

## Electrophilic Additions to Multiple Bonds. 4. Effect of Alkyne Structure on the Rates of Bromination<sup>1</sup>

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The rates of bromination of acetylene and 16 substituted derivatives were measured in acetic acid at 25 °C in the absence of added bromide ion. The bromine concentrations were sufficiently low ( $<3 \times 10^{-4}$  M) that the rate law was overall second order, first order in both alkyne and bromine. The rate data for acetylene and 11 of the 12 alkyl-substituted acetylenes follow a simple Taft correlation whose equation is  $\log k_2 = -2.11 \sum \sigma^* - 2.64$ . The rates of bromination of the phenyl-substituted acetylenes do not fit this equation. The data support two different mechanisms for the bromination of alkynes. Bromination of alkyl-substituted acetylenes occurs via a bridged rate-determining transition state while bromination of phenylacetylenes occurs via an open vinyl-ion-like rate-determining transition state.

The mechanism of the electrophilic bromine addition to alkynes is known to involve at least two steps.<sup>2</sup> One of these is rate-determining. The effect of substrate structure upon the rate of reaction is one of the classical methods used to obtain a description of the rate-determining transition state.

For bromination, the available structure-reactivity data have been interpreted in terms of two different mechanisms.<sup>3</sup> One, for alkyl-substituted acetylenes, involves a bridged rate-determining transition state. The other, for phenyl-substituted acetylenes, involves an open vinyl-like transition state. We wish to present additional data that support these mechanistic conclusions.

### Results and Discussion

The rate law for the electrophilic bromination of alkynes contains all or part of eq 1 (A = alkyne), depending upon

$$-d[\text{Br}_2]/dt = k_2[\text{Br}_2][\text{A}] + k_3[\text{Br}_2][\text{A}]^2 + k_3'[\text{Br}^-][\text{Br}_2][\text{A}] \quad (1)$$

reaction conditions. In acetic acid as solvent, at low bromine concentrations (less than  $3 \times 10^{-4}$  M) and in the absence of bromide ion, only the first term in eq 1 makes a significant contribution to the observed rate. Both the  $k_2$  and  $k_3$  terms contribute to the overall rate equation at a bromine concentration of approximately  $1 \times 10^{-2}$  M. In the presence of added bromide ion, the third term becomes important.

Under conditions where overall second-order kinetics are followed, the rates of bromination of acetylene (1) and 16 substituted derivatives (2-17) were measured in acetic acid at 25 °C (see Table I). The rate data are given in Table II.

Bromination of alkynes in acetic acid usually occurs by an ionic mechanism.<sup>4</sup> However, brominations of alkenes and alkynes are also known to occur by a free-radical mechanism.<sup>5</sup> To establish that our rate data represent an ionic reaction, we measured the rates of addition of selected alkynes in the presence of free-radical initiators or inhibitors. It was found that isoamyl nitrite in con-

Table I

R <sub>1</sub> C≡CR <sub>2</sub>					
	R <sub>1</sub>	R <sub>2</sub>		R <sub>1</sub>	R <sub>2</sub>
1	H	H	9	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>
2	H	CH <sub>3</sub>	10	CH <sub>3</sub>	<i>i</i> -C <sub>4</sub> H <sub>9</sub>
3	H	C <sub>2</sub> H <sub>5</sub>	11	CH <sub>3</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub>
4	H	<i>i</i> -C <sub>4</sub> H <sub>9</sub>	12	C <sub>2</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>
5	H	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	13	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub>
6	H	<i>n</i> -C <sub>3</sub> H <sub>7</sub>	14	H	C <sub>6</sub> H <sub>5</sub>
7	H	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	15	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>
8	CH <sub>3</sub>	CH <sub>3</sub>	16	C <sub>2</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>
			17	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>

