

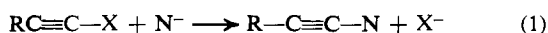
Nucleophilic Substitution at Acetylenic Carbon. Kinetics and Mechanism of the Arbuzov Reaction of Substituted Phenylbromo- and Phenylchloroacetylenes with Triethyl Phosphite^{1a,b}

Atsushi Fujii and Sidney I. Miller*^{1c}

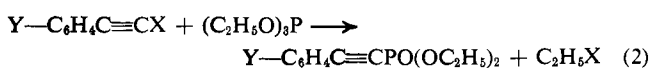
Contribution from the Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois 60616. Received August 3, 1970

Abstract: The kinetics of the Arbuzov reaction of four arylchloro- and three arylbromoacetylenes with triethyl phosphite in tetrahydrofuran (THF) was first order with respect to each reactant. Added halide had no effect on the rate. The activation parameters lie in the range $\Delta H^\ddagger = 17\text{--}18$ kcal/mol and $-\Delta S^\ddagger = 25\text{--}29$ eu. The halogen effect was small: $k(\text{PhC}\equiv\text{CCl})/k(\text{PhC}\equiv\text{CBr}) = 1.25$ at 79° . Hammett ρ values were found to be 1.98 and 1.56 at 102° for the arylchloro- and arylbromoethynes, respectively. To the extent that the Arrhenius and Hammett equations apply, the rate constants of arylchloroethynes are given by the expression $\log k = 0.858\sigma - 3941/T + 404\sigma/T + 7.42$. Toward triethyl phosphite, phenylchloroacetylene is about as reactive as ethyl iodide and far more reactive than ethyl chloride, β -bromostyrene, or bromobenzene. The absence of phenylethyne from the reactions of phenylchloroacetylene with triethyl phosphite in THF-ethanol was indicative of rate-determining nucleophilic attack on the α -carbon. However, the production of phenylethyne in the reaction of phenylbromoacetylene with triethyl phosphite in THF-ethanol was taken to be compelling evidence for some bromine abstraction in the overall process. Judging from changes in the product ratios of diethyl phenylethynylphosphonate to phenylethyne, rate-determining attacks on both α -carbon and bromine are plausible for phenylbromoacetylene. The reactions of phenylhaloethynes and 1-halo-3-methylbutyn-3-ols with sodium diethyl phosphite were much faster with the bromo compounds than the chloro compounds and are consistent with rate-determining attacks on halogen.

The synthetic utility and theoretical interest in nucleophilic substitution at an acetylenic carbon have developed only in the last decade.²⁻⁷ In 1962, phos-



phines,^{2a,3} thiolates,^{2a,b} amines,^{2a,3} phosphites,^{4a} and phosphides^{5f} were reported to effect the replacement of halide in eq 1 under surprisingly mild conditions. Since then, other examples have been found, several routes from reactant to product have been proposed, and a lively interest in the detailed mechanisms has developed.²⁻⁷ The particular systems (eq 2) of this paper permit us to explore a number of outstanding problems.



It may be recognized that eq 2 is an example of the Arbuzov reaction, whose normal path is given by eq 3.

(1) (a) Research supported by National Institutes of Health Grant GM07021; (b) abstracted from the Ph.D. thesis of A. F., 1970; (c) author to whom inquiries should be addressed.

(2) (a) C. E. Orzech, C. A. Welch, G. R. Ziegler, J. I. Dickstein, and S. I. Miller, *J. Amer. Chem. Soc.*, **84**, 2020 (1962); (b) A. K. Kuriakose and S. I. Miller, *Tetrahedron Lett.*, 905 (1962); (c) G. R. Ziegler, C. A. Welch, C. E. Orzech, S. Kikkawa, and S. I. Miller, *J. Amer. Chem. Soc.*, **85**, 1648 (1963); (d) H. G. Viehe, S. I. Miller, and J. I. Dickstein, *Angew. Chem.*, **76**, 537 (1964); (e) A. Fujii, J. I. Dickstein, and S. I. Miller, *Tetrahedron Lett.*, 3445 (1970); R. Tanaka and S. I. Miller, *ibid.*, 1753 (1971).

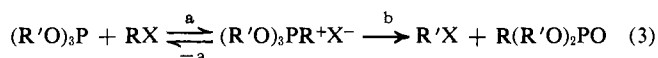
(3) H. G. Viehe and E. Franchimont, *Chem. Ber.*, **95**, 319 (1962).

