be obtained from solvolysis in acetic acid. The enol ether products were identified by ^{1}H NMR spectroscopy and GLC.

Acknowledgment. The continued financial support of the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged as are the awards of NRC Scholarships to G.M.

Registry No. 4-Chloro-2-methylacetophenone, 37074-38-7; 5-chloro-2-methylacetophenone, 58966-35-1; 2,6-dimethylbenzoic acid, 632-46-2; 2,6-dimethylbenzoyl chloride, 21900-37-8; 2,6-dimethylacetophenone, 2142-76-9; 4-bromo-2,6-dimethylbenzonitrile, 5757-66-4; 4-bromo-2,6-dimethylbenzoic acid, 74346-19-3; 4-bromo-2,6-dimethylbenzoyl chloride, 74346-20-6; 4-bromo-3,5-dimethylphenol, 7463-51-6; 4-bromo-3,5-dimethylanisole, 6267-34-1; 2,6-dimethyl-4-methoxyacetophenone, 60999-76-0; 2,6-dimethyl-4-methoxybenzoic acid, 37934-89-7; 2,6-dimethyl-4-methoxybenzoyl chloride, 31247-59-3; 1-(2-methylphenyl)vinyl chloride, 38379-19-0; 1,1-dichloro-1-(2-methylphenyl)ethane, 74346-21-7; *o*-methylphenylacetylene, 766-47-2; 1-(2-methylphenyl)vinyl bromide, 74346-22-8; 1-(2-methylphenyl)vinyl tosylate, 74331-76-3; 1-(4-methylphenyl)vinyl bromide, 51270-89-4; 1-(4-methoxy-2-methylphenyl)acetylene, 74331-69-4; 4-hydroxy-2-methylacetophenone, 875-59-2; 1-(4-methoxy-2-methylphenyl)vinyl chloride, 74346-23-9; 1-(4-methoxy-2-methylphenyl)vinyl bromide, 74346-24-0; 1-(4-methoxy-2-methylphenyl)vinyl tosylate, 74331-92-3; 1,1-dichloro-1-(4-chloro-2-methylphenyl)ethane, 74346-25-1; 1-(4-chloro-2-methylphenyl)vinyl bromide, 74346-26-2; 1-(4-chloro-2-methylphenyl)vinyl tosylate, 74346-27-3; 1-(5-chloro-2-methylphenyl)acetylene, 74331-72-9; 1-(5-chloro-2-methylphenyl)vinyl tosylate, 74346-28-4; 1-(5-chloro-2-methylphenyl)vinyl bromide, 74346-29-5; 1-(2,4-dimethylphenyl)acetylene, 16017-30-4; 2,4-dimethylacetophenone, 89-74-7; 1-(2,4-dimethylphenyl)vinyl chloride, 74346-30-8; 1-(2,4-dimethylphenyl)vinyl bromide, 51270-86-1; 1-(2,6-dimethylphenyl)acetylene, 74331-74-1; 1-(2,6-dimethylphenyl)vinyl chloride, 74331-79-6; 1,1-dichloro-1-(2,6-dimethylphenyl)ethane, 74346-31-9; 1-(2,6-dimethylphenyl)vinyl bromide, 74331-78-5; 1-(2,6-dimethylphenyl)vinyl tosylate, 74331-77-4; (4-bromo-2,6-dimethylphenyl)acetylene, 74331-75-2; 4-bromo-2,6-dimethylacetophenone, 53379-63-8; 1-(4-bromo-2,6-dimethylphenyl)vinyl chloride, 74346-32-0; 1-(4-bromo-2,6-dimethylphenyl)vinyl bromide, 74346-33-1; 1-(4-bromo-2,6-dimethylphenyl)vinyl tosylate, 74346-34-2; 1-(2,6-dimethyl-4-methoxyphenyl)vinyl chloride, 74331-91-2; 1-(2,6-dimethyl-4-methoxyphenyl)vinyl bromide, 74346-35-3; 1-(2,6-dimethyl-4-methoxyphenyl)acetylene, 74331-73-0; 1-(2,4-dimethylphenyl)vinyl tosylate, 51270-87-2; 1-(4-bromo-2-methylphenyl)vinyl tosylate, 74346-36-4; 2,6-dimethylaniline, 87-62-7; *o*-methylacetophenone, 577-16-2; 1-(4-methylphenyl)vinyl tosylate, 51270-88-3; 1-(4-chloro-2-methylphenyl)acetylene, 74331-71-8.

Supplementary Material Available: Listing of rate constants for all compounds studied (6 pages). Ordering information is given on any current masthead page.

