bromine–bromide/tribromide equilibrium constant.[20]

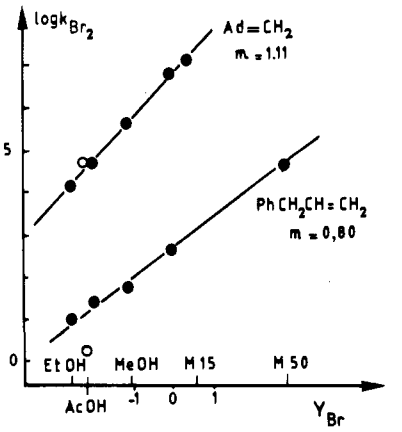
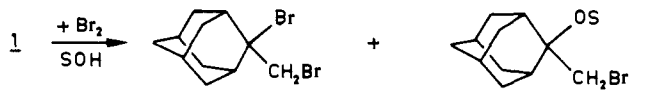


Figure 1. m_{Br} Y_{Br} plots for methylideneadamantane (Ad_EC1 mechanism) and allylbenzene (Ad_EC2-intermediate mechanism) bromination. Closed circles, alcohols and their aqueous mixtures; open circles, acetic acid.

Consequently, the rate data of Table I concern exclusively *the addition of molecular bromine, which may be assisted by the solvent but not by bromide.* Since the alcohols and their aqueous mixtures have approximately the same nucleophilicities (Table II), we tried to measure the rate constants in solvents of very different nucleophilic power, acetic acid and trifluoroethanol.[21] However, bromination of most alkenes is too fast in this latter solvent and kinetic data could only be obtained for allylbenzene and 1-pentene. The results are included in Table I.

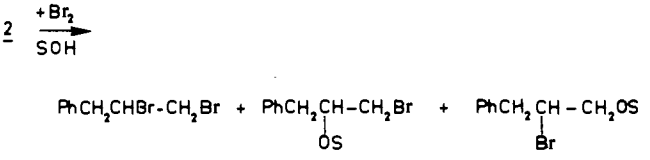
Kinetic Solvent Isotope Effects. Rates in deuterated alcohols were measured only by spectrophotometry because of the experimental limitations of amperometry. Since the highest rate constants available by this method are in the 10^3 M^{-1} s^{-1} range, MeOD or EtOD was used depending on the alkene reactivity. The kinetic solvent isotope effects given in Table III are average results of experiments carried out at several bromide ion concentrations. The bromide ion effect on these isotope effects is insignificant as compared to the errors on the bromination rate constants.

Product Formation. The bromination product distribution was also investigated in pure methanol and in acetic acid. Methylideneadamantane and allylbenzene lead exclusively to the expected solvent-incorporated and dibromo adducts in ratios shown in Table IV. Methylideneadamantane bromination is regiospecific: only 2-methoxy-2-(bromomethyl)adamantane or 2-acetoxy-2-(bromomethyl)adamantane (**5**) are obtained in methanol or in acetic



4 **5**

acid, respectively. This is in agreement with the well-established rule concerning the regiospecificity of *gem*-disubstituted alkene bromination.[22] In contrast, the solvent-incorporated product of allylbenzene bromination consists of two regioisomers, which have been detected but not separated from the product mixtures. No rearranged products (1,3-dibromo-2-phenylpropane or 1-methoxy-3-bromo-2-phenylpropane), which would suggest the occurrence of a bromomethylphenonium intermediate instead of the usual bromonium ion,[23] have been observed under these conditions.



(12) Bienvenue-Goëtz, E.; Dubois, J. E. *Tetrahedron* **1968**, *24*, 6777.
(13) Barbier, G.; Dubois, J. E. *J. Chim. Phys-Chim. Biol.* **1968**, *65*, 1989.
(14) Modro, A.; Schmid, G. H.; Yates, K. *J. Org. Chem.* **1977**, *42*, 3673.
(15) Ruasse, M. F. *Isr. J. Chem.* **1985**, *26*, 414.
(16) Ruasse, M. F.; Motallebi, S. *Bull. Soc. Chim. Fr.* **1988**, 349.
(17) Dubois, J. E.; Garnier, F. *Spectrochim. Acta, Part A* **1967**, *28A*, 2279.
(18) Dubois, J. E.; Ruasse, M. F.; Poupard, D. *J. Electroanal. Chem.* **1983**, *152*, 67.
(19) Bartlett, P. D.; Tarbell, D. S. *J. Am. Chem. Soc.* **1936**, *58*, 466. Dubois, J. E.; Huynh, X. Q. *Bull. Soc. Chim. Fr.* **1968**, 1436.
(20) Dubois, J. E.; Bienvenue-Goëtz, E. *Bull. Soc. Chim. Fr.* **1968**, 2089. Dubois, J. E.; Huynh, X. Q. *Tetrahedron Lett.* **1971**, 3369.
(21) Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7667.
(22) Dubois, J. E.; Chrêtien, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 3506.
(23) Norman, R. O. C.; Thomas, C. B. *J. Chem. Soc. B* **1967**, 598. Fain, D.; Dubois, J. E. *Tetrahedron Lett.* **1978**, 791.