(4) (a) B. I. Ionin and A. A. Petrov, *Zh. Obshch. Khim.*, **32**, 2387 (1962); (b) B. I. Ionin and A. A. Petrov, *ibid.*, **33**, 2863 (1963); (c) B. I. Ionin and A. A. Petrov, *ibid.*, **35**, 1917 (1965); (d) V. S. Zavgorodnii, B. I. Ionin, and A. A. Petrov, *ibid.*, **37**, 949 (1967).

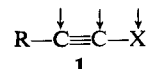
(5) (a) G. Sturtz, C. Charrier, and H. Normant, *Bull. Soc. Chim. Fr.*, 1707 (1966); (b) D. Seyferth and J. D. H. Paetsch, *J. Org. Chem.*, **34**, 1483 (1969); (c) D. W. Burt and P. Simpson, *J. Chem. Soc. C*, 2273 (1969); (d) P. Simpson and D. W. Burt, *Tetrahedron Lett.*, 4799 (1970); *J. Chem. Soc.*, in press; (e) G. Peiffer, A. Guillemonat, J.-C. Traynard, and M. Faure, *C. R. Acad. Sci., Ser. C*, **268**, 358 (1969); (f) K. Isslieb and G. Harzfeld, *Chem. Ber.*, **95**, 268 (1962).

(6) S. Y. Delavarenne and H. G. Viehe in "Chemistry of Acetylenes," H. G. Viehe, Ed., Marcel Dekker, New York, N. Y., 1969, Chapter 10.

(7) H. G. Viehe, *Angew. Chem., Int. Ed. Engl.*, **6**, 767 (1967).



Considering its wide application, few kinetic studies on this process are available.⁸⁻¹⁰ At the outset, it was not clear (to us) what mechanistic behavior we would find in the title system. Although it was recently established that $k_a \ll k_b$ in eq 3 when $\text{RX} = \text{EtI}$ or $i\text{-PrI}$, this opposed a tradition which held that $k_a \gg k_b$.¹⁰ As for process 1, at least three mechanistic possibilities have been considered for initial nucleophilic attack on the haloalkyne, namely, at halogen,



α -carbon, or β -carbon:²⁻⁷ the haloalkyne is *triphilic*. In this paper, we resolve some mechanistic questions involving both processes 1 and 3.

Experimental Section

The following instruments were used routinely: Beckman IR-8 for infrared (ir); Varian A-60 for nuclear magnetic resonance (nmr); Aerograph Model 700 for gas phase chromatography (gpc); Varian MAT-CH7 for mass spectroscopy (ms). Spectral checks were made on neat compounds, unless otherwise indicated.

Materials. Tetrahydrofuran (THF) was refluxed over sodium, fractionally distilled, and stored under nitrogen; our kinetic solvent had bp 66.5° , n_D^{20} 1.4070 (lit.¹¹ bp 66° , n_D^{20} 1.4073), and a single gpc peak. Triethyl phosphite was refluxed over sodium, fractionally distilled, and stored under nitrogen: it had bp 50° (48 mm), n_D^{20} 1.4119 (lit.¹² bp 65° (24 mm), n_D^{20} 1.4131), no

(8) A. J. Kirby and S. G. Warren, "The Organic Chemistry of Phosphorus," Elsevier, New York, N. Y., 1967, Chapter 3.

(9) A. N. Pudovik and L. M. Aladzheva, *Usp. Khim.*, **36**, 1499 (1967); (b) R. G. Harvey and E. R. DeSombre, *Top. Phosphorus Chem.*, **1**, 57 (1964).

(10) (a) G. Aksnes and D. Aksnes, *Acta Chem. Scand.*, **18**, 38 (1964); (b) G. Aksnes and D. Aksnes, *ibid.*, **19**, 898 (1965); (c) G. Aksnes and R. Eriksen, *ibid.*, **20**, 2463 (1966).

(11) "Tetrahydrofuran as A Reaction Solvent," E. I. Du Pont de Nemours and Co., Wilmington, Del., 1968.

(12) "Trialkyl Phosphites," Mobil Chemical Co., Industrial Chemistry Division, Richmond, Va., 1968.

extraneous nmr peaks, and no ir absorption in the $\nu_{\text{C}=\text{O}}$ region, 1200–1270 cm^{-1} . Tetraethylammonium chloride and bromide salts were recrystallized from absolute ethanol and anhydrous ether and dried under vacuum. Benzyl methyl ether, ethyl chloride, and diethyl phosphite were commercially available materials.