Vinyl Cation Intermediates in Solvolytic and Electrophilic Reactions. 2. Bromination of Arylacetylenes

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The kinetics of bromination of a series of ten ring-substituted phenylacetylenes were investigated in anhydrous acetic acid at 25 °C. All substrates were substituted with one or two methyl groups at the ortho position(s) for comparison with the behavior of analogously substituted α-arylvinyl tosylates, bromides, and chlorides, which generate formally very similar vinyl cation intermediates. The phenylacetylenes show wide variations in bromination rate, with second-order rate constants in the range 10^{-3}–10^4 M^{-1} s^{-1}. Activation parameters were also measured, with $\Delta S^{\ddagger}$ showing little variation with the number of ortho substituents. The rates of bromination correlate much better with σ^+ than with σ, yielding ρ values of −6.9 and −6.7 for the 2-methyl and 2,6-dimethyl series, respectively. The magnitudes of these ρ values are compared with those for the parent phenylacetylene series and with the corresponding values for α-arylvinyl–X solvolysis. The product distributions and stereochemistry are very similar to those found for phenylacetylenes with no *o*-methyl substituents.

As mentioned in the preceding paper,[1] vinyl cations are now well established as organic reaction intermediates. The present paper describes the generation of this type of intermediate by electrophilic addition of bromine to substituted phenylacetylenes for comparison with the behavior of structurally similar cationic intermediates formed during the solvolysis of α-arylvinyl derivatives. Although bromination of some substituted phenylacetylenes has already been investigated,[2] the present study deals exclusively with *o*-methyl and 2,6-dimethyl substituted phenylacetylenes for direct comparison with the solvolysis of similarly substituted α-arylvinyl systems, described in the preceding paper. In the latter systems, *o*-methyl groups were necessary to accelerate the solvolytic reactions to a conveniently measurable rate range with typical leaving groups.

Results and Discussion

Although it is well-known[3] that the kinetics of bromine addition to acetylenes generally follows the three-term expression of eq 1, the experimental conditions were adjusted in the present case so that eq 1 would reduce to a simpler pseudo-first-order rate equation (eq 2), where k_{obsd}

$$V = -\mathrm{d}[\mathrm{Br}_2]/\mathrm{d}t = [\text{acetylene}](k_1[\mathrm{Br}_2] + k_2[\mathrm{Br}_2]^2 + k_3[\mathrm{Br}_2][\mathrm{Br}^-]) \quad (1)$$

$$-\mathrm{d}[\mathrm{Br}_2]/\mathrm{d}t = k_{\mathrm{obsd}}[\mathrm{Br}_2] \quad (2)$$

$= k_1$[acetylene]. This was done by using low initial bro-

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[1] K. Yates and G. Mandrapilias, *J. Org. Chem.*, preceding paper in this issue.

[2] J. A. Pincock and K. Yates, *Can. J. Chem.*, 48, 3332 (1970).

[3] G. H. Schmid, "The Chemistry of the Carbon–Carbon Triple Bond", S. Patai, Ed., Wiley, New York, 1978, Chapter 8.

0022-3263/80/1945-3902$01.00/0

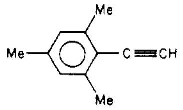
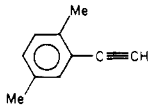
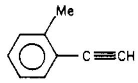
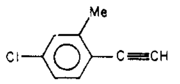
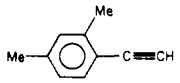
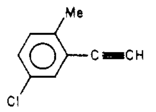
Table I. Rate Constants for the Bromination of Ring-Substituted Arylacetylenes in Acetic Acid

