Fraction II was redistilled and gave a colorless liquid, b.p. 53–55° (3.7 mm.), main fraction. Upon standing in the light for 2 days, this colorless oil took on a pinkish tinge which deepened to a pinkish red. The infrared spectrum of the colorless oil was free of any absorption between 2600 and 2000 cm.$^{-1}$ while the reddish material had a strong band at 2042 cm.$^{-1}$; 1-phenyldiazoethane absorbs strongly at 2040 cm.$^{-1}$.

Thermal Decomposition of 1-Phenyldiazoethane.—To 75 ml. of refluxing benzene was added 100 ml. of a hexane solution of 1-phenyldiazoethane [prepared from 30 g. (0.22 mole) of acetophenone hydrazone and 60 g. (0.30 mole) of mercuric oxide[3]]. After 12 hr., the nitrogen evolution had stopped and the color of the solution had changed from deep red to yellow, indicating that complete decomposition had occurred. The yellow solution was dried over anhydrous sodium sulfate and the solvent was evaporated *in vacuo;* acetophenone azine, m.p. 119–120°, m.m.p. 119–121°, was collected with the aid of small portions of hexane. More azine was obtained from the successive filtrates until almost no color remained in the filtrate. Evaporation of the last filtrate gave trace amounts of acetophenone (identified by comparison of its infrared spectrum with that of an authentic sample) and benzoic acid; mixture melting point with a commercial sample was 120–122°.

Photolysis of 1-Phenyldiazoethane.—A solution of 1-phenyldiazoethane prepared from 47.4 g. (0.35 mole) of acetophenone hydrazone and 112 g. (0.52 mole) of mercuric oxide[3] in 330 ml. of hexane was photolyzed at 0–5° by means of a Hanovia high pressure mercury immersion lamp (200 watts). The progress of the reaction was followed by the evolution of nitrogen and the disappearance of the red color. When the red color had changed completely to canary yellow, the irradiation was stopped and the precipitated azine was collected. Further concentration of the resulting filtrates gave more acetophenone azine, m.p. 120–121°. A total of about 17 g. of azine was collected. The yellowish residue was taken up in 100 ml. of hexane and passed through a column of alumina; elution with hexane and benzene gave, after the removal of the solvents *in vacuo*, an almost colorless oil ($\sim$5 ml.). Distillation of this oil *in vacuo* gave a colorless liquid ($\sim$1.5 ml.), b.p. 80–81° (0.1 mm.). This clear oily liquid on standing crystallized almost completely as tiny needles, m.p. 105–106°. The n.m.r. of this solid in carbon tetrachloride solution had two sharp singlets at τ 2.71 (aromatic protons) and 8.03 (methyl protons). The spectrum was consistent with that expected for *trans*-α,α'-dimethylstilbene, m.p. 106–107°. The colorless filtrate was too small to be characterized conclusively. Its infrared spectrum had strong absorptions at 3058 and 1027 cm.$^{-1}$ (cyclopropane) and was almost identical with that of the product prepared by the addition of phenyldiazomethane to α-methylstyrene, followed by thermal decomposition of the intermediate 1-pyrazoline; the expected 1,2-diphenyl-1-methylcyclopropane was obtained as a colorless oil, b.p. 113–114° at 1 mm., but was contaminated by some olefin and the isomeric cyclopropane (*dl-cis* and *-trans* are possible here). From the Dry Ice trap used during the distillation was obtained a colorless liquid having a strong odor of styrene, positively identified by its infrared, ultraviolet, and n.m.r. spectra. Bromination of this liquid gave styrene dibromide, m.p. 74–75°. The residue from the distillation was examined and only small amounts of acetophenone azine and polymeric material were present. No 2,3-diphenylbutane could be detected.

Acknowledgment.—We gratefully wish to acknowledge the support of this work by the National Science Foundation, Grant No. NSF G-17448 and the technical assistance of Mr. Ned Weinshenker.