Table II. Second-Order Rate Constants for the Bromination of Alkynes in Acetic Acid at 25 °C

alkyne	N <sup>d</sup>	k <sub>2</sub> , M <sup>-1</sup> s <sup>-1</sup>	k <sub>rel</sub>
HC≡CH (1)	3	(1.94 ± 0.01 <sup>a</sup> ) × 10 <sup>-5</sup>	1
CH <sub>3</sub> C≡CH (2)	3	(2.61 ± 0.01) × 10 <sup>-4</sup>	13.4
C <sub>2</sub> H <sub>5</sub> C≡CH (3)	2	(3.02 ± 0.03) × 10 <sup>-4</sup>	15.5
C <sub>4</sub> H <sub>9</sub> C≡CH (6)	4	(3.06 ± 0.03) × 10 <sup>-4</sup>	15.7
C <sub>4</sub> H <sub>9</sub> C≡CH (7)	6	(3.76 ± 0.01) × 10 <sup>-4</sup>	19.4
<i>i</i> -C <sub>4</sub> H <sub>9</sub> C≡CH <sup>b</sup> (4)	4	(6.50 ± 0.06) × 10 <sup>-4</sup>	33.5
<i>t</i> -C <sub>4</sub> H <sub>9</sub> C≡CH <sup>b</sup> (5)	4	(1.33 ± 0.01) × 10 <sup>-3</sup>	68.4
CH <sub>3</sub> C≡CCH <sub>3</sub> (8)	4	(2.33 ± 0.02) × 10 <sup>-3</sup>	120
CH <sub>3</sub> C≡CC <sub>2</sub> H <sub>5</sub> (9)	3	(3.87 ± 0.03) × 10 <sup>-3</sup>	199
C <sub>2</sub> H <sub>5</sub> C≡CC <sub>2</sub> H <sub>5</sub> (12)	3	(5.23 ± 0.03) × 10 <sup>-3</sup>	269
CH <sub>3</sub> C≡C- <i>i</i> -C <sub>4</sub> H <sub>9</sub> (10)	3	(5.74 ± 0.10) × 10 <sup>-3</sup>	296
CH <sub>3</sub> C≡C- <i>t</i> -C <sub>4</sub> H <sub>9</sub> (11)	2	(1.08 ± 0.06) × 10 <sup>-2</sup>	558
<i>t</i> -C <sub>4</sub> H <sub>9</sub> C≡C- <i>t</i> -C <sub>4</sub> H <sub>9</sub> (13)	4	(2.69 ± 0.05) × 10 <sup>-4</sup>	13.8
HC≡CC <sub>6</sub> H <sub>5</sub> <sup>c</sup> (14)		(4.33 ± 0.06) × 10 <sup>-3</sup>	223
CH <sub>3</sub> C≡CC <sub>6</sub> H <sub>5</sub> <sup>c</sup> (15)		(2.46 ± 0.06) × 10 <sup>-3</sup>	126
C <sub>2</sub> H <sub>5</sub> C≡CC <sub>6</sub> H <sub>5</sub> (16)	2	(6.31 ± 0.08) × 10 <sup>-3</sup>	325
C <sub>6</sub> H <sub>5</sub> C≡CC <sub>6</sub> H <sub>5</sub> (17)	2	(1.88 ± 0.04) × 10 <sup>-4</sup>	9.69

<sup>a</sup> Standard deviation. <sup>b</sup> Determined in the presence of isoamyl nitrite. See Table III and text for details. <sup>c</sup> Reference 3. <sup>d</sup> Number of determinations.

centrations of about 15 times larger than the concentrations of bromine used in kinetic runs ( $[\text{Br}_2] \approx 5 \times 10^{-4}$  M) effectively suppressed any free-radical pathway for these compounds. The rates obtained with and without radical inhibitors or initiators are compared in Table III. Only in the additions to 3-methyl-1-butyne (4) and 3,3-dimethyl-1-butyne (5) was there evidence of a competing free-radical process.