(2-Methylphenyl)acetylenes

substituent	T, °C	k_1, M^{-1} s^{-1}	$\sigma^{+\,a}$
4-OMe^b	24.8	$(4.3 \pm 0.40) \times 10^4$	−0.778
4-Me^b	39.2	$(2.97 \pm 0.03) \times 10$	
	29.9	$(2.02 \pm 0.05) \times 10$	
	24.8	$(1.67 \pm 0.05) \times 10$	−0.311
	21.9	$(1.30 \pm 0.04) \times 10$	
5-Me	35.9	$(4.22 \pm 0.20) \times 10^{-1}$	
	30.5	$(3.10 \pm 0.15) \times 10^{-1}$	
	24.8	$(2.36 \pm 0.10) \times 10^{-1}$	−0.069
	18.6	$(1.58 \pm 0.04) \times 10^{-1}$	
H	39.9	$(1.49 \pm 0.02) \times 10^{-1}$	
	30.8	$(8.00 \pm 0.40) \times 10^{-2}$	
	24.8	$(5.55 \pm 0.13) \times 10^{-2}$	0
4-Cl	29.6	$(2.08 \pm 0.05) \times 10^{-2}$	
	24.8	$(1.60 \pm 0.04) \times 10^{-2}$	+0.114
	18.6	$(1.11 \pm 0.02) \times 10^{-2}$	
	16.0	$(8.27 \pm 0.04) \times 10^{-3}$	
5-Cl	69.6	$(1.25 \pm 0.06) \times 10^{-2}$	
	59.6	$(6.80 \pm 0.34) \times 10^{-3}$	
	49.1	$(3.74 \pm 0.18) \times 10^{-3}$	
	24.8	$(7.19 \pm 0.50) \times 10^{-4\,c}$	+0.373
(2,6-Dimethylphenyl)acetylenes			
4-OMe^b	24.8	$\gtrsim 10^5$	−0.778
4-Me^b	45.5	$(5.25 \pm 0.22) \times 10^2$	
	40.3	$(3.43 \pm 0.15) \times 10^2$	
	35.9	$(3.13 \pm 0.10) \times 10^2$	
	24.8	$(2.07 \pm 0.10) \times 10^2$	−0.311
H^b	24.8	1.51	0
4-Br	24.8	0.16	+0.15

[a] Taken from ref 4. [b] Determined by stopped-flow measurements. [c] Extrapolated from values at other temperatures.

Table II. Activation Parameters for Bromination of Arylacetylenes in Acetic Acid

substrate	$\Delta H^{\neq}$, kcal mol^{-1}	$\Delta S^{\neq}$, eu mol^{-1}
	7.3 ± 1.4^a	-24 ± 4.6^a
	9.5 ± 0.3	-30 ± 1.2
	11.5 ± 0.1	-26 ± 2.0
	10.8 ± 1.0	-31 ± 2.5
	6.8 ± 0.3^a	-30 ± 0.9^a
	12.3 ± 0.3	-32 ± 2.1
PhC≡CH	11.7^b	-31^b

[a] Based on stopped-flow measurements. [b] Taken from ref 2.

mine concentrations (<5 × 10^{-4} M), by using large excesses of acetylene (≥50-fold), and by not adding any bromide salts to the system. In this way the simple second-order bromination rate constants, k_1, which are obtained are more directly comparable with the solvolytic rate constants for the α-arylvinyl systems of interest. The rates of bromination were determined in anhydrous acetic acid at different temperatures and in all cases showed simple pseudo-first-order kinetics over the whole range of reaction. Since the rate constants varied over more than seven powers of ten, as a function of the substituents, both conventional ultraviolet spectrophotometric and stopped-flow techniques were used to follow the rates. All runs were carried out in triplicate by using at least two different initial arylacetylene concentrations, and the rate constants agreed to within ±3%. The second-order rate constants for all the compounds investigated are given in Table I. It can be seen that the bromination rates span a very wide range of reactivity, with k_1 values from approximately 10^4 to 10^{-3} M^{-1} s^{-1}. For those compounds studied at several temperatures, the activation parameters are given in Table II. The values of both $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are in the same range as those reported by Yates and Pincock[2] for the parent phenylacetylenes. For a bimolecular reaction, values of $\Delta S^{\ddagger}$ of around −30 eu mol^{-1} are not unreasonable in terms of loss of vibrational and rotational degrees of freedom,[5] accompanied by some solvent reorganization leading to more restriction at the transition state. However, the important fact to be noted is that for the limited number of compounds studied, the $\Delta S^{\ddagger}$ terms are essentially invariant, within experimental error. This is irrespective of whether zero, one, or two o-methyl groups are present in the molecule. Thus, as in the case of the analogous solvolysis reactions, there is little or no hindrance to any essential solvation of the developing vinyl cation because of the presence of o-methyl substituents.

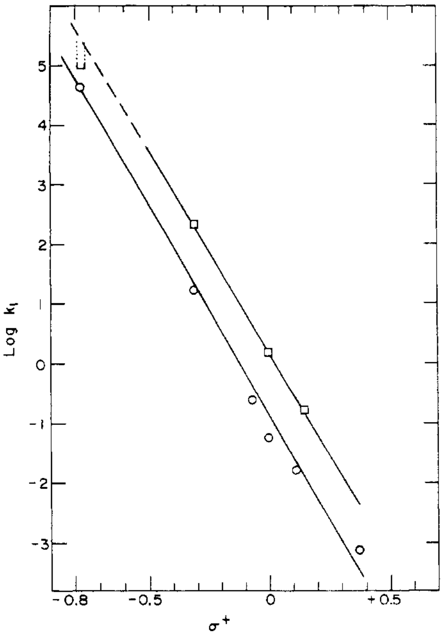


Figure 1. Plot of log k_1 vs. σ^+ for the bromination of substituted (2-methylphenyl)acetylenes (circles) and (2,6-dimethylphenyl)-acetylenes (squares) in acetic acid at 25 °C.

