Electrophilic Additions to Multiple Bonds.[1] 2. Medium Effect on Bromine Additions to Alkenes

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The rates of addition of bromine to a series of alkenes were obtained in acetic acid and in tetrachloroethane at 25 °C. Solvent effects on alkene reactivity have been evaluated by examination of relative rates with respect to ethylene in these two and five other solvents, covering a range of dielectric constants from about 2 to 80. The structural effects on reaction rates, for the bromination of alkenes, are approximately constant in all hydroxylic solvents, but are drastically enhanced in nonpolar solvents. The importance of specific solvation of the cyclic bromonium ion like transition state is examined.

The effect of solvent on the rate of bromine additions to alkenes has recently received increased attention.

It is well established that a change from a less to a more polar solvent results in an increase in the observed rate of bromination of a particular compound.[2] For example, the rate of bromine addition to 1-pentene varies from 1.17×10^{-3} M^{-1} s^{-1} in Freon 112 (1,2-difluorotetrachloroethane) to 11.3 M^{-1} s^{-1} in acetic acid and 2.5×10^{7} M^{-1} s^{-1} in water.[3]

Less well established experimentally is the effect of solvent upon the structural effects on the observed rates. Two different effects have been reported. Solvent independence of substituent effects on the rates of bromination of alkenes has been reported by Dubois.[3] On the other hand, reduced structural effects on rates of bromination of unsaturated compounds with a change of solvent from more polar to less polar were also reported recently.[4] The low selectivity of bromine addition to alkenes and alkynes in Freon 113 (1,1,2-trichlorotrifluoroethane) at −35 °C compared to high selectivity in methanol at 25 °C was interpreted by Olah in terms of a change in the structure of the rate-determining transition state of bromination from an alkene–bromine π complex in nonpolar media to a bromonium ion like σ complex in polar solvents.[4]

We would like to present experimental data that clearly establish that the structural effects on rates of bromination of alkenes are strongly reduced when going from nonhydroxylic to hydroxylic solvents and remain almost constant in the latter media.

Results and Discussion

The kinetic equation for polar additions of bromine to alkenes is presented in general form by eq 1, where [A] = [alkene]:[5]

$$-d[Br_2]/dt = k_2[Br_2][A] + k_3[Br_2]^2[A] + k_3'[Br_3^-][A] \quad (1)$$

In the absence of bromide ion and at low bromine concentrations ($[Br_2] < 10^{-3}$ M) in acetic acid, eq 1 reduces to the form:

$$-d[Br_2]/dt = k_2[Br_2][A] \quad (2)$$

In TCE, however, even under these conditions, only a third-order rate dependence is found:

$$-d[Br_2]/dt = k_3[Br_2]^2[A] \quad (3)$$

Even at the lowest bromine concentration at which we are able to measure rates ($[Br_2] = 2 \times 10^{-4}$ M), *no* second-order rate dependence is found.

The reason for this change in kinetic order is believed to be that protic solvents (such as methanol or acetic acid) can solvate the leaving bromide ion, thus stabilizing the ionic rate-determining transition state. In solvents which are not capable of such stabilization (e.g., TCE), a second bromine molecule may serve this function and the process then becomes third order (the Ad_E2–Br_2 assisted mechanism).[6] The second bromine molecule may then catalytically aid the Br–Br bond cleavage by formation of the more charge-dispersed tribromide ion.

The rate constants obtained in both solvents are collected in Tables I and II.

Separate experiments, carried out in the presence of oxygen or isoamyl nitrite, correspond to an ionic addition mechanism, and no contribution of a radical pathway was detected.

The logarithms of the rate constants correlate fairly well with the sum of Taft's polar substituent constants, $\Sigma\sigma^*$, for the alkyl groups substituted on the ethylene system. This remains in agreement with the commonly accepted model of a highly electron-deficient, bridged bromonium ion like transition state for the reaction. Nevertheless, steric effects upon the rate cannot be ignored, as demonstrated by the values of the k_{cis}/k_{trans} ratio which are generally greater than unity for pairs of geometrically isomeric alkenes (Table II). One of us has shown previously[8] that the initial enthalpy difference between the ground states of cis and trans isomers of 1,2-dialkyl-substituted ethylenes was increased at the transition state of bromination. This ruled out earlier assumptions about the partial loss of the ground-state energy difference between cis and trans isomers in the rate-determining transition state of addition. It may be possible to account for the somewhat faster rate of addition to the cis alkene relative to the trans isomer on the basis of steric interactions between the incoming electrophile and the alkyl groups on the double bond.[8,9]