Table I. Rate Constants (M^{-1} s^{-1}) for Free Bromine Addition to Alkenes **1**, **2**, and **3** at 25 °C in Various Protic Solvents

	k^a					
solvents	**1**	**3a**	**3b**	**3c**	**2**	*n*-PrCH=CH_2[b]
EtOH	1.4×10^4	1.3×10^2	3.5×10^6	9.7×10^4	1.0×10	1.3×10
EtOH(2.5)[d]	5.1×10^4	3.3×10^2	7.2×10^6	1.3×10^5	2.5×10	
EtOH(5.0)[d]			1.0×10^7			9.1×10
MeOH	4.2×10^5	1.4×10^3	2.5×10^7	5.7×10^5	5.3×10^e	3.8×10^2
M90[f]	5.5×10^6			4.8×10^6	4.4×10^2	2.8×10^3
M85[f]	1.3×10^7			1.0×10^7		
M80[f]				1.3×10^7		1.5×10^4
M70[f]		2.3×10^5				9.8×10^4
M50[f]					4.5×10^4	9.1×10^5
H_2O					$3.6 \times 10^{6\,g}$	2.3×10^7
AcOH	4.8×10^4	6.5×10^2	6.3×10^6	1.9×10^5	1.6^c	1.1×10
TFE3[h]					1.21×10^4	2.3×10^5

[a] Reprodubilicity is ±2% for constants smaller than 10^3 M^{-1} s^{-1} and ±5% for higher constants. [b] Reference 5a. [c] Reference 30. [d] EtOH(2.5) and EtOH(5.0), 2.5–97.5% and 5–95% H_2O–EtOH (v/v), respectively. [e] Reference 31. [f] M90, M85, M80, M70, M50, 10–90%, 15–85%, 20–80%, 30–70%, and 50–50% H_2O–MeOH (v/v), respectively. [g] Reference 12. [h] 3% aqueous trifluoroethanol (w/w).

Table II. *Y* and *N* Solvent Parameters in the Winstein–Grunwald and Bentley–Schleyer Scales

solvents	$Y_{t\text{BuCl}}$[a]	Y_{Br}[b]	N^c
EtOH	−2.03	−2.40	0.09
EtOH(2.5)[d]	−1.64	−1.90	0.08
EtOH(5.0)[d]	−1.36	−1.46	0.06
MeOH	−1.09	−1.10	0.01
M10[e]	−0.30	−0.10	0.02
M15[e]	0.00	0.30	0.00
M20[e]	0.38	0.70	−0.02
M30[e]	0.96	1.42	−0.07
M50[e]	1.97	2.61	−0.18
H_2O	3.49	4.44	−0.26
AcOH	−1.64	−2.10	−2.05
TFE3[f]	1.15	2.53	−2.59

[a] Reference 27. [b] Reference 28. [c] Reference 21. [d] EtOH(2.5), H_2O–EtOH, 2.5–97.5% v/v; EtOH(5.0), H_2O–EtOH, 5.0–95.0% v/v. [e] M90, H_2O–MeOH, 10–90% v/v; M85, H_2O–MeOH, 15–85% v/v; M80, H_2O–MeOH, 20–80% v/v; M70, H_2O–MeOH, 30–70% v/v; M50, H_2O–MeOH, 50–50% v/v. [f] 3% aqueous trifluoroethanol (w/w).

Table III. Experimental Data for the Kinetic Solvent Isotope Effects[a] on Bromination of Alkenes **1**, **2**, and **3** in Methanol and Ethanol

	k_{MeOH}/k_{MeOD}	k_{EtOH}/k_{EtOD}
1		1.35 ± 0.07
n-PrCH=CH_2	1.35 ± 0.07[b]	1.30 ± 0.05
3a	1.29 ± 0.04	
3c		1.13 ± 0.03
2	1.37 ± 0.08	
ϕ_{Br}[c]	1.35 ± 0.05	1.27 ± 0.06

[a] Average of kinetic measurements at several bromide ion concentrations. [b] Reference 32. [c] Limiting KSIE in bromination; see text.

Table IV. Product Distribution of the Bromination of Methylideneadamantane (**1**) and Allylbenzene (**2**) in Pure Methanol and Acetic Acid at 25 °C

		dibromide, %	mixed adduct, %
1[a]	MeOH	42[b]	58[c]
	AcOH	92[b]	8[d]
2[e]	MeOH	14[f]	86[g]
	AcOH	93[f]	7[h]

[a] From ^1H NMR measurements. [b] 2-Bromo-2-(bromomethyl)-adamantane. [c] 2-Methoxy-2-(bromomethyl)adamantane. [d] 2-Acetoxy-2-(bromomethyl)adamantane. [e] From GC measurements. [f] 1-Phenyl-2,3-dibromopropane. [g] Mixture of 1-phenyl-2-methoxy-3-bromopropane and 1-phenyl-2-bromo-3-methoxypropane. [h] Mixture of 1-phenyl-2-bromo-3-acetoxypropane and 1-phenyl-2-acetoxy-3-bromopropane.

Bromination products of isopropylideneadamantane (**3b**) have also been investigated. They correspond neither to the usual addition products nor to a homoallylic bromination of the methyl groups analogous to that observed in chlorination of the same alkene.[24] Instead, rearrangement of the adamantyl ring seems to be involved. The likelihood of this process is suggested by the several unusual products obtained in reactions involving a 2-adamantyl cation.[25] Attempts to identify the bromination products of **3b** have failed because of a marked dependence of their NMR spectra on the reaction conditions (temperature and concentrations). Similar difficulties have already been encountered in the bromination of tetrasubstituted alkenes.[26]

Table V. m_{Br} Correlations of Bromination Rates in Water, Ethanol, Methanol, and Their Aqueous Mixtures

alkene	m_{Br}	log k_0	r^a
1	1.11 ± 0.02	6.84	0.999
3a	0.85 ± 0.01	4.14	0.999
3b	0.63 ± 0.1	8.03	0.975
3c	0.76 ± 0.05	6.68	0.992
2	0.80 ± 0.03	2.80	0.996
n-PrCH=CH_2	0.95 ± 0.03	3.84	0.997

[a] Correlation coefficients.

mY Relationships and Nucleophilic Assistance Measurements. When either Winstein–Grunwald Y_{WG} values[27] or Bentley Y_{Br} values[28] (Table II) are used for nucleophilic alcoholic and aqueous solvents only, fairly linear *mY* relationships result. That both plots are linear is not unexpected since Y_{WG} values derived from *tert*-butyl chloride solvolysis are linearly related to Y_{Br} values based on 2-bromoadamantane ionization, for this limited set of solvents. m_{WG} values can therefore easily be converted to m_{Br} values, $m_{WG} = 1.25m_{Br}$. However, the second parameter scale is preferred since it does not involve any nucleophilic contribution of the solvent and because the leaving group is a bromide ion in solvolysis as in bromination. Results of the $m_{Br}Y_{Br}$ correlations are given in Table V. An example of the corresponding plots is shown in Figure 1.