From the rate data in Table II, it is clear that the substitution of one hydrogen on acetylene by an alkyl group leads to a rate enhancement of between 13 and 68. Replacement of both hydrogens leads to further rate enhancements. The rate constants for the alkyl-substituted acetylenes follow a simple Taft correlation<sup>6</sup> as illustrated

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Table III. Influence of Radical Inhibitors and Initiators on Rates of Bromination of Alkynes in Acetic Acid at 25 °C

alkyne	[inhibitor or initiator]/[Br <sub>2</sub> ]	$k_2, M^{-1} s^{-1}$	
		inhibitor or initiator present	inhibitor or initiator absent
<i>i</i> -AmONO			
HC≡C- <i>i</i> -C <sub>3</sub> H <sub>7</sub> (4)	16	$(6.50 \pm 0.063) \times 10^{-4}$	$(2.76 \pm 0.12) \times 10^{-2}{}^a$
HC≡C- <i>t</i> -C <sub>4</sub> H <sub>9</sub> (5)	15	$(1.33 \pm 0.014) \times 10^{-3}$	$(2.20 \pm 0.047) \times 10^{-2}{}^a$
CH <sub>3</sub> C≡CCH <sub>3</sub> (8)	16	$(2.42 \pm 0.026) \times 10^{-3}$	$(2.33 \pm 0.015) \times 10^{-3}$
CH <sub>3</sub> C≡CC <sub>2</sub> H <sub>5</sub> (9)	16	$(4.18 \pm 0.020) \times 10^{-3}$	$(3.87 \pm 0.033) \times 10^{-3}$
HC≡CC <sub>4</sub> H <sub>9</sub> (7)	13	$(4.22 \pm 0.066) \times 10^{-4}$	$(3.76 \pm 0.0075) \times 10^{-4}$
Bz <sub>2</sub> O <sub>2</sub>			
CH <sub>3</sub> C≡CCH <sub>3</sub> (8)	2.5	$(2.83 \pm 0.0069) \times 10^{-3}$	$(2.33 \pm 0.015) \times 10^{-3}$
( <i>t</i> -BuO <sub>2</sub> CO) <sub>2</sub>			
HC≡C- <i>i</i> -C <sub>3</sub> H <sub>7</sub> (5)	14	$(1.92 \pm 0.024) \times 10^{-2}$	$(2.76 \pm 0.12) \times 10^{-2}{}^a$

<sup>a</sup> No clean second-order rate plots were obtained. These values are calculated from the first 20% of the reaction where second-order rate plots were linear.

Table IV. Effect on the Rate of Bromination of Progressively Substituting Acetylenic Hydrogens

Me series	$k_{rel}$	Et series	$k_{rel}$	<i>t</i> -Bu series	$k_{rel}$	Ph series	$k_{rel}$
HC≡CH (1)	1.0	HC≡CH (1)	1.0	HC≡CH (1)	1.0	HC≡CH (1)	1.0
HC≡CCH <sub>3</sub> (2)	13.4	HC≡CC <sub>2</sub> H <sub>5</sub> (3)	15.6	<i>t</i> -C <sub>4</sub> H <sub>9</sub> C≡CH (5)	68	C <sub>6</sub> H <sub>5</sub> C≡CH (14)	218
CH <sub>3</sub> C≡CCH <sub>3</sub> (8)	120.1 <sup>a</sup>	C <sub>2</sub> H <sub>5</sub> C≡CC <sub>2</sub> H <sub>5</sub> (12)	270 <sup>b</sup>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> C≡C- <i>t</i> -C <sub>4</sub> H <sub>9</sub> (13)	14	C <sub>6</sub> H <sub>5</sub> C≡CC <sub>6</sub> H <sub>5</sub> (17)	10

<sup>a</sup> Equals 11.0<sup>2</sup>. <sup>b</sup> Equals 16.4<sup>2</sup>.