Table I. Specific Rate Constants[a] for the Addition of Bromine to Terminal Alkenes in CH_3COOH and in CCl_2H–CCl_2H at 25.0 °C

Alkene	k_2, M^{-1} s^{-1} in CH_3COOH	k_3, M^{-2} s^{-1} in TCE
$H_2C{=}CH_2$	0.221 ± 0.002	14.3 ± 0.69
$H_2C{=}CH(CH_3)$	17.6 ± 0.2	7820 ± 137
$H_2C{=}CH(C_2H_5)$	27.9 ± 0.4	3090 ± 26
$H_2C{=}CH(C_3H_7)$	16.5 ± 0.2	2930 ± 22
$H_2C{=}CH(i\text{-}C_3H_7)$	19.3 ± 0.2	4940 ± 30
$H_2C{=}CH(t\text{-}C_4H_9)$	10.2 ± 0.1	5680 ± 53
$H_2C{=}CH(CH_2\text{-}t\text{-}C_4H_9)$		479.0 ± 5.9
$H_2C{=}C(CH_3)_2$	1510 ± 33	345 000 ± 3500
$H_2C{=}CCH_3(C_2H_5)$	3410 ± 27	
$H_2C{=}C(C_2H_5)_2$	3350 ± 51	
$H_2C{=}CC_2H_5(i\text{-}C_3H_7)$	1330 ± 34	

[a] The rate constants are the average of two to nine independent kinetic runs.

Table II. The Specific Rate Constants[a] for the Addition of Bromine to Geometrically Isomeric Alkenes in CH_3COOH and in CCl_2H–CCl_2H at 25.0 °C

Alkene		k_2, M^{-1} s^{-1} in CH_3COOH	k_c/k_t	$k_3 \times 10^{-5}$, M^{-2} s^{-1}, in TCE	k_c/k_t
$CH_3CH{=}CHCH_3$	cis	1230 ± 20	1.31	5.38 ± 0.06	1.06
	trans	940 ± 9		5.05 ± 0.05	
$CH_3CH{=}CH(C_2H_5)$	cis	2530 ± 30	1.42	14.8 ± 0.15	1.20
	trans	1780 ± 20		12.3 ± 0.11	
$CH_3CH{=}CH(i\text{-}C_3H_7)$	cis	1300 ± 20	1.71	15.9 ± 0.10	1.36
	trans	760 ± 10		11.7 ± 0.10	
$CH_3CH{=}CH(t\text{-}C_4H_9)$	cis	1020 ± 20	3.40	19.3 ± 0.12	2.11
	trans	300 ± 4		9.16 ± 0.05	
$C_2H_5CH{=}CHC_2H_5$	cis	2830 ± 30	1.20	28.7 ± 0.20	1.01
	trans	2350 ± 10		28.4 ± 0.20	
$C_2H_5CH{=}CH(i\text{-}C_3H_7)$	cis	1340 ± 30	1.03	28.1 ± 0.18	1.03
	trans	1300 ± 30		27.4 ± 0.18	
$C_2H_5CH{=}CH(t\text{-}C_4H_9)$	cis	1250 ± 20	2.27	32.7 ± 0.32	1.71
	trans	550 ± 10		19.1 ± 0.15	
$(i\text{-}C_3H_7)CH{=}CH(i\text{-}C_3H_7)$	cis	270 ± 15	0.61	12.3 ± 0.11	0.22
	trans	440 ± 5		55.1 ± 0.84	
$(t\text{-}C_4H_9)CH{=}CH(t\text{-}C_4H_9)$	cis	517 ± 8	47.0		
	trans	11 ± 0.1		0.538 ± 0.005	

[a] The rate constants are the average of two to seven independent kinetic runs.