Nucleophilic solvent assistance is evaluated conventionally[10,29] from the *R* ratios, $(k_{aqEtOH}/k_{AcOH})_Y$, of the rate constant in acetic acid and in the appropriate water–ethanol mixture in which the rate has been calculated from the $m_{Br}Y_{Br}$ relationship above. The *R* values correspond, therefore, to the deviations of the acetic acid points from the log k/Y_{Br} plots used to calculate the m_{Br} values.

(24) Meijer, E. W.; Kellog, R. M.; Wynberg, H. *J. Org. Chem.* **1982**, *47*, 2005.
(25) Lenoir, D.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1970**, 941. Boyd, J.; Overton, K. H. *J. Chem. Soc., Perkin Trans. 1* **1972**, 2533. Gassman, P. G.; Saito, K.; Talley, J. J. *J. Am. Chem. Soc.* **1980**, *102*, 7615.
(26) (a) Mayr, H.; Will, E.; Heigh, U. W.; Schade, C. *Tetrahedron* **1986**, *42*, 2519. (b) Lenoir, D. *Chem. Ber.* **1978**, *111*, 411. (c) Andersen, L.; Berg, U.; Petterson, I. *J. Org. Chem.* **1985**, *50*, 493. (d) Brown, R. S.; Slebocka-Tilk, H.; Bennett, A. J.; Bellucci, G.; Bianchini, R.; Ambrosetti, R. *J. Am. Chem. Soc.* **1990**, *112*, 6310.
(27) Fainberg, A. H.; Winstein, S. *J. Am. Chem. Soc.* **1956**, *78*, 2770.
(28) Bentley, T. W.; Carter, G. E. *J. Am. Chem. Soc.* **1982**, *104*, 5741.
(29) Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7658.
(30) Zhang, B. L. Doctoral Thesis, University Paris 7, 1981.
(31) Bienvenue-Goëtz, E.; Dubois, J. E. *Tetrahedron* **1978**, *34*, 2021.

Table VI. m_{Br}, R, and Kinetic Solvent Isotope Effects for **1**, **2**, and **3** Bromination, as Mechanistic Criteria of Solvent Assistance and Return in Free Bromine Addition to Alkenes

	m_{Br}	R^a	KSIE
1	1.11	0.9	1.35
2	0.80	8.3[b]	1.37
3a	0.85	0.4	1.29
3b	0.63	0.8	
3c	0.76	0.6	1.13

[a] $R = (k_{aqEtOH}/k_{ACOH})_Y$. [b] $(k_{aqMeOH}/k_{TFE})_Y = 8.7$.

It is noticeable that R depends significantly on the choice of the Y scale. In principle, the less nucleophilic trifluoroethanol (TFE) would have been better than acetic acid for evaluating nucleophilic solvent assistance. However, it appears that R values from either $(k_{aqEtOH}/k_{AcOH})_Y$ or $(k_{aqMeOH}/k_{TFE})_Y$ are very similar for allylbenzene and 1-pentene. This suggests that nucleophilicities of acetic acid and TFE are not very different in bromination. However, R as evaluated here are probably underestimates of the nucleophilic solvent assistance.

Discussion

The main role of a protic solvent in the rate-limiting step of bromination has been identified as an electrophilic assistance to bromide ion departure. This was established from the high solvent sensitivity of the rate[5a,6,8c] and from the large solvent isotope effect[32,33] of 1-pentene bromination in methanol and acetic acid. Nucleophilic solvent involvement was excluded at that time because the m value ($m_{WG} = 1.16$) was greater than unity. Later, it was found for a variety of alkenes that there are good log/log correlations[12,13] between the rates in methanol, water, and 70% aqueous methanol; it was concluded that m_{WG} does not vary with the double-bond substituents or with the alkene reactivity. In other words, whatever the alkene structure, the mechanism is Ad_ECl with electrophilic solvent assistance only.

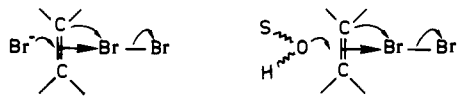
However, since there are some similarities between ionization processes involved in bromination and solvolysis, a progressive change in mechanism, parallel to the S_N2, S_N2-intermediate, S_N1 spectrum, is expected to result from variations in nucleophilic solvent assistance in bromination. The occurrence of bromide ion assistance,[20] as revealed by the reactivity dependence of the bromide effect coefficient, appears to support the idea that the nucleophilic requirements of bromination vary with the alkene reactivity.

Criteria for Nucleophilic Solvent Assistance. In solvolysis, mechanistic changes are revealed mainly by variations in m values and by comparison of the rates in pairs of solvents with similar ionizing powers but different nucleophilicities.[10,29] The same procedures can be applied in bromination if we know the values of these criteria (which are not necessarily identical for both reactions) for limiting situations with or without nucleophilic solvent assistance. These values are based on allylbenzene (**2**) and methylideneadamantane (**1**) bromination, respectively (Table VI).

In contrast with what was observed when solvents of various nucleophilicities are included in the same correlations, there are significant differences in m_{Br} for **1** and **2** when only alcoholic and aqueous solvents are considered. An m_{Br} value greater than unity associated with an R ratio close to unity, as found for **1**, is taken as a criterion of the nucleophilically unassisted Ad_ECl mechanism. When m_{Br} is smaller than 1 and R markedly greater, the solvent is nucleophilically involved in the ionization step, as required by an Ad_EC2–intermediate mechanism. By associating these two criteria, it is, therefore, possible to distinguish kinetically two bromination mechanisms, differing in solvent assistance to the rate-limiting step.

