standard perchloric acid, and 1:1 buffers of varying NEP concentration were prepared from this by appropriate dilution. The proper volume of a standard solution of lithium perchlorate in 60% dioxane was added to these solutions as required to achieve the desired ionic strength. The procedure used for following the kinetics of the disappearance of **1b** in 60% dioxane has already been described.[10] The hydrolyses were all slow enough at 25° to be followed by conventional, rather than stopped-flow, spectrophotometry.

Besides the various runs in 1:1 NEP-NEPH$^+$ buffers we also carried out a single series of runs in 60% dioxane in a set of 1:1 Et_3N-Et_3NH^+ buffers of varying triethylamine concentration in order to verify that we could obtain kinetic results on this system in adequate agreement with those reported earlier by Kice and Kasperek.[2]

Registry No. 1b, 10409-06-0; **3a,** 1153-45-3.

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The Addition of 2,4-Dinitrobenzenesulfenyl Chloride to 1-Phenylpropyne and Related Compounds

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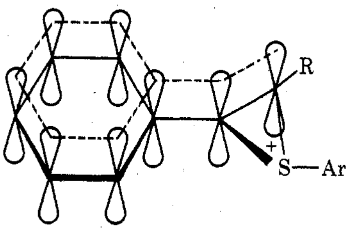
Electrophilic additions of 2,4-dinitrobenzenesulfenyl chloride (1) to 1-phenylpropyne (4) and its ring-substituted derivatives (p-OCH_3, p-Cl, and m-Cl) have been studied kinetically in acetic acid. The effects of the ring substituents on the reaction rate of 4 conformed to the Hammett $\rho\sigma$ relationship with the reaction constant $\rho = -1.46$ at 40°. Additions of 1 to phenylacetylene (5), 1-hexyne (7), and 2-heptyne (6) were also studied for the sake of comparison. It was found that the methyl substitution on the acetylenic carbon enhances the reactivity by a factor of 10 to 20. The secondary kinetic isotope effects were examined for 5 and styrene (10) with use of α- and β-deuterated substrates. The value $k_H/k_D \sim 0.95$ for each deuteration was obtained. These results were compared with those found in the related electrophilic addition reactions. It is concluded that the sulfenyl sulfur attacks the isolated π bond of phenylacetylenes to form an unsaturated episulfonium ion.

Electrophilic addition reactions of acetylenes are closely related to those of olefins in character. The acid-catalyzed hydration of both phenylacetylene[1] and styrene[2] involves a carbonium ion intermediate stabilized by the benzyl conjugation. Yates, *et al.*,[3] have recently compared the reactivities of some olefin–acetylene pairs in electrophilic addition reactions, pointing out the similarity and the difference of the two systems. Intermediacy of an episulfonium ion was concluded in the additions of sulfenyl halides to both classes of compounds.[3-9]

We have recently found that 2,4-dinitrobenzenesulfenyl chloride (1) adds exclusively to the terminal double bond of phenylallene, whose nodal plane is orthogonal to that of the phenyl ring.[10] This aroused our interest in the problem as to which of the two acetylenic π bonds of phenylacetylene (parallel or orthogonal to the phenyl pπ orbitals) is the more amenable to the electrophilic attack of sulfur. The phenyl group could stabilize the unsaturated episulfonium ion either by conjugation with the intact double bond as in 2 or by interaction with the ring as in 3.

Hassner, *et al.*,[11] have recently suggested the intermediacy of iodonium ion of type 2 in the ionic addition of IN_3 to 1-phenylpropyne to explain the orientation. Their claim was later criticized in a review.[12] Nevertheless, the possible intermediacy of the onium ion of type 2 will be well conceivable in some cases, because the intermediate 2 is considered to be more stable owing to the conjugation.