Attempts to correlate the log k_1 values from Table I with σ substituent constants showed a very poor correlation. However a plot of log k_1 vs. Brown's σ^+ scale[4] showed a very good correlation, as can be seen from Figure 1. Least-squares analysis gave $\rho = -6.92 \pm 0.28$ with a correlation coefficient of 0.996. Some scatter of the points is not surprising when the overall range of reactivity (>10^7) is considered as well as the fact that two different kinetic techniques were used to obtain the data.

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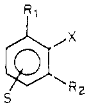
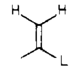
(4) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, 80, 4979 (1958).

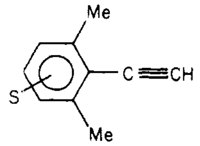
(5) K. B. Wiberg, "Physical Organic Chemistry", Wiley, New York, 1964, p 386–388.

Table III. Comparison of ρ Values[a] for Solvolyses of α-Arylvinyl Systems and Electrophilic Additions to Arylacetylenes

	X^b = 	X^c = C≡CH
$R_1 = R_2 = H$	$\rho = -5.3^d$ (L = Br)	$\rho = -5.2^e$
$R_1 = H$, $R_2 = Me$	$\rho = -3.9^f$ (L = OTs)	$\rho = -6.9$
$R_1 = R_2 = Me$	$\rho = -4.3^g$ (L = OTs), -4.4^h (L = OTs), -5.1^i (L = Br), -4.5^i (L = Cl)	$\rho = -6.7$

[a] Versus σ^+. [b] Solvolysis of ArX. [c] Bromine addition to ArX in acetic acid at 25 °C. [d] In 80:20 ethanol–water at 100 °C. Data taken from ref 10, except for point for *p*-amino group which was omitted. [e] Taken from ref 2. [f] In 50:50 methanol–water at 58 °C. [g] In 50:50 methanol–water at 36.5 °C. [h] In 80:20 ethanol–water at 88 °C. [i] In 50:50 methanol–water at 88 °C.

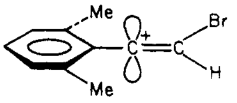
A much more limited series of 2,6-dimethyl-substituted compounds (I) was also studied (with S = H, Me, Br, and OMe).[6]



I

It can be seen from Figure 1 that although only a few points are available, they nonetheless lie on a good straight line, with a slope identical with that for the 2-methyl-substituted phenylacetylenes, within experimental error. The ρ value calculated for this series (vs. σ^+) is −6.7.

The ρ values obtained for both series are significantly more negative than that obtained for the parent phenylacetylene series[2] (i.e., with no *o*-methyl substituents) as shown in Table III. These values are also much larger in absolute magnitude than typical ρ values for aromatic side-chain reactions and, in fact, are comparable with those obtained in some aromatic electrophilic substitution reactions.[7] One explanation for this could be that steric inhibition of solvation by the ortho groups places a greater demand on the ring for charge dispersal. This type of phenomenon has been observed for the ionization of ortho-substituted benzoic acids.[8] However, several pieces of evidence seem to rule out this explanation. First, if *o*-methyl groups were significantly hindering solvation of the developing vinyl cation, a distinctly more negative ρ value would have been expected for the 2,6-dimethyl series than for the 2-methyl series. This is clearly not the case, as can be seen from Figure 1. Second, as pointed out earlier, the $\Delta S^{\ddagger}$ values in Table II are all fairly close to −30 eu mol^{-1}, irrespective of the number of *o*-methyl groups. Finally, the product distributions (see Experimental Section) show that approximately equal amounts of *cis*- and *trans*-dibromo adducts were formed as well as solvent-incorporated products in some cases. These results on (2-methylphenyl)- and (2,6-dimethylphenyl)acetylenes are very similar to those obtained by Yates and Pincock[2] for the parent phenylacetylenes. Complementary to the product studies on the Ad_E2 process of principal interest are the product distributions obtained in the presence of added LiBr (see Experimental Section) where the bromide-catalyzed Ad_E3 process is dominant.[9] Again the product distributions are very similar to those from the parent phenylacetylenes. It can be seen from space-filling models that the intermediate vinyl cation (II) should be



II

relatively unhindered with respect to solvent (or nucleophile) approach to C_α from above or below the plane of the benzene ring. It therefore appears that steric inhibition cannot be a major factor in causing the large (negative) ρ values in the 2-methyl and 2,6-dimethyl series.