Most of our acetylenic compounds were prepared by published procedures. Phenylacetylene could be directly chlorinated or brominated at the ethynyl carbon but the other arylacetylenes had to be converted to their mercuric derivatives and then halogenated; the procedure failed for the *p*-methoxyphenylbromoacetylene. Phenylacetylene had bp 33–34° (0.3 mm), n_{D}^{25} 1.5478, and $\nu_{\text{C}=\text{C}}$ 2118 cm^{-1} ;¹³ phenylchloroacetylene had bp 26° (0.25 mm), n_{D}^{20} 1.5740, and $\nu_{\text{C}=\text{C}}$ 2250 cm^{-1} ;¹⁴ phenylbromoacetylene had bp 45° (0.35 mm), n_{D}^{25} 1.6018, and $\nu_{\text{C}=\text{C}}$ 2204 cm^{-1} .¹⁵ *p*-Methoxyphenylacetylene had mp 29°, δ^{CCl_4} 3.73 (1 H, s) and 2.84 (3 H, s);¹⁶ mercuric *p*-methoxyphenylacetylide had mp 206–208° dec and $\nu_{\text{C}=\text{C}}^{\text{KBr}}$ 2135 cm^{-1} ;¹⁷ *p*-methoxyphenylchloroacetylene (91% pure) had bp 73–81° (0.1 mm) and $\nu_{\text{C}=\text{C}}$ 2226 cm^{-1} .¹⁸ *p*-Chlorophenylacetylene had bp 82° (19 mm), δ^{CCl_4} 2.97 (1 H, s);¹⁶ mercuric *p*-chlorophenylacetylide had mp 221–222° dec and $\nu_{\text{C}=\text{C}}^{\text{KBr}}$ 2145 cm^{-1} ;¹⁷ *p*-chlorophenylchloroacetylene had mp 75.8–76.2° and $\nu_{\text{C}=\text{C}}^{\text{CCl}_4}$ 2229 cm^{-1} ;¹⁹ *p*-methylphenylbromoacetylene (20 mm), δ 2.13 (3 H, s) and 3.00 (1 H, s);¹⁶ mercuric *p*-methylphenylacetylide had mp 208.5–209.5° dec and $\nu_{\text{C}=\text{C}}^{\text{KBr}}$ 2150 cm^{-1} .¹⁷ *p*-Methylphenylchloroacetylene had bp 39–52° (0.2–0.15 mm), n_{D}^{25} 1.5676, and $\nu_{\text{C}=\text{C}}$ 2224 cm^{-1} ;²⁰ *p*-methylphenylbromoacetylene (a new compound, 92% pure by nmr) had bp 54.0–54.5° (0.15 mm) and $\nu_{\text{C}=\text{C}}^{\text{CCl}_4}$ 2200 cm^{-1} .

Diethyl phenylethynylphosphonate was prepared from phenylbromoacetylene and triethyl phosphite in THF at 110° in 75% yield,^{4a,c} and from phenylchloroacetylene and sodium diethyl phosphite in THF at 0° in 61% yield.^{5a} It had bp 120–120.3° (0.09 mm); n_{D}^{18} 1.5282 (lit.^{5a} n_{D}^{20} 1.5267); δ^{CCl_4} 1.37 (6 H, m), 4.19 (4 H, m), and 7.48 (5 H, m); ν 2187, 1260, 1165, 1030, and 970 cm^{-1} ; mass spectrum m/e 238 (P^+), 210 ($\text{C}_{10}\text{H}_{11}\text{O}_3\text{P}$), 195 ($\text{C}_{10}\text{H}_{11}\text{O}_2\text{P}$), 165 ($\text{C}_8\text{H}_5\text{O}_2\text{P}$), 129 (C_{10}H_9), 128 (C_{10}H_8), 102 (C_8H_6).

Infrared analyses for the four diethyl arylethynylphosphonates of this study were carried out in THF solutions (see below). The para substituents and $\nu_{\text{C}=\text{C}}^{\text{THF}}$ are indicated: H, 2165 cm^{-1} ; CH_3 , 2164 cm^{-1} ; Cl, 2168 cm^{-1} ; CH_3O , 2161 cm^{-1} .