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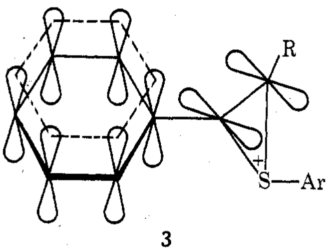
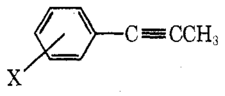
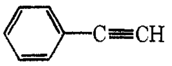


3

In the present paper, we will report the results of the kinetic studies on the electrophilic addition of 1 to 1-phenylpropyne (4) and its related compounds 5–7. The secondary isotope effects on the reaction rate of 5 were also measured with use of phenylacetylene-β-d (5β), in comparison with those observed for the styrene system. The kinetic information obtained here has provided a useful basis to determine which form of intermediate, 2 or 3, is the more closely related to the transition state of the reaction.



4, X = H
4a, X = p-OCH$_3$
b, X = p-CH$_3$
c, X = p-Cl
d, X = m-Cl



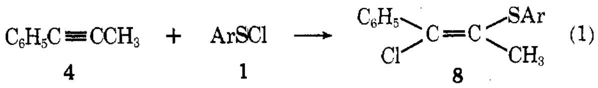
5

n-$C_4H_9C\equiv CCH_3$
6

n-$C_4H_9C\equiv CH$
7

Results

The reaction of 1 with 4 in acetic acid yielded a 1:1 adduct, 1-phenyl-*trans*-1-chloro-2-(2,4-dinitrophenylthio)-propene (8), in >98% yield. Structure of the product was determined by nmr spectroscopy.[13] The addition was specifically anti and Markovnikov-type.

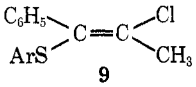


$$C_6H_5C\equiv CCH_3 + ArSCl \longrightarrow \begin{matrix} C_6H_5 & & SAr \\ & C{=}C & \\ Cl & & CH_3 \end{matrix} \qquad (1)$$

4 1 8

Ar = 2,4-dinitrophenyl

In chloroform as solvent, the same reaction gave 6% of the anti-Markovnikov-type isomer (9) along with 8.[13] The variation in the yield of 8 relative to 9 is consistent with the general trend of solvent effects.[14]



9

The rates of additions of 1 to 4 and other acetylenic derivatives were measured in glacial acetic acid at 30–55° by following the disappearance of 1 with use of the titration method.[15] The reaction was second order, *i.e.*, first order in each reactant, as observed previously.[15] The initial concentrations of reactants were varied in different rate runs, but no indication of deviation from the simple second-order kinetics was observed.

The second-order rate constants, k_2, obtained are summarized in Table I. The enthalpies and entropies of activation, ΔH^* and ΔS^*, were calculated in a usual manner (by plots of $\ln k/T$ *vs.* $1/T$) and are given in Table I.

Secondary kinetic isotope effects were evaluated from the rate measurements on 5β. Isotope effects were also measured with styrene (10), styrene-α-d (10α), and styrene-β,β-d_2 (10β) for the sake of comparison.

The results are summarized in Table II.

Discussion

Secondary Isotope Effect. As is given in Table II, small inverse isotope effects were observed for both 5 and 10. The effects may be ascribed mainly to the partial hybridization change sp → sp^2 (or sp^2 → sp^3) of the carbon atom attached to the hydrogen in question.[16] This would best be rationalized by assuming the transition state resembling an episulfonium ion intermediate.

In the acid-catalyzed hydration of 5, whose transition state resembles an open carbonium ion, $k_H/k_D = 1.11$ was observed and the prevalent contribution of hyperconjugative effect over rehybridization effect was considered.[17] The inverse effects observed in the present reaction indicate that the hyperconjugative effect is only a minor or negligible contribution, in accord with the assumption of episulfonium type activated complex of rather small electron deficiency at the carbon atom.