The fact that m_{Br} for Ad_ECl bromination is slightly greater than for S_N1 solvolysis is probably not significant since there are noticeable differences between the mechanisms of the two reactions. In particular, the ground states, alkyl halides on one hand, alkenes and bromine on the other hand, are likely to be differently solvated because of their different polarizabilities. This solvent effect should be very small as compared with that on the highly charged transition states. Moreover, in bromination the ionization step is preceded by the formation of a charge-transfer complex between bromine and the ethylenic bond. According to the few relevant data,[6,34] it is reasonable to assume that solvent effects on this preequilibrium are negligible with respect to those on the ionization step.[35]

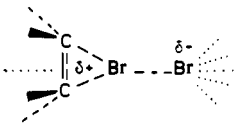
If the bromination–solvolysis analogy is pushed to the limit, an Ad_EC2 mechanism with no intermediate should be expected for highly deactivated ethylenic compounds. This hypothesis has not been considered until now since bromonium ions are thought to be implied whatever the double-bond substituents. This seems reasonable a priori, the bromide ion being an excellent neighboring group that can stabilize charge development efficiently, even if the substituents strongly destabilize it. However, bromide ion effects (β term in eq 2) have been discussed at length in terms of competition between tribromide ion addition and bromide-assisted molecular bromine addition,[8a,20,38] two processes kinetically indistinguishable. It is now accepted that for highly deactivated alkenes, the second process is preponderant.[39] It is, therefore, likely that a similar mechanism where the assistance is provided by the solvent could exist for the bromination of poorly nucleophilic and unhindered alkenes in highly nucleophilic solvents.



However, similar transition states are expected for Ad_EC2 and Ad_EC2-intermediate processes, differing only as to the occurrence or not of a very short-lived intermediate. The usual difficulties in showing whether a reaction goes through an intermediate[40] are expected for bromination. In any case, there are at present no bromination data that can be interpreted unambiguously in terms of an Ad_EC2 mechanism. Only for alkynes whose electrophilic reactions are much slower have exclusive bromine-assisted brominations been demonstrated.[33,41]

Evaluation of the Electrophilic Solvent Assistance. The kinetic solvent isotope effects are similarly high for the two mechanisms identified (Table VI), showing that electrophilic solvent assistance is equally important in both.[33] The absence of any relationship between electrophilic and nucleophilic solvent involvement is expected since solvent hydrogen bonding to the leaving bromide ion in the transition state cannot be hindered by the double-bond substituents.

(32) Garnier, F.; Donnay, R.; Dubois, J. E. *J. Chem. Soc. D* **1971**, 829.
(33) Modro, A.; Schmid, G. H.; Yates, K. *J. Org. Chem.* **1979**, *44*, 4221.
(34) For example, the equilibrium constant of the cyclohexene–bromine CTC is enhanced by a factor of 1.3 on going from hexane to 1,2-dichloroethane whereas the bromination rate of the same alkene is calculated to be 10^5 larger in the second than in the first solvent.[4b,36] A similarly small solvent effect on tetraisobutylethylene CTC formation has recently been measured.[26d]
(35) It has recently been argued[37] that neglect of substituent effects on CTC formation can be misleading in the interpretation of rate data. This suggestion is based on the observation of a very large equilibrium constant (K = 289 M^{-1}) in dichloroethane for the CTC from adamantylideneadamantane whereas previously known K were in the 5–10 M^{-1} range in the same solvent. This highly congested olefin is atypical; it is difficult to generalize from this finding.
(36) Bellucci, G.; Bianchini, R.; Ambrosetti, R. *J. Am. Chem. Soc.* **1985**, *107*, 2464.
(37) Bellucci, G.; Bianchini, R.; Chiappe, C.; Marioni, F.; Ambrosetti, R.; Brown, R. S.; Slebocka-Tilk, H. *J. Am. Chem. Soc.* **1989**, *111*, 2640.
(38) Nozaki, K.; Ogg, R. A. *J. Am. Chem. Soc.* **1942**, *64*, 697, 704, 709. Kanyaev, K. *Zh. Obshch. Khim.* **1959**, *29*, 841. Bell, R. P.; Pring, M. *J. Chem. Soc. B* **1966**, 1119. Buckles, R. E.; Miller, J. L.; Thurmaier, R. J. *J. Org. Chem.* **1967**, *32*, 888. Fahey, R. C.; Paine, M. T.; Lee, D. J. **1974**, *39*, 1124. De la Mare, P. B. D.; Wilson, R. D. *J. Chem. Soc., Perkin Trans. 2* **1977**, 2048, 2055, 2062.
(39) DeYoung, S.; Berliner, E. *J. Org. Chem.* **1979**, *44*, 1088.
(40) Jencks, W. P. *Acc. Chem. Res.* **1980**, *13*, 161.
(41) Pincock, J. A.; Yates, K. *J. Am. Chem. Soc.* **1968**, *90*, 5643; *Can. J. Chem.* **1970**, *48*, 3332. Erlich, S. J.; Berliner, E. *J. Am. Chem. Soc.* **1978**, *100*, 1525. Modena, G.; Rivetti, F.; Tonellato, U. *J. Org. Chem.* **1978**, *43*, 1521.

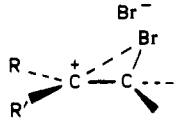


The magnitude of this assistance is directly related to the charge on the leaving bromide so that the kinetic solvent isotope effect is a direct measure of the charge development at the transition state.[32,33] The highest possible value for this isotope effect, corresponding to a fully developed bromide ion, is given by the ϕ_{Br^-} factor (Table III), which is the change in the transfer energy of bromide on going from the isotopically normal to the deuterated solvent. The experimental kinetic isotope effects for **1** and **2** are both very close to ϕ_{Br^-}. We conclude that the transition states for assisted and unassisted mechanisms are similarly late and closely resemble the ionic intermediates.[8c]

Solvation energies of bromide ions[42] are ~60 kcal/mol at 25 °C. The very high kinetic solvent isotope effects observed in bromination imply that the rate contribution of electrophilic solvent assistance is of the same order of magnitude.