1-Chloro-3-methylbutyn-3-ol had bp 43–44° (4.5 mm); δ^{CCl_4} 4.40 (1 H), 1.50 (6 H); ν 3350 and 2239 cm^{-1} . The 2-tetrahydropyranyl ether of 1-chloro-3-methylbutyn-3-ol had bp 54–55° (0.35 mm); n_{D}^{25} 1.4636; δ^{CCl_4} 1.50 (12 H, m), 3.60 (2 H, m), and 5.01 (1 H, t); ν 2237 and 2231 cm^{-1} .²¹

p-Chlorophenylbromoacetylene. To a stirred solution (200 ml) of mercuric *p*-chlorophenylacetylene (15 g) in carbon tetrachloride, bromine (10 g) in carbon tetrachloride was added dropwise over a period of 1.5 hr. After the white precipitate was filtered, the mother liquor was evaporated to give the bromoacetylene. This white solid (91%) had mp 88.5–89.4° from ethanol and $\nu_{\text{C}=\text{C}}$ 2225 cm^{-1} .

Anal. Calcd for $\text{C}_8\text{H}_4\text{BrCl}$: C, 44.58; H, 1.87. Found: C, 44.34; H, 1.83.

Reaction of 1-Chloro-3-methylbutyn-3-ol with Triethyl Phosphite. In a 100-ml flask, which was preflushed with nitrogen, the chlorobutynol (0.08 mol) and triethyl phosphite (0.12 mol) were heated to ca. 75°. Heating was stopped briefly to temper the vigorous reaction. The reaction mixture was kept at 80° for 4 hr. The excess triethyl phosphite was removed at 30° (0.4 mm) and the residue was fractionated. Only the last fraction (ca. 2 ml), bp 58–62° (0.05 mm), showed ir absorption at 2000–2200 cm^{-1} : ν 3450 (broad, weak), 3160, 2950–2910 (three peaks), 2185, 2070, 1960, 1265, 1030, 970 cm^{-1} . The peaks at 3160, 2070, and 1265

cm^{-1} were assigned to $\text{HC}\equiv\text{CP}(\text{O})(\text{OEt})_2$ ^{4c} and those at 3450 and 2185 cm^{-1} to $(\text{CH}_3)_2\text{C}(\text{OH})\text{C}\equiv\text{CP}(\text{O})(\text{OC}_2\text{H}_5)_2$.^{5a} It has been reported that diethyl ethynylphosphonate is a product of the thermal decomposition of the butynylphosphonate.^{5a}

Diethyl 3-(3-Methylbutynyl)phosphite. In a 500-ml three-necked flask, freshly cut sodium (0.13 g-atom) was added piece by piece to the mixture of dry THF (200 ml) and freshly distilled diethyl phosphite (20 ml, bp 71–72° (14 mm)). The reaction mixture was allowed to stand at ca. 25° overnight under nitrogen to consume the sodium. To the homogeneous solution at ca. 78°, freshly distilled 3-methyl-3-chlorobutynol ((14.2 g), bp 44–45° (4.5 mm)) was added dropwise. Since no reaction was observed at –70° or at ca. 25° for 1 day, the solution was kept at 106° for 5 hr. After three distillations, the product (33%) was obtained and had bp 67–69° (0.06 mm); n_{D}^{20} 1.4304 (lit.^{5a} n_{D}^{20} 1.4303), $\nu_{\text{C}=\text{C}}^{\text{neat}}$ 3285, 3210, 2120 cm^{-1} , δ^{CCl_4} 1.33 (6 H, sextet), 1.70 (6 H, s), 2.82 (1 H, s), 4.03 (4 H, octet). When the same reaction was carried out with equimolar ethanol, the yield of product was increased to 56%.