Of more interest is a comparison between the ρ values for electrophilic addition and those from the preceding paper[1] for α-arylvinyl-X solvolyses. The values are summarized in Table III along with available values from the two parent series containing no *o*-methyl substituents. At first sight there appears to be poor correspondence between the ρ values for two types of reaction (S_N1 and Ad_E2) generating very similar vinyl cationic intermediates (and presumably similar transition states). For example, the solvolytic reactions give ρ values in the range −4 to −5, whereas the electrophilic additions show significantly more sensitivity to structural change, with ρ's in the range −5 to −7. However, there are two important differences in the reaction conditions under which these ρ's were obtained, both of which would tend to make the solvolysis values less negative. One is that because of generally low rates for vinyl solvolysis, elevated temperatures were used in most cases, whereas all the electrophilic additions were measured at 25 °C. Whether isokinetic phenomena are to be expected or not, ρ values generally decrease in absolute magnitude with increasing temperature. Thus, all the solvolysis ρ values would be more negative at 25 °C than the values listed in Table III. The second factor is that all the solvolysis rates were measured in highly polar water–alcohol mixtures, whereas the electrophilic reactions were studied exclusively in anhydrous acetic acid, which is a much poorer ionizing solvent. Even though only (or primarily) electrophilic solvation of the leaving group may be important in the S_N1 reactions, with no rear-side nucleophilic assistance, the better solvents used for these reactions should result in less demand being placed on the ring to achieve a given degree of charge development or separation at the transition state and hence less negative ρ values.

When the above factors are considered as well as the enormous differences in rates[11] for the two quite different ways of generating structurally similar vinyl cations, the

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[6] The *p*-methoxy compound reacted too rapidly to be followed by the stopped-flow apparatus. Therefore its rate constant must be of the order of 10^6 M^{-1} s^{-1} or greater.

[7] J. G. Hoggett, R. B. Moodie, J. R. Penton, and K. Schofield, "Nitration and Aromatic Reactivity", Cambridge University Press, New York, 1971, p 194.

[8] H. V. Bekkum, P. E. Verkade, and B. M. Wepster, *Recl. Trav. Chim. Pays-Bas*, **78**, 815 (1959).

[9] J. A. Pincock, and K. Yates, *J. Am. Chem. Soc.*, **90**, 5643 (1968).

[10] C. A. Grob and G. Cseh, *Helv. Chim. Acta*, 47, 194 (1964).

[11] It is difficult to estimate this difference in reactivity precisely, because of the frequently different reaction conditions used, but for three pairs of compounds with identical substituents which have been studied in anhydrous acetic acid at similar temperatures, the rate constants for Ad_E2 reactions are anywhere from 10^5 to 10^9 times as large as those for the corresponding S_N1 reactions. Strictly speaking, it is the half-lives which should be compared not the rate constants, since the solvolyses are first order and the electrophilic reactions second order. For example, for 1-(2-methyl-4-methoxyphenyl)vinyl tosylate in HOAc at 36.5 °C, $t_{1/2}$ is 3.09 h, whereas for (2-methyl-4-methoxyphenyl)acetylene in HOAc at 24.8 °C, $t_{1/2}$ is 0.0016 s. Thus the reactivity ratio in this case, at a common temperature, would probably be greater than 10^6 in favor of the Ad_E2 process for any reasonable range of initial bromine concentrations.

correspondence between the two sets of ρ values in Table III is probably as good as could be expected. Both types of reaction follow σ^+ much better than σ, and both series give strongly negative reaction constants. It may be that the weakly exothermic or thermoneutral nature of the solvolysis reactions leads to somewhat earlier transition states with less charge development and hence somewhat less negative ρ values. In the case of the Ad_E2 reactions, the transition state for electrophilic addition may be much closer in structure to that of the vinyl cation itself and hence give a more negative ρ. However, it must be pointed out that none of the foregoing factors give any explanation of why the ρ values for the Ad_E2 reactions of substrates with *o*-methyl substituents are so much more negative than that for the parent series.

Experimental Section

General experimental details and procedures were exactly as described in the preceding paper.[1] Preparation of all but three of the phenylacetylene substrates has already been described in this paper. The remaining phenylacetylenes were all synthesized by starting from the corresponding α-chlorostyrenes, prepared as described in the preceding paper.[1]

(2,5-Dimethylphenyl)acetylene. The α-chlorostyrene was dehydrochlorinated as described previously[1] by using potassium *tert*-butoxide in dry Me_2SO to give the acetylene: 97% yield; bp 72 °C (15 mm) [lit.[12] bp 49 °C (2 mm)]. The acetylene was redistilled to greater than 99.5% purity by GLC.