As for styrene, both α- and β-deuteration exerted rate enhancement of the same magnitude ($k_H/k_D = 0.95$) by the single deuteron. The effect of α-deuteration has recently been examined by the competitive measurements, giving the results in complete agreement with ours.[18]

Table I
Rate Constants and Activation Parameters for the Reaction of 1 with Acetylenes in Acetic Acid

Acetylene	Temp, °C	$10^4 k_2$, M^{-1} sec^{-1}	ΔH^*,[a] kcal/mol	ΔS^*,[a] eu
4	30.0	0.811	16.8 ± 0.8	−22.3 ± 2.5
	40.0	1.90		
	50.0	4.83		
4a	40.0	14.4		
4b	40.0	4.03		
4c	40.0	0.760		
4d	40.0	0.431		
5	45.0	0.309	23.7 ± 1.3[b]	−3.3 ± 4.1[b]
6	35.0	13.7	15.6 ± 1.2	−21.4 ± 4.0
	45.0	31.4		
7	34.9	0.490	19.8 ± 0.8	−14.6 ± 2.5
	40.1	0.941		
	45.0	1.57		
	55.0	3.85		

[a] Errors are given by standard deviations. [b] Data taken from ref 15.

Table II
Secondary Kinetic Isotope Effects in the Reaction of 1 with 5 and 10 in Acetic Acid

Substrate	Temp, °C	$10^4 k_2$, M^{-1} sec^{-1}	k_H/k_D
5	45.0	0.309 ± 0.018	
5β	45.0	0.336 ± 0.011	0.92 ± 0.06
10	25.0	72.4 ± 0.09	
10α	25.0	7.64 ± 0.28	0.95 ± 0.04[a]
10β	25.0	7.96 ± 0.19	0.91 ± 0.03 (0.95 per D)

[a] The value of 0.95 ± 0.01 is reported by the competitive measurements at 40°.[18]

These results indicate confirmatively the involvement of an episulfonium type activated complex in styrene sulfenylation, in accord with the previous conclusion.[4-10] Furthermore, the identical k_H/k_D values observed for α- and β-deuteration appear to reflect the symmetrical nature of the activated complex; similar degrees of bond formation of S with α-C and β-C are observed.

General Mechanism. The mechanism involving the rate-determining formation of episulfonium ion has already been established for the sulfenyl chloride addition to olefins and acetylenes.[3-9,13] This is further confirmed above by the results of secondary isotope effects. Furthermore, the linear correlation between ΔH^* and ΔS^* obtained for the reaction in acetic acid was found for a wide variety of substrates, including both olefins and acetylenes (Figure 1). This kind of isokinetic relationship is considered to be a criterion of the mechanistic uniformity of the reactions under study.[19] The isokinetic temperature was found to be *ca.* 400°K. Although the significance of the relationship is somewhat controversial,[20] we would like to point out that the correlation shown in Figure 1 extends over a wide range of ΔH^* and ΔS^* values and appears not to be trivial.

Effects of the β-Methyl Substitution. Summarized in Table III are the kinetic data [$k(CH_3)/k(H)$] for the effects of β-methyl substitution on the reactivities of various electrophiles toward styrene and phenylacetylene. Although the effects of the cis and trans methyl groups differ somewhat in olefinic compounds, only the latter effects are listed here for the sake of simplicity.

As can be seen in Table III, the value of $k(CH_3)/k(H)$ varies with the nature of electrophile as well as substrate. The additions of ArSCl and Br$_2$ to styrene are slightly accelerated by the β-methyl group, while the acid-catalyzed hydration is considerably retarded. The rate retardation