Derivatives of Sulfenic Acids. XLIV. The Kinetics of the Reaction of 2,4-Dinitrobenzenesulfenyl Chloride with Phenylacetylene and 3-Hexyne[1]

NORMAN KHARASCH AND C. N. YIANNIOS

The Department of Chemistry, University of Southern California, University Park, Los Angeles, California

Received December 5, 1963

The rates of additions of 2,4-dinitrobenzenesulfenyl chloride (I) to phenylacetylene and 3-hexyne, in dry acetic acid at 45° and 55°, follow second-order kinetics, $-d(\text{ArSCl})/dt = k[\text{ArSCl}][\text{RC}{\equiv}\text{CR}']$. Addition of I to phenylacetylene is about 1/100th as fast as to styrene, while the addition to 3-hexyne is about 1/10th as fast as to cyclohexene. The addition of I to diphenylacetylene is also slower than are those of I to the stilbenes. Values for the activation energies and entropies of activation for the reactions of I with the acetylenes are given and compared with recorded values of these parameters for olefin additions. The rates of reactions of I with alkynes and alkenes are compared with available comparable data for bromine additions, and the need for further study of selected examples is noted. The structure of the adduct of I to phenylacetylene was shown to be $C_6H_5C(Cl){=}CH(SAr)$, where Ar = 2,4-dinitrophenyl, with a *trans* disposition of ArS and Cl groups assumed.

Earlier studies from this laboratory concerned additions of 2,4-dinitrobenzenesulfenyl chloride (I) to styrene,[2] *p*-substituted styrenes,[2a] and certain related compounds, including some symmetrical alkynes.[3–5] Studies of the reactions of I with cyclohexene were described by Hogg and Kharasch,[6] with *cis*- and *trans*-2-butene by Kharasch and Havlik,[7,8] with the *cis*- and *trans*-stilbenes by Slobodkin and Kharasch,[9] and with olefin oxides by Peters and Kharasch.[10] Related reactions with several olefins[11,12] and some bicyclic olefins[11–13] have also been examined.

For several additions of I to olefins, the kinetics of the reactions were investigated and the mechanism of addition to the carbon–carbon double bond was discussed.[2,6,9] Interest in the corresponding additions to the carbon–carbon triple bond prompted the present study. Phenylacetylene was selected because kinetic data are available for quantitative comparison with styrene, the corresponding olefin. Reaction rates for the addition of I to 3-hexyne were also determined, although quantitative data for the reaction with the corresponding olefin, 3-hexene, are not available.

---

(1) This study was supported by grants from the National Science Foundation and the Office of Army Research (Durham).

(2) (a) W. L. Orr and N. Kharasch, *J. Am. Chem. Soc.*, **75**, 6030 (1953); (b) **78**, 1201 (1956).

(3) N. Kharasch and S. J. Assony, *ibid.*, **75**, 1081 (1953).

(4) N. Kharasch and S. J. Assony, *ibid.*, **77**, 3390 (1955).

(5) S. J. Assony and N. Kharasch, *Chem. Ind.* (London), 1388 (1954).

(6) D. R. Hogg and N. Kharasch, *J. Am. Chem. Soc.*, **78**, 2728 (1956); *cf.* D. S. Campbell and D. R. Hogg, *J. Chem. Soc.* (submitted).

(7) N. Kharasch and A. J. Havlik, *J. Am. Chem. Soc.*, **75**, 3734 (1953).

(8) A. J. Havlik and N. Kharasch, *ibid.*, **78**, 1207 (1956).

(9) N. R. Slobodkin and N. Kharasch, *ibid.*, **82**, 5837 (1960).

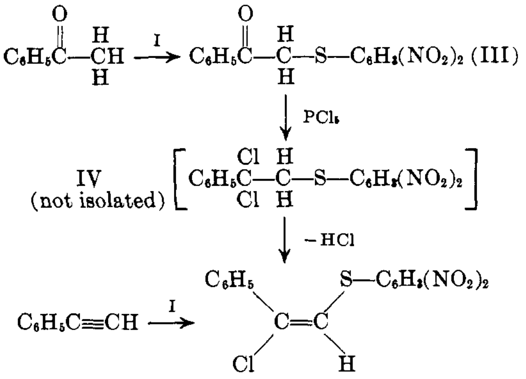
(10) D. Peters and N. Kharasch, *J. Org. Chem.*, **21**, 590 (1956).