Kinetic Criteria for Return in Bromination in Protic Solvents. In the foregoing discussion it has been implicitly assumed that the formation of the bromocations from **1** and **2** is irreversible. Now, in the solvolysis of 2-adamantyl derivatives significant return has been found.[9] The differences in the structures of bromination and solvolysis intermediates suggest, however, that return should be less important in electrophilic addition than in solvolytic ionization.

Return in bromination implies bromide attack on the charged bromine atom of the bromonium ion, leading to molecular bromine and alkene. However, it has been calculated[43] and indirectly shown from product data[22] that the bromination intermediates of *gem*-disubstituted alkenes resemble β-bromo carbocations, the charge of which is mainly borne by the most substituted carbon atom and not by the bromine atom. As a consequence, the bromide counterion in the intimate ion pair should attack the carbocationic site to give the reagents.



Reversibility of bromonium ion formation should, therefore, be disfavored with respect to product formation, unless the last step is made energetically difficult by some particular features, such as those described below, steric crowding or poor reactivity of the trapping nucleophiles. The unimportance of return in bromination of **1** is supported by the results obtained for adamantylidenealkanes **3**.

In Table VI are listed the values of the three kinetic criteria observed in the bromination of a series of alkenes more congested than **1**, the mechanism of which should be a priori Ad_ECl. The reaction of **3** cannot be and is not nucleophilically assisted, as is shown by the very small R ratios. For solvolytic reactions, it has been suggested[10,29] that R values smaller than unity, as are those obtained in bromination of **3**, could indicate reversible formation of the intimate ion pair. Moreover, the m values for **3** fall unexpectedly in the range of an Ad_EC2-intermediate bromination and the isotope effects are significantly smaller. This picture is consistent with return.

The inhibition of nucleophilic solvent involvement by congested alkyl substituents can play a role in the ionization step[11] and also in the last product-forming step of bromination. For moderately crowded alkenes, it is reasonable to assume that the ionic intemediate is trapped rapidly. For highly congested alkenes such as **3** it is probable that the nucleophilic attack on the bromonium

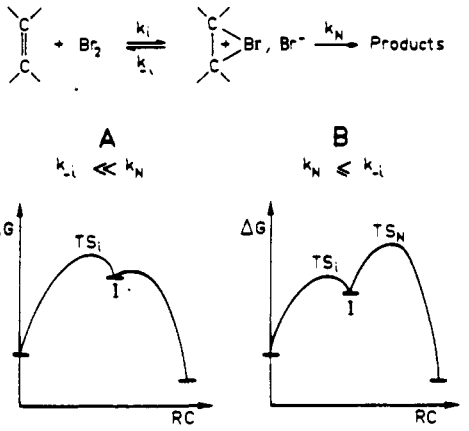


Figure 2. Free energy profiles of bromination with (a) rate-limiting bromonium ion formation and (b) reversible bromonium ion formation.

ions is difficult so that the product-forming step is now of higher energy, as is shown in Figure 2. In fact, the absence of any addition product in the bromination of **3** suggests that the products do not arise from the usual nucleophilic attack but from bromide-promoted rearrangements as proposed by Wynberg[24] et al. and more recently, by Brown et al. for tetraalkylethylene halogenation.[26d] In particular, a substantial kinetic isotope effect has been observed by comparing the bromination of tetraisobutylethylene with that of the analogous alkene in which the eight allylic positions are deuterated, showing that proton abstraction is involved in the rate-limiting step.[26] The energy profile of congested alkene bromination must, then, resemble that of Figure 2B, implying return from the ionic intermediate I. Under these circumstances, the kinetic data and the criteria deduced therefrom are not only related to the ionization process but also to the last step, as shown in eqs 3 and 4, where the subscripts i and N refer

$$k = (k_i/k_{-i})k_N \qquad m = m_i m_N \tag{3}$$

to the ionization step and to the last nucleophilic step, respectively. Since m_i is probably not different from the m value for the Ad_ECl mechanism, the experimental m values suggest that m_N is in the range of −0.2 to −0.3 at least. The negative value of this solvent effect is easily understood, the charge on the bromide counterion decreasing from the intermediate to the final transition state. This charge decrease is also consistent with the kinetic solvent isotope effect, which is found to be significantly smaller for bromination of **3** than for the other two alkenes.

Return in bromination of **3** is also strongly suggested by the olefin series **1**, **3**, and **6**. There is a continuous increase in double-bond crowding on going from **1** to **3** and finally to **6**, adamantylideneadamantane. It is well-known that in the bromination of **6** nucleophilic attack is totally inhibited since the reaction stops at the bromonium ion.[45] It is probable, therefore, that the mechanism of **3** involves a marked increase in the activation free energy of the product-forming step.

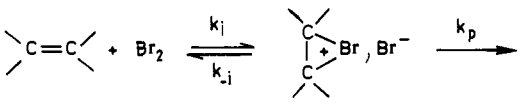
The fact that the Winstein–Grunwald relationships remain linear even when there is return in bromination deserves comment. Equation 3 assumes that an mY relationship holds for the nucleophilic step. In the case of bromination, the solvent can affect the last step by changing the nucleophilicity of the bromide ion. This could arise from changes in the magnitude of the energy of counter-bromide solvation, a process clearly included in the Y parameters. Consequently, bromination is probably a particular situation as regards the description of return by mY correlations.