Table III. The Solvent Dependence of Bromination Rates on Alkene Structure

Alkene	Registry no.	k^{rel} in Freon 112[a]	k^{rel} in TCE[b]	k^{rel} in CH_3COOH[b]	k^{rel} in MeOH[c]	k^{rel} in MeOH/H_2O[d] (7/3)	k^{rel} in H_2O[e]	k^{rel} in Freon 113[f]
$H_2C{=}CH_2$	74-85-1	1.0	1.0	1.0	1.0	1.0	1.0	1.0
$H_2C{=}CH(CH_3)$	115-07-1		5.5×10^2	8.0×10	6.1×10	2.5×10	2.6×10	1.4×10
$H_2C{=}CH(C_2H_5)$	106-98-9		2.2×10^2	1.3×10^2	9.6×10			2.0×10
$H_2C{=}CH(C_3H_7)$	109-57-1	1.3×10^3	2.0×10^2	7.5×10	6.9×10	2.3×10	6.4×10	1.2×10
$H_2C{=}CH(i\text{-}C_3H_7)$	563-45-1		3.5×10^2	8.8×10	5.6×10	2.2×10	2.2×10	
$H_2C{=}CH(t\text{-}C_4H_9)$	558-37-2		4.0×10^2	4.6×10	2.7×10			
$H_2C{=}CH(CH_2\text{-}t\text{-}C_4H_9)$	762-02-9		3.3×10					
$H_2C{=}C(CH_3)_2$	115-11-7		2.4×10^4	6.9×10^3	5.4×10^3	5.4×10^3		2.0×10^2
$H_2C{=}CCH_3(C_2H_5)$	563-46-2			1.5×10^4				
$H_2C{=}C(C_2H_5)_2$	760-21-4			1.5×10^4				
$H_2C{=}CC_2H_5(i\text{-}C_3H_7)$	7357-93-9			6.0×10^3				
cis-$CH_3CH{=}CHCH_3$	590-18-1		3.8×10^4	5.6×10^3	2.6×10^3	1.8×10^3		3.2×10^2
trans-$CH_3CH{=}CHCH_3$	624-64-6		3.5×10^4	4.3×10^3	1.7×10^3	1.1×10^3		2.0×10^2
cis-$CH_3CH{=}CHC_2H_5$	627-20-3	1.1×10^5	1.0×10^5	1.1×10^4	4.1×10^3	2.3×10^3		8.8×10^2
trans-$CH_3CH{=}CHC_2H_5$	646-04-8		8.6×10^4	8.1×10^3	2.6×10^3			
cis-$C_2H_5CH{=}CHC_2H_5$	7642-09-3		2.0×10^5	1.3×10^4	6.4×10^3			8.5×10^2
trans-$C_2H_5CH{=}CHC_2H_5$	13269-52-8		2.0×10^5	1.1×10^4	3.7×10^3			6.8×10^2
cis-$CH_3CH{=}CH(i\text{-}C_3H_7)$	691-38-3		1.1×10^5	5.9×10^3	1.5×10^3	1.4×10^3		
trans-$CH_3CH{=}CH(i\text{-}C_3H_7)$	674-76-0		8.1×10^4	3.5×10^3	1.2×10^3	1.1×10^3		
cis-$CH_3CH{=}CH(t\text{-}C_4H_9)$	762-63-0		1.3×10^5	4.6×10^3	1.3×10^3	9.3×10^2		
trans-$CH_3CH{=}CH(t\text{-}C_4H_9)$	690-08-4		6.4×10^4	1.4×10^3	1.6×10^2	1.3×10^2		
cis-$C_2H_5CH{=}CH(i\text{-}C_3H_7)$	15840-60-5		2.0×10^5	6.1×10^3				
trans-$C_2H_5CH{=}CH$-$(i\text{-}C_3H_7)$	692-24-0		1.9×10^5	5.9×10^3				
cis-$C_2H_5CH{=}CH(t\text{-}C_4H_9)$	690-92-6		2.3×10^5	5.7×10^3	2.0×10^3	1.3×10^3		
trans-$C_2H_5CH{=}CH$-$(t\text{-}C_4H_9)$	690-93-7		1.3×10^5	2.5×10^3	2.1×10	1.6×10^2		
cis-$(i\text{-}C_3H_7)CH{=}CH$-$(i\text{-}C_3H_7)$	10557-44-5		8.6×10^4	1.2×10^3				
trans-$(i\text{-}C_3H_7)CH{=}CH$-$(i\text{-}C_3H_7)$	692-70-6		3.8×10^5	2.0×10^3				
cis-$(t\text{-}C_4H_9)CH{=}CH$-$(t\text{-}C_4H_9)$	692-47-7			2.4×10^3				
trans-$(t\text{-}C_4H_9)CH{=}CH$-$(t\text{-}C_4H_9)$	692-48-8		3.8×10^3	5.2×10				
$CH_3CH{=}C(CH_3)_2$	513-35-9	2.1×10^6			1.3×10^5	2.7×10^3		2.3×10^3
$(CH_3)_2C{=}C(CH_3)_2$	563-79-1	5.2×10^7			9.2×10^5			5.7×10^3