(11) N. Kharasch and C. M. Buess, *J. Am. Chem. Soc.*, **71**, 2724 (1949).

(12) E. W. Malmberg and F. G. H. Lee, paper presented before the Organic Division, at the 127th National Meeting of the American Chemical Society, Minneapolis, Minn., April, 1955.

(13) H. Kwart and R. K. Miller, *J. Am. Chem. Soc.*, **78**, 5682 (1956).

The reaction of I with phenylacetylene in acetic acid led to a high yield of 1:1 adduct which was shown to be 2-chloro-2-phenylethenyl 2′,4′-dinitrophenyl sulfide (II), $C_6H_5(Cl)C{=}C(H){-}S{-}C_6H_3(NO_2)_2$. The question as to whether the chlorine and ArS moieties are *cis* or *trans* in II has not been fully resolved. However, in view of the *trans* additions of I to olefins and the ionic nature of the reactions, the *trans* configuration is suggested. The basis for assigning the attachment of chlorine in II was the reaction of III with phosphorus pentachloride, which gave II as the major product.[14]



The product of the reaction of I with 3-hexyne has been reported previously as 4-chloro-3-(2′,4′-dinitrophenylthio)-3-hexene, isolated in 93% yield.[3] This adduct is also tentatively assumed to have the *trans* configuration for the ArS and Cl groups.

Kinetic Data.—The rates of addition of I to phenylacetylene and 3-hexyne were determined in dry acetic acid solution. The reactions were followed by measuring the rates of disappearance of the sulfenyl chloride (I) by the methods previously described.[1,15]

The reaction with phenylacetylene was inconveniently slow at 35 and 45°, but satisfactory rate measurements were obtained at the latter temperature and at 55°. The reaction with 3-hexyne was considerably faster and the rates were measured conveniently at 35 and 45°. Data for typical rate runs are given in Tables I and II and are shown in Fig. 1 and 2, plotted as second-order reactions—first order in each reactant. Concentrations were varied in the different rate runs and, although only a limited number of runs were made, there was no indication of deviations from simple second-order kinetics. The calculated second-order rate constants for the reactions of I with the acetylenes are therefore directly comparable to the second-order rate constants previously reported for the reactions of I with olefins.

The rate constants for the reactions of I with phenylacetylene and 3-hexyne are summarized in Table III, together with the derived values for the energy and entropy of activation.

Besides the reactions already mentioned, the rate of reaction of I with diphenylacetylene was explored in a single experiment. In acetic acid at 45°, the reaction was found to be extremely slow and the reaction was followed to only 10% completion. The rate appears

Table I

Reaction of 2,4-Dinitrobenzenesulfenyl Chloride with Phenylacetylene in Acetic Acid at 55.00 ± 0.02°

Time, sec.	Concn. of ArSCl, moles/l. $(b - x)$	Concn. of acetylene, moles/l. $(a - x)$	$\log \frac{b(a-x)}{a(b-x)}$	k, (moles/l.$^{-1}$) sec.$^{-1}$ $\times 10^5$
0	0.03985	0.20000		
6,900	0.03522	0.19537	0.04346	9.06
11,100	0.32151	0.19266	0.07217	9.35
15,000	0.03070	0.19085	0.09295	8.91
17,160	0.02980	0.18995	0.10381	8.70
21,000	0.02739	0.18754	0.13490	9.24
25,200	0.02619	0.18634	0.15157	8.65
			Mean k =	8.98