(2,4,6-Trimethylphenyl)acetylene. The corresponding α-chlorostyrene was dehydrochlorinated in the same way as described previously[1] to give the acetylene: 81% yield; bp 82 °C (12 mm) [lit.[12] bp 62–63 °C (2.5 mm)]. Redistillation gave a product of 99.9% purity by GLC.

(2,6-Dimethyl-4-methoxyphenyl)acetylene. The corresponding α-chlorostyrene was dehydrochlorinated in the same way as above to give the acetylene in 85% yield. Recrystallization from ethanol–water followed by sublimation gave a final product, mp 50–52 °C.

The ^1H NMR and IR spectral data on all three of the above compounds were consistent with the assigned structures.

Kinetic Measurements. The brominations of the slower reacting compounds were studied by conventional UV spectrophotometry by following the decrease in bromine absorbance at 490 nm on a Cary 16 instrument. This wavelength was chosen since in some cases hydrogen bromide is formed along with the solvent-incorporated products. This complexes with Br_2 to give Br_3^-, which absorbs strongly[13] at lower wavelengths (λ_{max} = 390 nm) and can lead to erroneous rate measurements. To avoid higher order terms in Br_2, we had to use low initial concentrations ($2-4 \times 10^{-4}$ M), necessitating use of a 10-cm thermostated cell. Initial acetylene concentrations were in the range 50–200-fold in excess of starting bromine concentrations to ensure pseudo-first-order kinetics. All bromine solutions were protected from direct light by aluminum foil. The reactions were followed for 3 half-lives, and infinity values of the absorbance taken after 10 half-lives. Rate constants were obtained from least-squares plots of ln $(A - A_\infty)$ vs. time. In all cases two to four runs were carried out with different initial acetylene concentrations, and the derived second-order rate constants were found to agree to within ±3%. At least four temperatures were used to determine the activation parameters by use of least-squares plots of log (k/T) vs. $1/T$.

For the more reactive acetylenes, the rates of bromination were followed by the stopped-flow method with a Durrum stopped-flow kinetics spectrophotometer. Output from the photomultiplier tube was coupled to a Tektronix storage oscilloscope, with the vertical axis linear in absorbance and the horizontal axis linear in time. Again the UV absorbance of Br_2 at 490 nm was used to monitor the reaction. After several reproducible oscilloscope traces of a given run were obtained, the scope was set on the storage mode and the next trace recorded with a Tektronix Polaroid oscilloscope camera. Runs were followed to 2 or 3 half-lives and infinity values taken after 10 half-lives. The reactions were again studied under pseudo-first-order conditions and the rate constants obtained as before. Between two and four runs were carried out at different initial acetylene concentrations, and the derived second-order rate constants agreed to within ±3%.

Table IV. Bromination Product Distributions

phenyl-acetylene	reaction conditions	% products[a]		
		dibromides		
		trans	cis	SI[b]
2,4-dimethyl	HOAc	51	43	6
	HOAc/0.1 M LiBr	88	16	trace
2,5-dimethyl	HOAc	46	44	10
	HOAc/0.1 M LiBr	86	14	trace
2,4,6-trimethyl	HOAc	56	44	
	HOAc/0.1 M LiBr	71	29	
4-methyl	HOAc[c]	56	44	
	HOAc/0.1 M LiBr	81	19	

[a] Results were obtained from integration ratios of the ^1H NMR spectra of the product mixtures; estimated error ±5%. [b] 1-Acetoxy-2-bromo-1-arylethylenes. [c] Data from ref 2.

Product Distributions. The main purpose of the product studies was to determine the effect of one or two *o*-methyl groups on the stereochemistry of addition, as compared with that of the parent phenylacetylenes. Analyses were routinely carried out by ^1H NMR spectroscopy. Attempts to separate the isomeric *cis*- and *trans*-dibromides by preparative GLC were not successful due to the instability of these compounds at the high temperature (≃200 °C) and long retention times required for separation. Thus extensive purification and physical property measurements were not attempted. The product distributions are summarized in Table IV, and the details of the identifications of individual products were as follows.