[a] Data from ref 3, k_2 for $CH_2{=}CH_2$ was calculated from the equation taken from ref 7 and k_2 for $CH_2{=}CH_2$ in methanol.[11] [b] This paper. [c] Data from ref 11. [d] Data taken from ref 12, k_2 for $CH_2{=}CH_2$ being calculated on the basis of appropriate equation[12] and k_2 ($CH_2{=}CH_2$) in methanol.[11] [e] Data taken from ref 13. [f] Data taken from ref 4.

Table IV. Observed Proton Magnetic Resonance Parameters for Products from the Bromination of Olefin Pairs in Acetic Acid

Compound			Dibromoalkane[e]					Bromoacetoxyalkane[f]				
					Chemical shifts, δ, ppm					Chemical shifts, δ, ppm		
R^1	R^2	cis trans	Stereochemistry	Registry no.	H^1	H^2	Coupling constants, Hz, $J_{H^1H^2}$	Stereochemistry	Registry no.	H^1	H^2	Coupling constants, Hz, $J_{H^1H^2}$
CH_3	CH_3	cis	dl	598-71-0	4.45	4.45	3.2	threo	19773-39-8	4.10	4.95	4.0
		trans	meso	5780-13-2	4.23	4.23	7.6	erythro	37906-78-8	4.21	4.90	6.0
C_2H_5	CH_3	cis	threo	22415-73-2	4.13	4.35	3.0	threo	63569-56-2	4.83–5.20	4.83–5.20	*a*
		trans	erythro	22415-74-3	3.88–4.45	3.88–4.45	*a*	erythro	63569-57-3	4.73–5.19	4.73–5.19	*a*
C_2H_5	C_2H_5	cis	dl	16230-28-7	3.98–4.28	3.98–4.28	*a*	threo	63569-58-4	3.95	4.87	3.4
		trans	meso	16230-27-6	3.90–4.28	3.90–4.28	*a*	erythro	63569-59-5	3.81–4.30	4.85	6.0
i-C_3H_7	i-C_3H_7	cis	dl	40084-92-2	3.70–3.85	3.70–3.85	8.2[d]	threo	40084-95-5	3.91	4.87	5.0[b]
		trans	meso	40084-93-3	4.16	4.16	11.8[d]	erythro	40084-94-4	3.91	5.08	10.2[b]
C_3H_7	CH_3	cis	threo	58608-83-6	3.77	4.25	3.5	threo	63569-60-8	3.6–4.0	5.03	6.5
		trans	erythro	58608-84-7	4.15	4.26	10	erythro	63569-61-9	4.8–5.1	4.8–5.1	*a*
i-C_3H_7	C_2H_5	cis	threo	63569-54-0	3.77	4.07	3.0	threo	63569-62-0	5.0[d]	4.0[c]	6.0
		trans	erythro	63569-55-1	4.03–4.23	4.03–4.23	*a*	erythro	63569-63-1	3.95	5.00	4.0
t-C_4H_9	CH_3	cis	threo	7694-05-5	3.85	4.40	1.3	threo	63569-64-2	3.87	5.20	1.5
		trans	erythro	7694-04-4	4.40	4.61	*a*	erythro	63569-65-3	4.4	5.1–5.36	*a*
t-C_4H_9	C_2H_5	cis	threo	40084-97-7	3.93	3.9–4.3	1.6[b]	threo	63569-66-4	3.80	5.00	1.1[b]
		trans	erythro	40084-96-6	4.23	4.38	1.9[b]	erythro	63569-67-5	3.99	4.7–5.1	3.1[b]
t-C_4H_9	t-C_4H_9	cis	dl	40085-00-5	4.17	4.17	1.0[b]	threo	40085-01-6	3.97	4.95	1.0[b]
		trans	d									

[a] The value of the coupling constants is nonmeasureable. [b] Data taken from ref 8. [c] The regiochemistry of the product: (i-C_3H_7)-BrHC–CH($OCOCH_3$)(C_2H_5). [d] The reaction product is a complex mixture, but neither the *dl*-dibromide nor *threo*-acetoxy bromide could be detected 8. [e] $R^1H^1C(Br)$–$(Br)CH_2R^2$. [f] $R^1H^1C(OCOCH_3)$–$(Br)CH^2R^2$.