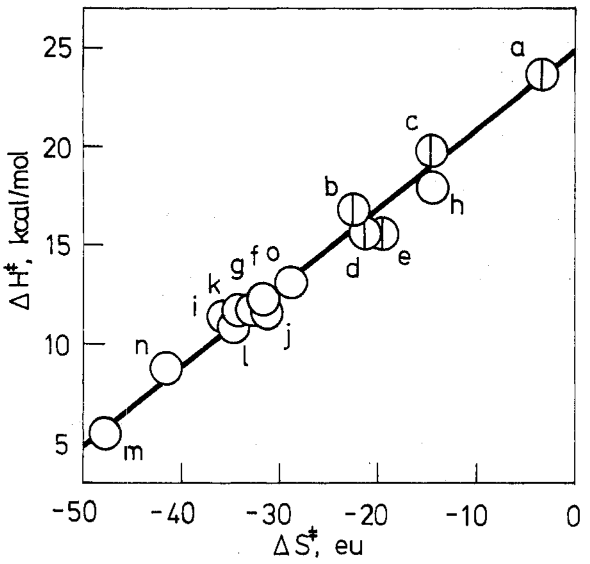


Figure 1. Correlation of ΔH^* and ΔS^* for the reaction of 1 with acetylenes (⦶) and olefins (○) in acetic acid: a, 5;[15] b, 4; c, 7; d, 6; e, 3-hexyne;[15] f, 10;[25] g and h, *trans*- and *cis*-phenylpropenes;[24] i, allylbenzene;[24] j, cyclohexene [D. R. Hogg and N. Kharasch, *J. Amer. Chem. Soc.*, 78, 2728 (1956)]; k, 1-hexene;[24] l and m, *trans*- and *cis*-2-heptenes;[24] n and o, *trans*- and *cis*-stilbenes [N. R. Slobodkin and N. Kharasch, *J. Amer. Chem. Soc.*, 82, 5837 (1960)].

Table III
Effects of the β-Methyl Substitution on the Reactivities of Styrene and Phenylacetylene in Some Electrophilic Addition Reactions

Reaction	Electrophile	$k(CH_3)/k(H)$	
		$C_6H_5CH{=}CHR$[a]	$C_6H_5C{\equiv}CR$
Hydration	H_3O^+	0.05[b]	0.033[c]
Cationic polymerization	C^+	0.2–0.7[d]	
Bromination	Br^+	1.10[e]	0.57[f]
Sulfenylation	ArS^+	1.83[g]	11

[a] The trans isomer for 1-phenylpropene. [b] T. Okuyama and T. Fueno, unpublished results. [c] Reference 1. [d] A. Mizote, T. Higashimura, and S. Okamura, *J. Polym. Sci., Part A-1*, **6**, 1825 (1968). [e] J. H. Rolston and K. Yates, *J. Amer. Chem. Soc.*, **91**, 1469 (1969). [f] Reference 23. [g] Reference 24.

in the latter reaction can be interpreted in terms of the decreasing hyperconjugative stabilization of the intermediate carbonium ion.[21] The acceleration in the former was taken as evidence for the formation of cyclic onium ion intermediate.[22]

The situation is somewhat different in the acetylenic compounds. The β-methyl substitution on 5 diminishes the rate of bromination, in contrast to the results for the case of styrene. This was accounted for by assuming a transition state resembling a benzylic vinyl cation, an assumption which is consistent with a large negative ρ value of −5.17 observed for ring-substituted derivatives of 5.[23] Thus it seems that a cyclic halonium intermediate is less important in acetylenic systems than in the corresponding olefinic analogs. By contrast, the sulfenyl chloride addition to 5 is markedly accelerated by the β-methyl substitution. The magnitude of this rate enhancement $k(CH_3)/k(H) = 11$ (at 45°) is definitely greater than that of styrene and as large as that of alkene by the cis methyl group $[k(CH_3)/k(H) \sim 14]$.[24]

The nature of the transition state in the reaction of ArSCl with 5 thus appears to be more closely related to that for alkene than for styrene. The considerably large rate enhancement $[k(CH_3)/k(H) = 20$ at 45°] in alkylacetylenes (6 relative to 7) is interesting to note in this connection. All these results can best be understood if we assume that the addition of sulfenyl chloride to phenylacetylenes takes place on the "orthogonal" π bond, thus forming the cyclic intermediate ions of type 2.

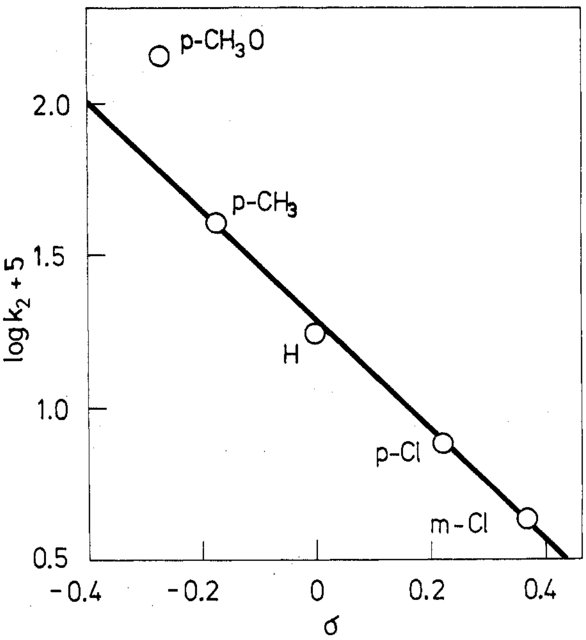
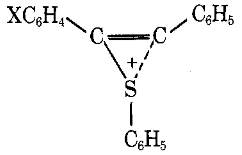