In conclusion, return for bromination in protic solvents can be evidenced by kinetic criteria whose values are markedly different from those obtained when there is no return. High crowding of the double bond enforces the reversibility of bromonium ion formation.[46] This is an indirect argument for the absence of

(42) Abraham, M. H. *J. Chem. Soc., Faraday Trans. 1* **1978**, 1064.
(43) Galland, B.; Evleth, E. M.; Ruasse, M. F. *J. Chem. Soc., Chem. Commun.* **1990**, 898.
(44) Kevill, D. N.; Kamil, W. A.; Anderson, S. W. *Tetrahedron Lett.* **1982**, *23*, 4635.
(45) Strating, J.; Wieringa, J. H.; Wynberg, H. *J. Chem. Soc., Chem. Commun.* **1969**, 907. Slebocka-Tilk, H.; Ball, R. G.; Brown, R. S. *J. Am. Chem. Soc.* **1985**, *107*, 4504.

kinetically significant return in bromination of moderately crowded alkenes, at least in alcoholic solvents.

In acetic acid in the presence of added bromide ions, reversible formation of a bromonium–bromide ion pair has been found by Brown et al.[7a] Free bromine, rapidly trapped by a highly reactive alkene, is obtained from the cyclohexene bromonium ion solvolytically generated under these experimental conditions. The kinetic results associating m_{Br}, R, and KSIE values establish the absence of return in alcoholic and aqueous media but not necessarily in acetic acid.[47] Nevertheless, R ratios are similar in acetic acid and trifluoroethanol, two solvents in which the importance of return is expected to be different since they are both poor nucleophiles but have different ionizing and dissociating powers. Consequently, at least for allylbenzene and 1-pentene, the main factor that determines R values is probably nucleophilic assistance and not return. Conclusively, as regards return in acetic acid, the two series of results from either product or kinetic data seem to be contradictory unless the ratio k_{-i}/k_p (eq 4), which



Products (4)

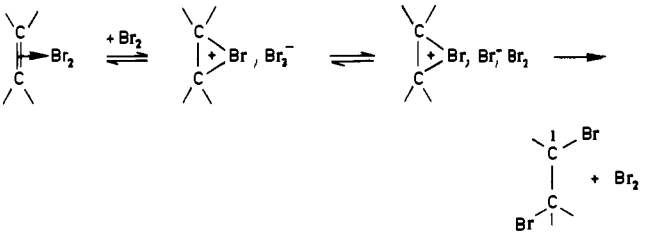
determines the kinetic significance of return, is sensitive to the reaction conditions and, in particular, to bromide ion concentrations.

Enforced Return in Bromination in Nonprotic Solvents. Recent data on bromination of uncongested alkenes suggest that uncrowded bromonium ions are formed reversibly *in halogenated solvents*.[7b] This is in contrast with the conclusion that in protic solvents return is only observed for the reaction of congested alkenes. In terms of the energy profile, return involves a product-forming step energetically more expensive than the ionization step. Increase in the kinetic barrier of the last bromination step arises from steric inhibition of nucleophile attack on the cationic intermediate. But a similar increase can also be achieved by decreasing the nucleophilicity of the species that traps the bromonium ion.

Whereas in protic media the charge-transfer complex (CTC) ionization is promoted by electrophilic solvent assistance to the leaving bromide ion, in halogenated solvents the ionization is provided by a second bromine molecule.[48] Consequently, in the first solvents the bromonium counterion is a solvated bromide and in the second a tribromide anion.[45,48] In the first case, the intermediate is readily trapped by the nucleophilic bromide; in the second case, the electrophilic tribromide species has to dissociate, at least partly, into bromide to give the dibromo adduct by reacting with the bromonium ion. It is well-known that, particularly in halogenated solvents where the equilibrium constant of eq 5 (K_f = k_1/k_{-1}) can be as high as 10^4–10^7 M^{-1}, the dissociation process

$$Br_3^- \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} Br^- + Br_2 \qquad (5)$$

(k_{-1}) is slow whereas the reverse reaction (k_1) is very fast, close to diffusion-controlled.[49] It is, therefore, not unexpected that the product-forming step, where bromide and not tribromide ion is necessarily involved, is highly energetic as compared with the return to tribromide–bromonium ion pair and to the reagents. A possible mechanism in halogenated solvents is shown in the following scheme where total dissociation of tribromide is postulated.



Concluding Remarks. It is well-known experimentally[50] and theoretically[51] that the formation of a bromonium ion from an ethylenic bond and a bromine molecule is impossible in the gas phase. Since bromination is very fast in solution, the solvents play a crucial role in promoting the reaction. In protic media, the main driving force is electrophilic solvent assistance to bromide ion departure, as shown by the KSIE. This participation provides an important (close to 60 kcal/mol) contribution to the reaction rate, regardless of the substituents. Nucleophilic assistance to positive charge development contributes also but to a smaller extent. The data in this paper give only an underestimate of this solvent contribution which, in contrast, is markedly substituent-dependent.

In halogenated solvents, the driving force is probably bromine assistance via a process analogous to electrophilic solvent assistance to the CTC ionization. This results in a tribromide anion, formation of which from fully developed bromide and bromine is almost diffusion-controlled.[49] As a consequence, the product-forming step is energetically difficult and the previous bromonium ion forming step is reversible.

In a previous paper[1] we found that steric effects of branched substituents such as *tert*-butyl are significantly higher in adamantylidenealkane than in acyclic alkene brominations. The results obtained here show that this is to be attributed, at least in part, to the occurrence of return in the reaction of the highly congested adamantylethylenes. Due to the reversible formation of their bromonium ions, the experimental rates are smaller than the ionization rates. The steric effects appear, therefore, to be greater since they are evaluated by comparing their measured rates with that of the less congested alkene **1** for which both rates are identical.

Finally, it cannot be considered that the bromination mechanism is unique and as simple as taught in textbooks. It depends on the properties—protic or aprotic, nucleophilic or nonnucleophilic—of the solvent and on the ethylenic bond substituents. With the help of the criteria obtained here, it should be possible to reinvestigate how solvent involvement is governed by the alkene reactivity. Work is in hand to obtain more quantitative information on the balance between the several contributions of the reaction medium and the olefin structure to the bromination rates and products.