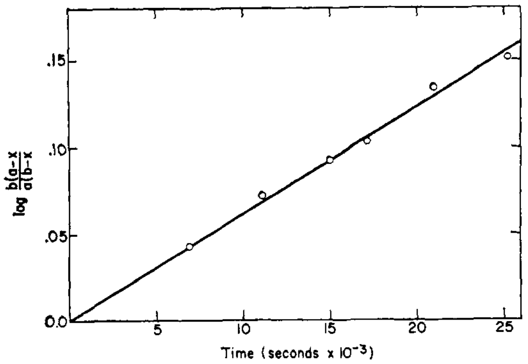


Fig. 1.—Second-order plot for the reaction of phenylacetylene with 2,4-dinitrobenzenesulfenyl chloride at 55 ± 0.02°.

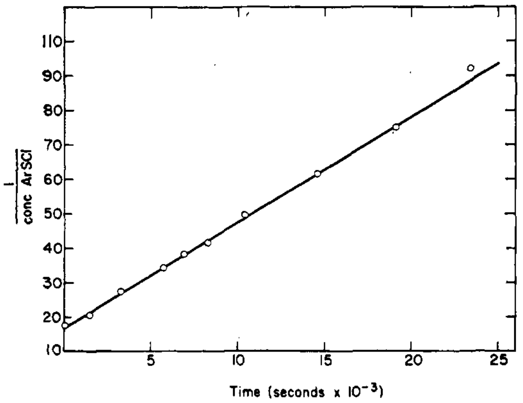


Fig. 2.—Second-order plot for the reaction of 3-hexyne with 2,4-dinitrobenzenesulfenyl chloride at 45 ± 0.02°.

Table II

Reaction of 2,4-Dinitrobenzenesulfenyl Chloride with 3-Hexyne in Acetic Acid at 45.00 ± 0.02°

Time, sec.	Concn. of ArSCl,[a] moles/l. $(a - x)$	$1/(a - x)$	k, (moles/l.)$^{-1}$ sec.$^{-1}$ $\times 10^3$
0	0.05690	17.57	
1,440	0.04876	20.51	(2.04)[b]
3,240	0.03642	27.46	3.05
5,700	0.02920	34.25	2.93
6,900	0.02619	38.19	2.99
8,280	0.02408	41.53	2.89
10,380	0.02017	49.59	3.08
14,700	0.01625	61.52	2.97
19,080	0.01330	75.17	3.02
23,400	0.01080	92.29	(3.19)[b]
		Mean k =	2.99

[a] Both reactants were at equal initial concentrations. [b] Values in parentheses were neglected in calculating the mean value of k.

---

(14) A small amount of an isomer of II, presumably the *cis* isomer, was also isolated from the reaction of III with phosphorus pentachloride (see Experimental).

(15) N. Kharasch and M. M. Wald, *Anal. Chem.*, **27**, 996 (1955).

TABLE III

RATE CONSTANTS AND ARRHENIUS PARAMETERS FOR THE REACTION OF 2,4-DINITROBENZENESULFENYL CHLORIDE WITH ACETYLENES IN ACETIC ACID

Acetylene	Temp., °C.	k, (moles/l.)$^{-1}$ sec.$^{-1}$	E_a, kcal./mole[a]	log A	ΔS^*, cal./deg.[b]
Phenylacetylene	45.00 ± 0.02	2.55×10^{-5}			
		2.79×10^{-5}			
		Av. (2.67×10^{-5})			
	55.00 ± 0.02	8.98×10^{-5}			
		8.25×10^{-5}			
		Av. (8.61×10^{-5})	24.3 ± 1.3	12.12	−3.3 ± 4.1
3-Hexyne	35.00 ± 0.02	1.27×10^{-3}			
		1.32×10^{-3}			
		Av. (1.29×10^{-3})			
	45.00 ± 0.02	2.89×10^{-3}			
		2.99×10^{-3}			
		Av. (2.94×10^{-3})	16.1 ± 0.7	8.52	−19.7 ± 2.2

[a] Calculated from the Arrhenius equation in the form $k = Ae^{-E_a/RT}$. [b] Calculated from the value of A by the equation $A = (kT/h)e^{\Delta S^*/R}$.

to be about one-half that of phenylacetylene under comparable conditions. The estimated rate constant was 1.6×10^{-5} (moles/l.)$^{-1}$ × sec.$^{-1}$, at 45°.