2,4-Dimethylphenylacetylene. In a typical experiment, 2.0 g (0.0154 mol) of (2,4-dimethylphenyl)acetylene was dissolved in 30 mL of dry acetic acid. This solution was slowly added to an equimolar amount of bromine in 30 mL of acetic acid with rapid stirring, so that the resulting solution remained a very pale yellow color. This ensures that low bromine concentrations (as in the kinetic measurements) were always maintained. The reaction mixture was left stirring for an additional 30 min before it was poured into 20 mL of water, and this was followed by extractions with methylene chloride (2 × 50 mL). The extracts were washed (water, 5% $NaHCO_3$) and dried with M_2SO_4 before removal of the solvent under vacuum. This yielded 2.7 g of reaction products, which were directly analyzed by ^1H NMR. The mixture was found to consist of *trans*-1,2-dibromo-1-(2,4-dimethylphenyl)ethylene (51%), *cis*-1,2-dibromo-1-(2,4-dimethylphenyl)ethylene (43%), and (*E*)- and (*Z*)-1-acetoxy-2-bromo-1-(2,4-dimethylphenyl)ethylene (6%). No other products were indicated by either the ^1H NMR or IR spectrum.

The bromination was also studied in the presence of 0.1 M LiBr. After being worked up as described above, the mixture was shown to consist of the *trans*-dibromide (88%), the *cis*-dibromide (12%), and only traces of the acetoxy bromides. In both cases, a check of the product distribution as a function of reaction time indicated no isomerization of the dibromides or their subsequent reaction to produce acetoxy bromides was occurring.

Since the dibromides could not be separated by preparative GLC, distillation of the first reaction mixture yielded 59% of the *trans*-dibromide and 41% of the cis isomer at 88–90 °C (100 torr). Anal. Calcd for $C_{10}H_{10}Br_2$: C, 41.41; H, 3.48; Br, 55.11. Found: C, 41.58; H, 3.36; Br, 55.04. The stereochemistry of these two isomers was established by ^1H NMR only. The olefinic proton signal of the trans isomer is a singlet at δ 6.68 and that of the cis isomer is a singlet at δ 6.63. This is in agreement with previous observations that β-olefinic protons cis to the aromatic ring occur at lower field than those trans to the ring. The ^1H NMR signal at δ 6.45 was assigned to the acetoxy bromide product, in agreement with previous assignments.[2]

(2,5-Dimethylphenyl)acetylene. The reaction and workup were as described above. ^1H NMR analysis of the product mixture

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[13] J. H. Rolston and K. Yates, *J. Am. Chem. Soc.*, **91**, 1483 (1969).

showed it to consist of 46% of the *trans*-dibromo adduct, 44% of the *cis*-dibromo adduct, and 10% of the acetoxy bromide mixture. Distillation of the reaction mixture yielded 55% of *trans*-dibromide and 45% of *cis*-dibromide at 95–97 °C (200 torr). Anal. Calcd for $C_{10}H_{10}Br_2$: C, 41.41; H, 3.48; Br, 55.11. Found: C, 41.29; H, 3.50; Br, 54.96. The olefinic proton of the trans isomer is a singlet at δ 6.69 and that of the cis isomer occurs at δ 6.64. The peak at δ 6.51 was assigned to the olefinic proton of the acetoxy bromide product.

(2,4,6-Trimethylphenyl)acetylene. The reaction and workup were carried out as before. ^1H NMR analysis showed the reaction mixture to consist of 56% of the *trans*-dibromo adduct and 44% of the cis isomer. The olefinic protons of the two isomers are singlets at δ 6.68 and 6.5, respectively. No other products were found to be present.

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Registry No. (4-Methoxy-2-methylphenyl)acetylene, 74331-69-4; (2,4-dimethylphenyl)acetylene, 16017-30-4; (2,5-dimethylphenyl)acetylene, 74331-70-7; (2-methylphenyl)acetylene, 766-47-2; (4-chloro-2-methylphenyl)acetylene, 74331-71-8; (5-chloro-2-methylphenyl)acetylene, 74331-72-9; (4-methoxy-2,6-dimethylphenyl)acetylene, 74331-73-0; (2,4,6-trimethylphenyl)acetylene, 769-26-6; (2,6-dimethylphenyl)acetylene, 74331-74-1; (4-bromo-2,6-dimethylphenyl)acetylene, 74331-75-2; 1-(2-methylphenyl)vinyl tosylate, 74331-76-3; 1-(2,6-dimethylphenyl)vinyl tosylate, 74331-77-4; 1-(2,6-dimethylphenyl)-1-bromoethene, 74331-78-5; 1-(2,6-dimethylphenyl)-1-chloroethene, 74331-79-6; 4-methylphenylacetylene, 766-97-2; (*E*)-1,2-dibromo-1-(2,4-dimethylphenyl)ethylene, 74331-80-9; (*Z*)-1,2-dibromo-1-(2,4-dimethylphenyl)ethylene, 74331-81-0; (*E*)-1,2-dibromo-1-(2,5-dimethylphenyl)ethylene, 74331-82-1; (*Z*)-1,2-dibromo-1-(2,5-dimethylphenyl)ethylene, 74331-83-2; (*E*)-1,2-dibromo-1-(2,4,6-trimethylphenyl)ethylene, 74331-84-3; (*Z*)-1,2-dibromo-1-(2,4,6-trimethylphenyl)ethylene, 74331-85-4; (*E*)-1,2-dibromo-1-(4-methylphenyl)ethylene, 74331-86-5; (*Z*)-1,2-dibromo-1-(4-methylphenyl)ethylene, 74346-16-0; (*E*)-1-acetoxy-2-bromo-1-(2,4-dimethylphenyl)ethylene, 74331-87-6; (*Z*)-1-acetoxy-2-bromo-1-(2,4-dimethylphenyl)ethylene, 74331-88-7; (*E*)-1-acetoxy-2-bromo-1-(2,5-dimethylphenyl)ethylene, 74331-89-8; (*Z*)-1-acetoxy-2-bromo-1-(2,5-dimethylphenyl)ethylene, 74331-88-7; 2,5-dimethyl-α-chlorostyrene, 74331-90-1; 2,4,6-trimethyl-α-chlorostyrene, 5312-67-4; 2,6-dimethyl-4-methoxy-α-chlorostyrene, 74331-91-2; 1-(2-methyl-4-methoxyphenyl)vinyl tosylate, 74331-92-3.