Figure 2. The Hammett plots for the reaction of 1 with 4 in acetic acid at 40.0°.

Effects of Ring Substituents. Plots of log k_2 of several ring-substituted compounds 4 against Hammett's σ values show a fairly good linear relationship except for the p-OCH_3 derivative (Figure 2). The reaction constant ρ was −1.46 at 40°. The ρ value is significantly smaller in magnitude than the values for olefinic analogs, 1-phenylpropenes (ρ = −2.64),[24] and styrenes (ρ = −2.41),[25] and is closer to those for nonconjugated allylbenzenes (ρ = −0.91)[24] and phenylallenes (ρ = −2.0).[10,24] The same reaction of tolane derivatives was reported to have a ρ value of −1.3 to −1.8 in less polar solvents.[26] These results imply that, in the case of 5, the electronic delocalization to the positive sulfur is occurring from the π bond which is orthogonal to the phenyl group. Should the reaction take place at the other π bond in conjugation with the phenyl group, the ρ value would be closer in magnitude to that of the styrene system.

The above-mentioned difference in ρ cannot be attributed solely to the difference in the types of the reacting bonds, an sp^2–sp^2 bond in olefin and an sp–sp bond in acetylene. For instance, the acid-catalyzed hydration was found to have a ρ value even greater in magnitude for phenylacetylenes (−3.8)[1] than for styrene derivatives (−3.2).[2] An alternative reasoning that the electrophilic sulfur adds to the π bond orthogonal to the phenyl group of phenylacetylene seems to be more plausible. This in turn implies that the transition state should structurally resemble 2. The upward deviation of the p-OCH_3 point from the linearity (Figure 2) is probably attributable to a partial contribution of the type 3 interaction to the transition state because of the strong electron-donating ability of the anisyl group.

Modena and Tonellato[27] have recently reported that an unsymmetrical episulfonium ion like 11 is an intermediate in the SN1 solvolysis of 1,2-diaryl-2-arylthiovinyl 2,4,6-trinitrobenzenesulfonates. The effects of ring substituents of the 2-aryl group on the rates were found to obey the Hammett relationship with a ρ value of −1.25. The substituent effect observed is probably the one characteristic of indirect conjugation between the delocalized positive charge and the 2-aryl group. Our ρ value (-1.46) observed for the sulfenyl chloride addition to **4** agrees closely with theirs (-1.25) for the solvolysis. This would lend further support to the view that the reaction of our concern proceeds through the episulfonium ion of type **2**.



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In conclusion, the "orthogonal π bond" of **4**, which is essentially an isolated unsaturated bond, should be considered to constitute the reaction center toward sulfenyl ions.

Experimental Section

Materials. Glacial acetic acid was refluxed over phosphorus pentoxide overnight and distilled. 2,4-Dinitrobenzenesulfenyl chloride (**1**) was prepared by the method of Kharasch and Langford.[28]

Phenylacetylene (**5**), 2-heptyne (**6**), 1-hexyne (**7**), and styrene (**10**) were obtained commercially (Nakarai Chemicals). They were purified by fractional distillation and purities were checked by vpc analysis.