Experimental

Materials and Methods.—Dry acetic acid and 2,4-dinitrobenzenesulfenyl chloride (I) were prepared by techniques previously reported.[1] Phenylacetylene (Eastman Organic Chemicals) was redistilled, 47–48° at 24 mm., using a few drops of octylic alcohol to prevent foaming. The 3-hexyne (Farchan Research Laboratories) was redistilled at atmospheric pressure. The center cut, distilling at 80–80.5°, was used. Diphenylacetylene was prepared in pure form by the method in "Organic Syntheses."[16]

Rate runs were made by essentially the same procedures and techniques as used by Orr and Kharasch.[1,2] Stock solutions of sulfenyl chloride and unsaturated compounds were prepared by dissolving weighed amounts of freshly purified materials in the desired volume of dry acetic acid at the temperature of each run. The second-order rate constants were calculated in the usual manner, as described previously.[1,2]

Adduct of I and Phenylacetylene. 2-Chloro-2-phenylvinyl-2′,4′-dinitrophenyl Sulfide (II).—To 1.0 g. (0.0042 mole) of 2,4-dinitrobenzenesulfenyl chloride in 20 ml. of acetic acid, 1.6 g. (0.0156 mole) of phenylacetylene was added. The reaction mixture was allowed to stand for 2 days at room temperature (28°) until the iodine-starch test was negative. The mixture was then poured into 100 g. of ice–water. The yellow oil which first separated solidified while being washed with water to remove acetic acid. The crude dry product (1.13 g., 79% yield, m.p. 119–124°) was recrystallized from 95% ethanol, yielding a yellow solid, m.p. 124–130°. Further purification was achieved by chromatography on a 20-cm. column of alumina using Skellysolve A–benzene mixture, 1:1 by volume, for development and elution. The residue from the eluent was recrystallized from 95% ethanol yielding yellow needles, m.p. 138.7–141°. Further recrystallizations gave a constant melting point of 139–141°.

Anal. Calcd. for $C_{14}H_9ClN_2O_4S$: C, 49.94; H, 2.69; Cl, 10.54; N, 8.3; S, 9.5. Found: C, 50.27; H, 2.77; Cl, 10.79.

A similar experiment carried out at 80° was complete in 3 hr. and gave a 91% yield of crude product.

2,4-Dinitrophenyl Phenacyl Sulfide (III).—Ten grams of I was dissolved in 130 ml. of glacial acetic acid and an excess of acetophenone (10 g.) was added. The mixture was heated at 82–85° until the iodine–starch test for the sulfenyl chloride was negative (5 hr.). The major portion of the product precipitated upon cooling and was removed by filtration. A small additional amount was precipitated by dilution of the filtrate with water. The total yield of crude product was 10 g., 75% yield. Recrystallization from acetic acid gave 9 g. of product, m.p. 170–170.5°, lit.[17] m.p. 168°

Reaction of 2,4-Dinitrophenyl Phenacyl Sulfide with Phosphorus Pentachloride.—Phosphorus pentachloride, 4.0 g. (0.02 mole), was dissolved in 25 ml. of carbon tetrachloride by heating in a 100-ml. three-necked flask equipped with a thermometer, condenser, and mechanical stirrer. A solution of 3.0 g. (0.0094 mole) of 2,4-dinitrophenyl phenacyl sulfide in 20 ml. of ethylene chloride was added, and the mixture refluxed for 24 hr. The solution was transferred to a separatory funnel, washed twice with water, and dried over anhydrous sodium sulfate; the solvent was removed by aspiration. The yellow residue (2.78 g., m.p. 129–144°) was dissolved in Skellysolve A–benzene (1:1 by volume) and chromatographed through a 20-cm. alumina column. The yellow material was eluted with the same solvent mixture. The residue from the eluent, upon recrystallization from methyl alcohol, deposited a mixture of both yellow plates and needles. The plates and needles were separated mechanically, with the aid of a microscope. Melting points for the needles and plates, respectively, were 122–130° and 157–158°. A second chromatographic separation of this mixture on a 45-cm. column and using a 3:1 mixture of Skellysolve A–benzene for elution resolved the mixture into two bands, a pale yellow band, followed by a deep yellow band. The material from the pale yellow band was recrystallized from 95% ethanol to obtain light yellow needles with a constant melting point of 141.5–142°. Chlorine analysis, melting point, and the infrared spectrum established that this product was identical with the adduct II obtained from the reaction of 2,4-dinitrobenzenesulfenyl chloride with phenylacetylene.