Experimental Section

Materials. Commercially available (Aldrich) allylbenzene was purified by GC before use. Alkenes **1** and **3a–c** were synthesized and purified as previously reported.[1] Salts (sodium and lithium bromide) were Merck products; they were dried at 120 °C before use. Solvents (ethanol, methanol, acetic acid, and water) were purified as previously described;[11,18] trifluoroethanol from Baker was used without further purification.

Kinetic Experiments. Rate constants above 5×10^3 M^{-1} s^{-1} were measured by couloamperometry;[18] smaller constants were obtained by following the overall (free bromine + tribromide ion) bromine uptake

(46) Anomalous kinetic bromide ion effects in the methanolic bromination of congested tri-*tert*-butylethylene and α-acetoxycholestene can also be interpreted in terms of return: Dubois, J. E.; Loizos, M. *C. R. Séances Acad. Sci., Ser. C* **1972**, *274*, 1130. Calvet, A.; Josefowicz, M.; Levisalles, J. *Tetrahedron* **1983**, *39*, 103.

(47) A reviewer has pointed out that return is more probable from intimate ion pairs than from dissociated ions, that is, more likely in the poorly dissociating acetic acid. In this solvent, dibromo adduct formation from an intimate ion pair would require translocation of the counterion, a process energetically expensive as compared to return. However, a direct attack of the intimate ion pair by external nucleophiles (solvent, added salts) is also possible. For example, in the presence of 0.5 M added chloride ions, allylbenzene bromination in acetic acid gives 90% of the bromo chloro adduct. Clearly, the reaction of bromonium–bromide ion pairs can involve many pathways: return, dissociation, external and internal nucleophile trapping, etc. In the absence of systematic data on the product-forming step, it is difficult to rigorously describe the many possible routes leading from the first ion pair to the reaction products. This problem can be expressed in similar terms for bromination and for solvolysis.

(48) Bellucci, G.; Berti, G.; Bianchini, R.; Ingrosso, G.; Yates, K. *J. Org. Chem.* **1981**, *46*, 2315, and references cited therein.

(49) Ruasse, M. F.; Aubard, J.; Galland, B.; Adenier, A. *J. Phys. Chem.* **1986**, *90*, 4382.

(50) Angelini, G.; Speranza, M. *J. Am. Chem. Soc.* **1981**, *103*, 3792.

(51) Yamabe, S.; Minato, T.; Inagaki, S. *J. Chem. Soc., Chem. Commun.* **1988**, 532.

spectrophotometrically at a wavelength between 300 and 400 nm, depending on the alkene reactivity. Kinetic experiments were carried out at 25 ± 0.1 °C, under second-order conditions (first order in each reagent) and in the presence of excess bromide ions. Bromine concentrations ranged from 10^{-7} to 5×10^{-4} M depending on the method and on the alkene reactivity. Alkene concentrations were about half the bromine concentration. Bromide ion concentration was varied from 2.5×10^{-2} to 5×10^{-1} M. The experimental rate constants, k_{exp}, were obtained with a reproducibility generally better than 2%.

***k* Determinations.** Equation 2 expresses the bromide ion effect. The rate constant, k_{exp}, was measured at several (three or four) bromide ion concentrations. Rate constants, k, for free bromine addition are[19] α, the intercepts of the linear plots (correlation coefficients better than 0.999) of $k_{exp}(1 + K[Br^-])$ against $[Br^-]$. K, the equilibrium constant of tribromide ion formation from bromine and bromide, is 16, 50, 92, 177, and 400 in water,[49] trifluoroethanol,[52] acetic acid,[8a] methanol,[49] and ethanol,[49] respectively; for aqueous alcoholic mixtures, they are either interpolated or obtained directly from ref 53.

Bromination Products. 2-Bromo-2-(bromomethyl)adamantane was synthesized by adding the stoichiometric amount of bromine slowly to a solution (2×10^{-2} M) of methylideneadamantane (**1**) in methylene chloride at room temperature. After solvent evaporation, the resulting dibromide (99% yield) was twice recrystallized from pentane: mp 72 °C; ^{1}H NMR ($CDCl_3$, TMS) δ 1.75–2.20 (m, 12 H), 2.3–2.5 (m, 2 H), 4.18 (s, 2 H). Anal. Calcd for $C_{11}H_{16}Br_2$: C, 42.86; H, 5.19; Br, 51.90. Found: C, 42.97; H, 5.03; Br, 51.34.

2-Methoxy-2-(bromomethyl)adamantane. A stoichiometric amount of bromine dissolved in methylene chloride (2 mL) was slowly added to **1** (800 mg, 5.5 mmol) in methanol (100 mL) at room temperature. The residue obtained after solvent evaporation was dissolved in pentane and chromatographed on silica gel. After elution of dibromide in pentane, 2-methoxy-2-(bromomethyl)adamantane was eluted in 50:50 pentane–ether in 55% yield: mp 42.5 °C (pentane); ^{1}H NMR ($CDCl_3$, TMS) δ 1.5–1.85 (m, 12 H), 2.0–2.1 (m, 2 H), 3.19 (s, 3 H), 3.78 (s, 2 H). Anal. Calcd for $C_{12}H_{19}BrO$: C, 55.60; H, 7.33; O, 6.18; Br, 30.88. Found: C, 55.75; H, 7.63; O, 6.32; Br, 30.84.

2-Acetoxy-2-(bromomethyl)adamantane. To a solution of **2** (500 mg, 3.5 mmol) in methylene chloride (10 mL) and acetic acid (100 mL) was added lithium perchlorate (17.6 g). The stoichiometric amount of bromine dissolved in methylene chloride (10 mL) was added dropwise at room temperature. The resulting solution was then diluted in pentane (200 mL), carefully washed with water, and dried. After solvent evaporation, the residue was chromatographed on silica gel. Dibromide was first eluted with pentane and then followed by 2-acetoxy-2-(bromomethyl)adamantane in 40% yield by elution with 50:50 pentane–ether: mp 75–76 °C (pentane); ^{1}H NMR ($CDCl_3$, TMS) δ 1.06–2.05 (m, 12 H), 2.08 (s, 3 H), 2.54 (s, 2 H), 4.26 (s, 2 H). Anal. Calcd for $C_{13}H_{19}BrO_2$: C, 54.36; H, 6.62; O, 11.15; Br, 27.87. Found: C, 54.92; H, 6.74; O, 11.01; Br, 27.64.