Attempted Reaction of the 2-Tetrahydropyranyl Ether of 1-Chloro-3-methylbutyn-3-ol with Diethyl Sodium Phosphite. The reaction was carried out in THF on a 0.1-mol scale at 108° for 3 hr. Work-up and distillation gave the starting chlorobutynol (45%) and left a residue with no $\nu_{\text{C}=\text{C}}$ but ν 1620 (strong) and 1250 cm^{-1} ir bands (polyenephosphonate?). It has been reported that reaction with the bromo compound takes place at –70° and yields the butynyl phosphonate.^{5a}

Analyses. The rates of formation of product in eq 2 were followed by ir analysis²² on a Perkin-Elmer Model 257 spectrophotometer with a scan speed of 100 $\text{cm}^{-1}/\text{min}$ and specified resolution of 5 cm^{-1} . Beer's law (eq 4) was found to hold for 0.1 and 0.7 mm

$$D = \log T_0/T = \epsilon lc \quad (4)$$

thick cells with sodium chloride windows.^{1b} The average optical density (D) of three scans was used in a given determination: $D = 0.5970 \pm 0.009$, say, at 0.0997 *M* phenylethynylphosphonate in THF, is based on 0.5953, 0.5971, 0.5975, and 0.5980. To minimize errors, our actual analyses were always made on solutions in which T was greater than 30% and usually less than 75%.²²

Quantitative analyses of product mixtures containing phenylchloro- or phenylbromoacetylene and phenylacetylene were carried out by gpc: the 5-ft \times 0.25 in. aluminum column contained 10% QF-1 on 60–80 mesh firebrick. Benzyl methyl ether was used as an internal standard. With a carrier gas of helium at 60 ml/min, injector 170°, column at 99–100°, detector at 265°, retention times (minutes) were ethanol (0.6), THF (2.2), phenylacetylene (7.0), triethyl phosphite (8.5), benzyl methyl ether (16.4), phenylchloroacetylene (20.4), and phenylbromoacetylene (37.4). Standard solutions containing benzyl methyl ether, phenylchloro- and phenylbromoacetylene, and phenylacetylene were used to obtain curves of peak area vs. concentration. Peak areas were taken as (peak height) \times (width at half-height). The lower limit of detection of a standard sample of phenylacetylene was 0.002 *M*. Average deviations in points on the calibration curves were ca. 5%; the uncertainty for an actual run may be somewhat higher, because the phenylacetylene peak is superimposed on the tail of the strong solvent (THF) peak and may also be distorted by the onset of the triethyl phosphite peak, when the concentrations of the latter are high.

Kinetic Procedures. Haloacetylene and triethyl phosphite were weighed in a volumetric flask (25 ml) and diluted with dry THF at 20.5°. This solution was distributed among ampoules (1 ml) and these were sealed. To minimize contact with air, all containers were preflushed with nitrogen. The ampoules were left in regulated baths ($\pm 0.05^\circ$); calibrated thermometers were used to obtain the temperatures. To stop the reaction, the ampoules were quickly cooled in Dry Ice–acetone.

Reaction 2 was assumed to be first order both with respect to arylhaloacetylene and triethyl phosphite. By using an excess of the phosphite, we were able to process our data according to the first-order relation eq 5, in which D is the optical density of $\nu_{\text{C}=\text{C}}$

$$k_d t = 2.303[\log D_\infty - \log (D_\infty - D)] \quad (5)$$

for the arylethynylphosphonate. This also had the advantage that the initial concentrations of our reactant arylhaloacetylenes did

(13) J. C. Hessler, "Organic Syntheses," Collect. Vol. I, Wiley, New York, N. Y., 1941, p 438.

(14) R. Truchet, *Ann. Chim.*, (10) 16, 309 (1931).

(15) S. I. Miller, G. R. Ziegler, and R. Wielesek, *Org. Syn.*, 45, 86 (1965).

(16) A. D. Allen and C. D. Cook, *Can. J. Chem.*, 41, 1084 (1963); R. W. Bott, C. Eaborn, and D. R. M. Walton, *J. Chem. Soc.*, 384 (1965).

(17) I. Iwai and Y. Yura, *Takamine Kenkyusho Nempo*, 10, 30 (1958); *Chem. Abstr.*, 55, 4400 (1961); J. R. Johnson and W. L. McEwen, *J. Amer. Chem. Soc.*, 48, 469 (1926).

(18) E. Ott and W. Bossaller, *Chem. Ber.*, 76, 88 (1943).

(19) D. Woodcock, *J. Chem. Soc.*, 203 (1949).

(20) H. H. Wenzke and C. J. Wilson, *J. Amer. Chem. Soc.*, 56, 2025 (1934).

(21) M. Julia and J. M. Surzur, *Bull. Soc. Chim. Fr.*, 1620 (1956).

(22) H. H. Willard, L. L. Merritt, Jr., and J. A. Dean, "Instrumental Methods of Analysis," 4th ed, D. Van Nostrand, New York, N. Y., 1965, pp 85–95.