1-Phenylpropyne (**4**) and its ring-substituted derivatives were prepared according to the literature.[29] **4** had bp 68° (11 mm) [lit.[29] bp 113° (84 mm)]; nmr (CCl_4) δ 2.01 (3 H, s), ~7.25 (5 H, m); ir (thin film) 2280 cm^{-1} (C≡C). 1-*p*-Methoxyphenylpropyne (**4a**) had bp 101° (7 mm); nmr (CCl_4) δ 1.95 (3 H, s), 3.70 (3 H, s), 6.5–7.4 (4 H, m); ir (thin film) 2240 cm^{-1} (C≡C). 1-*p*-Methylphenylpropyne (**4b**) had bp 75° (12 mm); nmr (CCl_4) δ 2.00 (3 H, s), 2.3 (3 H, s), ~7.1 (4 H, m); ir (thin film) 2250 cm^{-1} (C≡C). 1-*p*-Chlorophenylpropyne (**4c**) had bp 86° (14 mm); nmr (CCl_4) δ 2.0 (3 H, s), 7.2 (4 H, s); ir (thin film) 2270 cm^{-1} (C≡C). 1-*m*-Chlorophenylpropyne (**4d**) had bp 89.5° (11 mm); nmr (CCl_4) δ 2.0 (3 H, s), ~7.3 (4 H, m); ir (thin film) 2240 cm^{-1} (C≡C).

Phenylacetylene-*β*-*d* (**5*β***) was prepared by the repetitive isotope exchange (four times) in NaOD-D_2O. Nmr analysis showed the isotopic purity to be ~99%, bp 75–76° (89 mm), mass spectrum molecular ion at *m*/*e* 103.

Styrene-*α*-*d* (**10*α***) and -*β*,*β*-d_2 (**10*β***) were prepared by the dehydration of appropriate deuterio alcohols.[30] *α*-Phenylethyl alcohol-*α*-*d* was obtained by the reduction of acetophenone with lithium aluminum deuteride (Merck) in anhydrous ether. *α*-Phenylethyl-*β*-d_3 alcohol was synthesized by the reduction of acetophenone-*α*-d_3, which was obtained by the repetitive isotope exchange (three times) in NaOD-D_2O. The nmr spectra of **10*α*** and **10*β*** were those expected and showed an isotopic purity of >99%: **10*α***, bp 68–70° (66 mm), mass spectrum molecular ion at *m*/*e* 105; **10*β***, bp 70–72° (71 mm), mass spectrum molecular ion at *m*/*e* 106.

Reaction of 1 and 4. To 1.876 g (8 mmol) of **1** in 100 ml of acetic acid, 0.928 g (8 mmol) of **4** was added at room temperature. The reaction mixture was allowed to stand for 2 days at 40°. The mixture was then poured into 500 g of ice-water. The yellow oil which first separated out was solidified while being washed with water to remove acetic acid. The crude dry product (2.38 g, 85% yield as a 1:1 adduct, mp 153°) was recrystallized from 95% ethanol, yielding yellow needles, mp 160.5°. *Anal.* Calcd for $C_{15}H_{11}O_4N_2ClS$: C, 51.33; H, 3.14; N, 7.99; Cl, 10.12; S, 9.14. Found: C, 51.49; H, 3.38; N, 8.03; Cl, 10.13; S, 9.07. Nmr ($CDCl_3$): δ 2.33 (3 H, s), 7.3 (5 H, s), 7.6 (1 H, d), 8.4 (1 H, q), 9.6 (1 H, d). The melting point and nmr spectrum of the product coincide with those reported for 1-phenyl-*trans*-1-chloro-2-(2,4-dinitrophenylthio)propene (**8**).[13]

Kinetic Measurements. The reaction rates were measured by the titration method according to Kharasch, *et al.*[15,25] The measurements were carried out at least three times. The second-order rate constants were calculated by using the usual integrated second-order rate equation.[31]

Acknowledgment. We wish to thank Mr. Yoshiharu Kawashima for his able technical assistance.

Registry No. 1, 528-76-7; **4,** 673-32-5; **4a,** 2749-94-2; **4b,** 2749-93-1; **4c,** 2809-65-6; **4d,** 43136-84-1; **5,** 536-74-3; **6,** 1119-65-9; **7,** 628-71-7; **8,** 20047-60-3; **10,** 100-42-5.

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