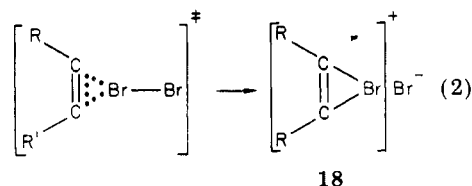
in Figure 1. Acetylene and 11 of the 12 alkyl-substituted derivatives lie on the straight line whose equation is

$$\log k_2 = -2.11 \sum \sigma^* - 2.64$$

A correlation of  $r = 0.996$  is obtained. The point for 2,2,5,5-tetramethyl-3-hexyne, 13, lies off the line. Such a relationship implies that only the polar effect of substituents is important in the rate-determining transition state. Steric effects are important only when both substituents are bulky. The phenyl-substituted acetylenes do not follow a simple Taft correlation.

In accord with previous findings,<sup>7</sup> the rate of bromination of alkynes is slower than that of similarly substituted alkenes. The effect of substituents is slightly greater upon the rate of addition to alkenes than to alkynes. This is in contrast to the effect of these same substituents upon the rate of addition of 4-chlorobenzenesulfonyl chloride to alkynes,<sup>8</sup> a reaction that involves a bridged rate-determining transition state.

The ionic mechanism of the bromination of alkyl-substituted acetylenes has been postulated<sup>3</sup> to involve a bridged rate-determining transition state leading to a bromonium ion intermediate (18, eq 2). The data in Table



R = R' = H or alkyl group

II support such a mechanism. The effect of progressively substituting the hydrogens of acetylene by methyl and ethyl groups is cumulative, as shown in Table IV. This suggests that the charge distribution is similar on both acetylenic carbon atoms in the rate-determining transition

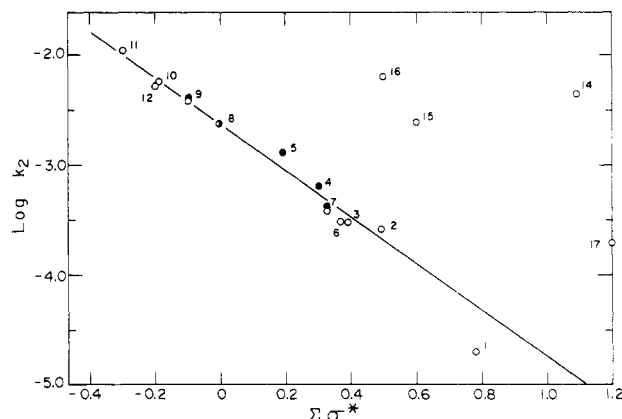
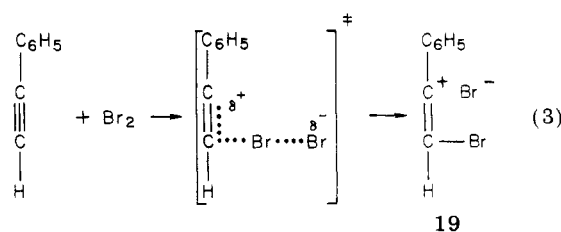


Figure 1. Taft plot of the rates of bromination of alkynes. The numbers correspond to those in the text. The solid circles refer to rates obtained in the presence of isoamyl nitrite. The point for 2,2,5,5-tetramethyl-3-hexyne is off the figure. Compounds 14, 15, 16, and 17 are not included in the equation of the line (see text).

state, consistent with a bridged structure. In the *tert*-butyl series, replacing the second hydrogen of acetylene by another *tert*-butyl group causes a decrease in the rate. Such an effect is well documented in electrophilic additions<sup>8,9</sup> and has been ascribed to steric hindrance.

The mechanism of the bromination of phenyl-substituted acetylenes has been postulated<sup>3</sup> to involve a vinyl-cation-like rate-determining transition state leading to an open vinyl cation (19, eq 3). The data support such a



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mechanism. Substituting the acetylenic hydrogen of

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phenylacetylene by a methyl or an ethyl group has little effect upon the rate. This suggests that acetylenic carbon C-2 has very little positive charge in the rate-determining transition state, consistent with an open-ion-like structure.