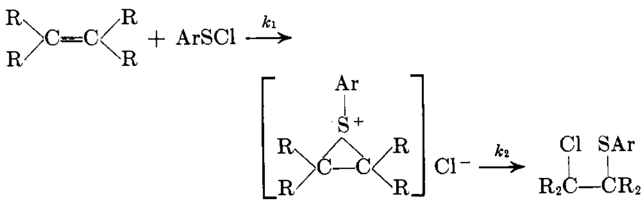
Anal. Calcd. for $C_{14}H_9ClN_2O_4S$: Cl, 10.54. Found: Cl, 11.07.

The product from the deep yellow band reached a constant melting point of 154.5–156° after several recrystallizations from ethanol. Chlorine analysis and the infrared spectrum suggest that this product is an isomer of II, presumably the *cis* isomer.

Anal. Calcd. for $C_{14}H_9ClN_2O_4S$: Cl, 10.54. Found: Cl, 10.47.

Discussion

There is now considerable evidence which indicates that addition of 2,4-dinitrobenzenesulfenyl chloride to olefins in acetic acid solution proceeds by a polar mechanism, represented as a two-step process in which the electrophilic attack on the double bond is believed to be the rate-determining step.[1,2]



---

(16) L. I. Smith and M. M. Falkof, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 350; *cf. Org. Syn.*, **34**, 42 (1954).

(17) N. Kharasch, H. L. Wehrmeister, and H. Tigerman, *J. Am. Chem. Soc.*, **69**, 1612 (1947).

The direction of addition to unsymmetrical olefins, the demonstration of stereospecific addition, and the effect of substituents on the reaction velocities are consistent with this mechanism, which is entirely analogous to the generally accepted mechanism for bromine addition to olefins in polar solvents.[18]

While the reactions at ethylenic and acetylenic bonds are formally analogous, it has long been suggested that the unsaturation electrons of acetylenes are more tightly held then are those of corresponding alkenes.[19]

Hence the rates of electrophilic attack by ArSCl, or Br_2, may be expected to be slower than similar reactions with olefins. While it is somewhat surprising that this phenomenon has not been more fully studied, both the present results for the additions of I to acetylenes and the earlier data of Robertson, *et al.*,[20] for rates of bromine addition, in acetic acid, confirm the lower reaction rates for the alkynes.

Rate data for the reaction of I with a number of olefins are collected in Table IV for reference. Comparison of the present results for the addition of I to acetylenes (Table III) with those for the appropriate olefins shows significantly lower reaction velocities for the acetylenes. Thus, the rate ratio for styrene–phenylacetylene is about 106. Using the approximate value for the reaction of diphenylacetylene, the rate ratio for the pair, *trans*-stilbene–diphenylacetylene, is about 7. Robertson's data[20] for bromine addition in acetic acid at 25° show the same trends, but with considerably greater differences in reactivity between the ethylenes and acetylenes. For examples, the rate ratios for the pairs styrene–phenylacetylene and stilbene–diphenylacetylene were reported as about 3000 and 250, respectively, in this reaction.