If the particularly sterically hindered *trans*-di-*tert*-butylethylene is excluded,[10] the values of ρ^* for additions in acetic acid and TCE are -2.8 ± 0.3 and -4.1 ± 0.3, respectively.

Relative rates ($k^{rel} = k^{alkene}/k^{ref\ alkene}$) are a more sensitive measure of selectivity than the reaction constants ρ^*, which involve logarithmic relationships. The relative rates of bromine addition to alkenes compared to ethylene in seven solvents are presented in Table III. For all alkenes studied, the selectivity of bromination decreases in solvent order: Freon 112 > TCE > CH_3COOH > MeOH > 70% MeOH/30% H_2O > H_2O > Freon 113.

This surprising result is not only in disagreement with Olah's postulate about bromination selectivity of alkenes in polar and nonpolar solvents, but is inconsistent with the proposed change in the mechanism of bromination in polar and nonpolar solvents (σ- and π-complex type transition state). Further, the solvent order shown above does not follow any known solvent polarity scale.[14]

Our rate data in acetic acid and in TCE, as well as the reported data in all but the last column of Table III, were obtained by direct kinetic measurements, while the relative rates in Freon 113 represent values obtained by competition experiments.[4]

It has been frequently pointed out[1,15] that relative rates obtained by the competitive technique can be influenced by several external factors (rate of mixing, concentrations, etc). This tends to result in a smaller span of rate constants compared to those obtained from direct kinetic measurements. In addition, the decrease of ρ values with an increase of temperature is a general feature of the addition of halogens to alkenes;[16] thus, kinetic data obtained at −35 °C in Freon 113 should show *increased* selectivity with respect to those at +25 °C.

It is also possible that the additions in Freon 113 at −35 °C in the dark proceed at least partly via radical mechanisms.[17] This would explain the high reaction rates and low selectivity observed. It has been reported that the free-radical bromination is facilitated by a decrease in temperature.[18] Bromine addition to the double bond of [4.3.1]propell-3-ene in CH_2Cl_2 at −78 °C in the dark has been demonstrated to be of a radical nature.[19] It has been pointed out that the radical character of the addition does not have to be externally induced, but "a solely free-radical reaction initiated by interaction between reactants" [20] may occur.

The rate data in Freon 113 at −35 °C simply do not make any sense in terms of an ionic mechanism. However, if the data in Freon 113 are neglected, the interpretation of the remaining results concerning the role of solvent in determining the selectivity of bromination of alkenes becomes much clearer, and remains in agreement with the general organic reactivity–selectivity principle; in the better solvents, an increased reactivity and decreased selectivity is expected to occur.

In our opinion, there is no need to invoke different rate-determining transition-state structures for additions in polar and nonpolar media. The widely accepted cyclic bromonium ion like transition state accounts very well for the observed rates and exclusive antistereospecificity of the reaction in both polar and nonpolar solvents.[21]

The stereochemistry of the present additions was investigated by means of spectroscopic (NMR) analysis of the vicinal

dibromides formed as reaction products. For all 1,2-disubstituted ethylene derivatives, both in acetic acid and in TCE, exclusive antiaddition (>99%) was found. In acetic acid some bromoacetoxy products were also observed, in amounts not exceeding 5%, which is significantly less than the amounts of bromomethoxy compounds found for brominations in methanol.[22]