Such a conclusion is consistent with the rates of solvolysis of several  $\alpha$ -bromostyrene derivatives. The effect of  $\beta$ -substituents on the formation of a phenyl-stabilized cation is small.<sup>10</sup> Further support for this explanation is found in the effect of substituents upon the rate of addition of 4-chlorobenzenesulfonyl chloride to phenylacetylenes.<sup>11</sup> In this reaction, substituting the acetylenic hydrogen of phenylacetylene by a methyl group causes a rate increase of 35.

It is found that the rate of bromination of diphenylacetylene is slower than phenylacetylene. This effect of a second phenyl group on the rates of electrophilic additions to alkenes and alkynes has been found in other studies.<sup>11</sup> This may be due to an inductive electron-withdrawing effect of the second phenyl group of tolan.

### Summary

Systematic structure-reactivity data support the proposal that the rate-determining transition states of bro-

mine additions are different for alkyl- and phenyl-substituted acetylenes. An open vinyl-like rate-determining transition state is involved in the bromination of phenylacetylenes while a bridged-like rate-determining transition state is involved with alkyl-substituted acetylenes.

### Experimental Section

**Reagents.** The alkynes are 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 was distilled through a column.<sup>12</sup> Di-*tert*-butyl peroxyoxalate was kindly provided by Professor T. T. Tidwell of this department. All other reagents are commercially available.

**Kinetics.** The kinetics were carried out as previously reported.<sup>3</sup>

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**Registry No.** 1, 74-86-2; 2, 74-99-7; 3, 107-00-6; 4, 598-23-2; 5, 917-92-0; 6, 627-19-0; 7, 693-02-7; 8, 503-17-3; 9, 627-21-4; 10, 21020-27-9; 11, 999-78-0; 12, 928-49-4; 13, 17530-24-4; 16, 622-76-4; 17, 501-65-5; Br<sub>2</sub>, 7726-95-6.

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## Rearrangements of 1,6-Dihalotricyclo[4.2.2.0<sup>2,5</sup>]decanes. Synthesis of Tricyclo[5.3.0.0<sup>4,8</sup>]decane Derivatives<sup>1,2</sup>

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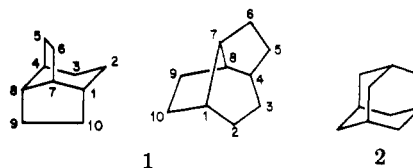
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1,8-Diiodotricyclo[5.3.0.0<sup>4,8</sup>]decane (**16**) was prepared by reaction of 1,6-dihalotricyclo[4.2.2.0<sup>2,5</sup>]decanes **9a** and **9b** with aluminum triiodide. Reduction of **16** with di-*n*-butyltin dihydride produced the tricyclic hydrocarbon tricyclo[5.3.0.0<sup>4,8</sup>]decane (**1**). Dichloride **9a** was prepared by a Diels-Alder reaction between 1,4-dichlorocyclohexa-1,3-diene (**10a**) and cyclobutene followed by catalytic hydrogenation of the adduct **12a**. The structure of **16** was determined by an X-ray diffraction study of a single crystal.

Adamantane (**2**) and its congeners have been the subject of numerous theoretical and experimental investigations.<sup>3</sup> The highly symmetrical diamondoid structure of adamantane, its striking physical properties, and the almost complete lack of strain have urged chemists to explore the interrelationships of its chemical and physical properties in exquisite detail. These researches have been encouraged

by the discovery that adamantane can be prepared by Lewis acid isomerization<sup>4-9</sup> of a variety of less stable isomeric hydrocarbons, such as tetrahydrodicyclopentadiene,<sup>4</sup> twistane,<sup>5</sup> perhydroquinacene,<sup>6</sup> and protoadamantane.<sup>7</sup>



(1) Taken in part from the Ph.D. Dissertation of J.J.V., The University of Michigan, 1978.

(2) The von Baeyer system is used to name and to number the bridged ring systems in this paper. The *Chemical Abstracts* name for **1** is 1,4-ethano-1,2,3,3a,4,5,6,6a-octahydropentalene. Derivatives of **1** with double bonds in the ethano bridge (2,3-position using the von Baeyer numbering scheme) are indexed under 1,4-ethenopentalene.



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