TABLE IV

SUMMARY OF KINETIC PARAMETERS FOR THE REACTIONS OF 2,4-DINITROBENZENESULFENYL CHLORIDE WITH OLEFINS IN ACETIC ACID AT 45°

Olefin	k, (moles/l.)$^{-1}$ sec.$^{-1}$ × 10^3	E_a, kcal./mole	log A	S^*, cal./mole	Ref.
Cyclohexene	27.6	11.1	6.06	−32.7	6
p-Methylstyrene	9.43[a]	12.0	6.20	−32.2	2
Styrene	2.90	12.9	6.34	−31.6	2
Stilbene (*cis*)	0.109[b]	13.8	5.52	−33.4	9
p-Chlorostyrene	0.093	15.9	7.91	−24.4	2
p-Nitrostyrene	0.0693	16.9	7.46	−26.5	2

[a] This is the experimental value for a single determination at 44.9°; the value of k calculated from E_a and log A is 9.1. [b] All rate constants in ref. 9 have been found to be high by a factor of ten. The values tabulated here have been corrected for this error, which was kindly pointed out to us by Dr. D. R. Hogg of the University of Aberdeen, Scotland. It should also be noted that the plot of log k *vs.* $1/T$ for the *trans*-stilbene reaction in ref. 9 showed a slight curvature. A subsequent determination of the rate at 35° by Hogg indicated that the curvature is real and sufficient to preclude the calculation of an activation energy for the reaction. The reported activation energy for the *trans*-stilbene reaction should thus be questioned. Further work to check these points is in progress.

The intrinsic mechanism of the addition of bromine, or of other electrophilic reagents, to acetylenes has not been established although much speculation exists on the subject. Robertson, *et al.*,[20] believed that the addition of bromine proceeds similarly to the addition to alkenes, *viz*, initiation by electrophilic attack, but he also stated that some acetylenic compounds may add bromine by a nucleophilic mechanism.[20,21] Bohlmann,[22] in discussing various reactions of acetylenes, favored an ionic mechanism for bromine addition to acetylenes in acetic acid, but suggested that the reaction was initiated by a nucleophilic attack of the bromine.

Sinn[23] reported the effect of *p*-nitro substituents in stilbenes and diphenylacetylenes (tolanes) on the rates of bromine addition. Whereas the reaction with stilbene was much faster than with *p,p'*-dinitrostilbene, as expected for an electrophilic attack by bromine, the reaction with *p,p'*-dinitrotolane was slightly *faster* than with tolane. The latter result was difficult to reconcile with an electrophilic attack, and Sinn, therefore, proposed a homolytic mechanism for the reaction with acetylenes. It is evident that further studies are required to clarify the mechanism, or mechanisms, of additions of bromine to acetylenes.

The direction of addition of I to phenylacetylene, as shown by the established structure of II, can be rationalized on the basis of an electrophilic attack on the acetylenic bond similar to the postulated mechanism for the reaction with ethylenes. The higher activation energies and less negative entropies of activation for the acetylene reactions, compared to the olefin reactions, are also in the direction consistent with the postulation of similar ionic addition mechanisms. Nevertheless, it is clear that further studies are desirable also in the case of sulfenyl halide additions to alkynes.

Acknowledgment.—We are deeply indebted to the National Science Foundation and to the Army Research Office (Durham) for support of this work, and to Dr. Wilson L. Orr for his assistance in verification of calculations and for helpful discussions.

---

[18] P. B. D. de la Mare, *Quart. Rev.* (London), **3**, 126 (1949).

[19] A. D. Welch, *Ann. Rept. Progr. Chem.* (Chem. Soc. London), **44**, 35 (1947); *Quart. Rev.* (London), **2**, 78 (1948).

[20] P. W. Robertson, W. E. Dasent, R. M. Milburn, and W. H. Oliver, *J. Chem. Soc.*, 1628 (1950).

[21] R. Daniels and L. Bauer, *J. Chem. Educ.*, **35**, 444 (1958).

[22] F. Bohlmann, *Angew. Chem.*, **69**, 82 (1957).

[23] H. Sinn, *ibid.*, **69**, 754 (1957).