Notes

Oxidation by Metal Ions. 6.[1a] Intramolecular Selectivity in the Side-Chain Oxidation of *p*-Ethyltoluene and Isodurene by Cobalt(III), Cerium(IV), and Manganese(III)

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Side-chain substitutions of alkylaromatic compounds by one electron oxidants such as Ce(IV), Mn(III), and Co(III) are generally thought to occur via a radical cation intermediate[2,3] (eq 1a–c). However, this hypothesis has been recently criticized.[4-6] It has been suggested that the benzyl radical may be directly formed by a hydrogen atom abstraction reaction (eq 2) promoted by one of the metal ligands.[4,6]

$$ArCH_3 + M^{n+} \rightleftharpoons ArCH_3^{+}\cdot + M^{(n-1)+} \tag{1a}$$

$$ArCH_3^{+}\cdot + B \rightarrow ArCH_2\cdot + BH^+ \tag{1b}$$

$$ArCH_2\cdot + M^{n+} \xrightarrow[\text{steps}]{\text{one or more}} \text{products} + M^{(n-1)+} \tag{1c}$$

$$ArCH_3 + M^{n+}L \rightarrow ArCH_2\cdot + M^{(n-1)+} + HL \tag{2}$$

Certainly, the difficulty of reaching firm conclusions depends also upon the fact that many of the main features of these reactions are scarcely known. For example, in oxidation of poly(alkyl)benzenes, the effects of the oxidizing metal ions on the intramolecular selectivities (relative reactivity of nonequivalent α-hydrogen atoms) are virtually unknown.[7]

It is believed that such information could be very useful for a better understanding of the mechanism of these reactions and also be of practical interest. Therefore, a study has been carried out on the isomeric product distribution for the reactions in acetic acid of *p*-ethyltoluene and isodurene (1,2,3,5-tetramethylbenzene) with ceric ammonium nitrate (CAN), manganic acetate (in the presence of 0.2 M H_2SO_4[10]), and cobaltic acetate. For comparison, we have also investigated the side-chain bromination of the same substrates with *N*-bromosuccinimide (NBS) which certainly involves a hydrogen atom abstraction step.[12]

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[1] (a) Part 6 of the series Oxidation of Aromatic Compounds by Metal Ions. Part 5: Baciocchi, E.; Mei, S.; Rol, C.; Mandolini, L. *J. Org. Chem.* **1978**, *43*, 2919. Part 4: Maini, S.; Mandolini, L.; Rol, C. *J. Org. Chem.* **1978**, *43*, 3236. (b) Università di Perugia. (c) Università di Roma.

[2] Kochi, J. K. *Free Radicals* **1973**, *1*, 643–648, and references cited therein.

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[7] Data of intramolecular selectivity are available only for the oxidation in acetic acid, under pressure at 105 °C, of *p*-cymene and *p*-ethyltoluene catalyzed by $Co(OAc)_2$[8] and for the reaction of Ce(IV) with isodurene.[9]

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[10] In the absence of H_2SO_4 the reaction of alkylaromatics with Mn(III) occurs only at high temperature and can lead to products derived by attack of the carboxymethyl radical generated by the thermolysis of $Mn(OAc)_3$.[11]

[11] Heiba, E. I.; Dessau, R. M.; Koehl, W. G., Jr. *J. Am. Chem. Soc.* **1969**, *91*, 138.

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