Structural effects on bromination rates in different solvents correlate linearly. Unfortunately, the limited number of data in H_2O as well as in Freon 112 do not allow the use of the most or least polar solvent as a reference for all the correlations. However, the rate data of each column in Table III correlate linearly with the appropriate rate data of the other columns. The slopes are close to unity for the hydroxylic solvents, and significantly higher for the nonpolar solvents, e.g.,

$$\log k_2^{rel}(CH_3COOH) = 1.09 \log k_2^{rel}(MeOH) + 0.15 \quad (4)$$

where $r = 0.971$, $s = 0.06$

$$\log k_3^{rel}(TCE) = 1.32 \log k_2^{rel}(MeOH) + 0.51 \quad (5)$$

where $r = 0.895$, $s = 0.16$

$$\log k_2^{rel}\ (Freon\ 112) = 1.23 \log k_2^{rel}\ (MeOH) + 0.37 \quad (6)$$

where $r = 0.992$, $s = 0.09$

Thus, although increased reactivity and decreased selectivity with a change from less to more polar solvent is observed for all the solvents of Table III (except for the data in Freon 113), the trend in slope does not show any uniform character. The larger slope value in the correlations 5 and 6 indicates a much larger charge development in the transition state of bromination in TCE and Freon 112 than in MeOH. This can be interpreted in terms of the absence of specific solvation of the transition state in nonhydroxylic solvents. This results in relative localization of the positive charge and therefore higher sensitivity to the electron-releasing effects of the substituents on the double bond.

The relative rate data presented in Table III indicate not only a general medium effect on the transition state of the reaction, but also a marked difference in the mode of solvation in nonpolar solvents with respect to the hydroxylic solvents.

The linear character of the correlations of structural effects in different solvents provides an additional argument in favor of a common σ-complex-like rate-determining transition-state structure in all solvents investigated.

We conclude that structural effects on reaction rates of bromination of alkenes are approximately constant in all hydroxylic solvents but are drastically enhanced when the reaction medium is changed to nonhydroxylic halogenated hydrocarbon-type solvent. This strongly indicates the importance of specific solvation of the transition states. Thus, it appears that the solvent has two roles in the rate-determining transition state. It solvates the departing bromide ion (electrophilic solvation) and specifically solvates the carbon portion (nucleophilic solvation).

Unfortunately, the detailed nature of the solvent–transition-state interactions cannot be evaluated on the basis of the present results. However, the importance of electrophilic solvation in bromination is emphasized by the fact that a termolecular process operates in nonprotic solvents like TCE, which are not capable of such solvation, so that the second bromine molecule has to serve the solvent function in removing the bromide ion.

Experimental Section

Reagents. The alkenes were commercially available (Chemical Samples) and their purity was verified by GLC and NMR. Acetic acid was purified by refluxing for several hours with chromium trioxide and acetic anhydride and then distilled through a column.[23] 1,1,2,2-Tetrachloroethane was purified as previously described.[24]

Kinetics. The rate constants were measured on a Durrum-Gibson stopped-flow spectrophotometer, as previously described.[6]

In order to inhibit the possible radical reaction, oxygen was passed through the TCE prior to preparing the solutions for a few control kinetic runs. No change of the reaction rate was observed.

The rates of bromine addition to 1-pentene and *cis*-3-hexene in TCE and in the presence of the radical inhibitor (isoamyl nitrite, concentration 5×10^{-3} M) were measured. The observed rates were not slower than in the regular TCE experiments.

Product Analysis. Identification of products from the addition of bromine in acetic acid to some cis and trans pairs of alkenes was carried out under conditions where the second-order process is dominant.[6] The products were isolated by pouring the reaction mixture into water, extraction with pentane, and washing with saturated $NaHCO_3$ solution and then water. The extracts were dried over $MgSO_4$ and the solvent was removed on a rotary evaporator at room temperature. The quantitative yield of products indicated 1:1 alkene–bromine adduct formation. IR and NMR spectra of the reaction mixture were in full agreement with the structure of the corresponding vicinal dibromides obtained in previous studies.[8]

In TCE, analyses were performed both by NMR and infrared spectroscopy on the reaction mixtures themselves. The magnitude of the vicinal coupling constant between the bromomethine hydrogens has been used as a criterion for distinguishing meso-*dl* and erythro-threo diastereomeric pairs of dibromoalkanes.[25] The stereochemistry of acetoxybromides was assigned on the basis of dimethine coupling constants and rotamer population by similar arguments as those for dibromoalkanes. Percentage compositions were determined from integrated areas of appropriate peaks or from peak-height ratios.

Erythro- and *threo*-acetoxy bromides used for identification as model compounds were prepared by addition of acetyl hypobromite to some alkenes.[26] NMR data necessary for product determination are collected in Table IV.

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Registry No.—Bromine, 7726-95-6.

References and Notes

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