1,2-Dibromo-3-phenylpropane. Dry lithium bromide (1.74 g) was dissolved in a solution of allylbenzene (1 g, 8.5 mmol) in acetic acid (100 mL). The stoichiometric amount of bromine diluted in acetic acid (15 mL) was then added dropwise at room temperature. After the same workup as that used for 2-acetoxy-2-(bromomethyl)adamantane, oily 1,2-dibromo-3-phenylpropane was obtained in 98% yield: ^{1}H NMR ($CDCl_3$, TMS) δ 3.10 (q, 2 H), 3.47 (q, 1 H), 3.58 (m, 1 H), 3.77 (m, 1 H), 7.27–7.31 (m, 5 H). Anal. Calcd for $C_9H_{10}Br_2$: C, 38.84; H, 3.60; Br, 57.55. Found: C, 39.05; H, 3.65; Br, 57.35.

(52) Hamdoun, M.; Ruasse, M. F., unpublished results.
(53) Dubois, J. E.; Garnier, F. *Bull. Soc. Chim. Fr.* **1965**, 1715.

Bromination of allylbenzene in methylene chloride gave a significant amount of rearranged 1,3-dibromo adduct,[23] in addition to the 1,2-dibromo adduct.

1-Bromo-2-methoxy-3-phenylpropane and 1-Methoxy-2-bromo-3-phenylpropane. Allylbenzene bromination was carried out by the procedure described above for methanolic bromination of methylideneadamantane. The oily product obtained by elution from silica gel with 50:50 pentane–ether (80% yield) was a mixture (~70:30) of two regioisomers, as shown by GC and the NMR spectrum ($(CDCl_3$, TMS) δ_{OCH_3} 3.37 and 3.39). Anal. Calcd for $C_{10}H_{13}O_{Br}$: C, 52.40; H, 5.68; O, 7.98; Br, 34.93. Found: C, 52.35; H, 5.77; O, 7.58; Br, 34.08.

1-Acetoxy-2-bromo-3-phenylpropane and 1-Bromo-2-acetoxy-3-phenylpropane. Dry lithium perchlorate (16.0 g) was added to allylbenzene (1 g, 8.5 mmol) in acetic acid (100 mL). The stoichiometric amount of bromine diluted in acetic acid (15 mL) was added dropwise at room temperature. After the same workup as that described above for the brominations in acetic acid, the oily liquid (25% yield) eluted with 50:50 pentane–ether was a mixture of two acetoxy bromo regioisomers (~75:25) as shown by its NMR spectrum ($(CDCl_3$, TMS) δ_{COCH_3} 2.06 and 2.10). Anal. Calcd for $C_{11}H_{13}O_2Br$: C, 51.36; H, 5.06; O, 12.45; Br, 31.12. Found: C, 51.18; H, 5.00; O, 12.17; Br, 33.92. The two regioisomers had identical retention times in analytical GC (SE 30 10%, 4 m; T, 130 °C; P, 1 bar).

Product Distribution of Methylideneadamantane Bromination. To a solution of **1** (50 mg, 0.34 mmol) dissolved in methanol or acetic acid (50 mL) and thermostated at 25 °C was added dropwise with stirring the stoichiometric amount of bromine diluted in methylene chloride (2 mL). Stirring was maintained a further 30 min after complete decolorization of the reaction mixture. When the solvent was MeOH, it was eliminated under vacuum at room temperature; the residue was dissolved in pentane, washed with water, and dried on $MgSO_4$. After careful elimination of pentane, the product mixture was dissolved in $CDCl_3$ to be analyzed by NMR. When acetic acid was used, pentane (200 mL) was added to the reaction mixture. The solution was very thoroughly washed with water to eliminate acetic acid. The organic layer was then dried and evaporated to dryness under vacuum. The product distribution was obtained by integration of the well-separated signals of the CH_2Br groups at δ 3.78, 4.18, and 4.26 for the methoxy bromo, dibromo, and acetoxy bromo adducts, respectively.

Product Distribution of Allylbenzene Bromination. To a 25 °C thermostated solution of **2** (50 mg, 0.43 mmol) in methanol or acetic acid (50 mL) containing *n*-heptadecane (50 mg, 0.21 mmol) as internal reference was added dropwise with stirring the stoichiometric amount of bromine dissolved in the same solvent (15 mL). After the end of the addition, the reaction mixture was worked up by the procedures described above for the bromination of **1**. The product mixtures were analyzed by GC on Apiezon L 10%, 1.4 m at 180 °C. Retention times increased in the following order: t_{MeOBr}, t_{DiBr}, t_{AcOBr}, and $t_{C_{17}H_{36}}$. The product distribution was obtained from the peak areas calibrated against the internal reference.

Acknowledgment. We are indebted to Dr. H. Maskill and Dr. J. S. Lomas for helpful and stimulating discussion of our data and to Professor R. S. Brown for communicating his results on tetraisobutylethylene before publication.

Registry No. 1, 875-72-9; **2**, 300-57-2; **3a**, 38424-21-4; **3b**, 20441-18-3; **3c**, 125413-49-2; **4**, 31482-53-8; **5** (S = Me), 132802-73-4; **5** (S = Ac), 132802-74-5; $PhCH_2CHBrCH_2Br$, 1586-98-7; $PhCH_2CH(OMe)CH_2Br$, 115333-02-3; $PhCH_2CHBrCH_2OAc$, 55510-09-3; $PhCH_2CHBrCH_2OMe$, 115333-03-4; $PhCH_2CH(OAc)CH_2Br$, 55510-08-2.