Table I. Rate Data for the Reactions of Arylhaloalkynes, p - $\text{Y-C}_6\text{H}_4\text{C}\equiv\text{CX}$, with Triethyl Phosphite in THF

p -Y, X	σ	Temp, $\pm 0.05^\circ$	$[\text{C}_6\text{H}_5\text{C}\equiv\text{CX}]$, $M \times 10^2$	$[(\text{C}_2\text{H}_5\text{O})_3\text{P}]$, $M \times 10$	No. of runs	$k \times 10^5$, a, b $M^{-1} \text{sec}^{-1}$	$\Delta H^\ddagger, a$ kcal/mol	$-\Delta S^\ddagger, eu$
Cl, Cl	0.227	102.30				250 ^c		
		77.23	3.74-7.28	3.90-10.0	4	457 ± 0.5		
		60.01	3.74-7.28	3.90-10.0	4	12.6 ± 0.3	17.0	0.2
		48.10	3.74-7.28	3.90-10.0	4	4.40 ± 0.13		26
Cl, Br	0.227	102.30	2.88-6.30	2.39-8.42	4	181 ± 2		
		102.25	1.42-8.90	1.30-6.63	7	85.3 ± 4.0^d		
H, Cl	0.0	79.40	1.42-8.90	1.30-6.63 ^{e, f}	7	17.5 ± 0.3^d		
		77.23				14.7 ^e		
		60.01				3.86 ^e	17.6	0.06
		59.72	1.44-8.99	4.55-7.31	6	3.71 ± 0.11		26
H, Br	0.0	102.25	1.84-7.75	1.31-8.85 ^{e, g, h}	5	73.2 ± 0.2		
		79.40	1.84-7.75	1.31-13.0 ^{e, i}	6	13.9 ± 0.2		
		59.72	1.95-13.5	6.55-16.5	5	2.96 ± 0.07	18.0	0.2
		102.30	4.99-7.05	6.29-9.17	4	46.3 ± 1.4		25
CH ₃ , Cl	-0.170	77.23	4.99-7.05	6.29-9.17	4	7.77 ± 0.3		
		60.01	6.83-7.11	7.94-14.1	4	2.07 ± 0.06	17.7	0.06
		102.30	4.88-8.18	4.90-1.33	4	40.8 ± 1.1		27
CH ₃ , Br	-0.170	102.30	5.42-10.6	6.18-11.9	4	25.3 ± 0.2		
		77.23	5.42-10.6	6.18-11.9	4	4.10 ± 0.14		
		60.01	6.91-6.78	14.9-30.1	3	1.12 ± 0.03	17.6	0.3
CH ₃ O, Cl	-0.269	102.30						
		77.23						
		60.01						29

^a The probable error from a least squares treatment is indicated. ^b k has been corrected for solvent expansion. ^c Calculated value. ^d One run contains $8 \times 10^{-4} M$ $(\text{C}_2\text{H}_5)_3\text{NCl}$. ^e Additional runs with higher $[(\text{C}_2\text{H}_5\text{O})_3\text{P}]$ are not included. See below for excluded k , in $M^{-1} \text{sec}^{-1}$ (M , $(\text{C}_2\text{H}_5\text{O})_3\text{P}$). ^f $k = 2.4 \times 10^{-4}$ (0.731 M). ^g One run contains $8.7 \times 10^{-4} M$ $(\text{C}_2\text{H}_5)_3\text{NBr}$. ^h $k = 7.6 \times 10^{-4}$ (1.65 M). ⁱ $k = 1.35 \times 10^{-4}$ (1.30 M); $k = 1.4 \times 10^{-4}$ (1.65 M).

not have to be known exactly. Reactions were followed for 1-3 half-lives and D_∞ was taken after 10 half-lives. Typical plots are given in the thesis.^{1b} Second-order rate constants were obtained from the slopes of least squares plots given by eq 6 and illustrated

$$k' = k_p[(\text{C}_2\text{H}_5\text{O})_3\text{P}] \quad (6)$$

in Figure 1. These k' values were then corrected to k for solvent (THF) expansion, using the factors ($^\circ\text{C}$) 1.000 (20.0 $^\circ$), 1.0463 (59.72 $^\circ$), 1.0704 (79.40 $^\circ$), and 1.0964 (102.25 $^\circ$).¹¹

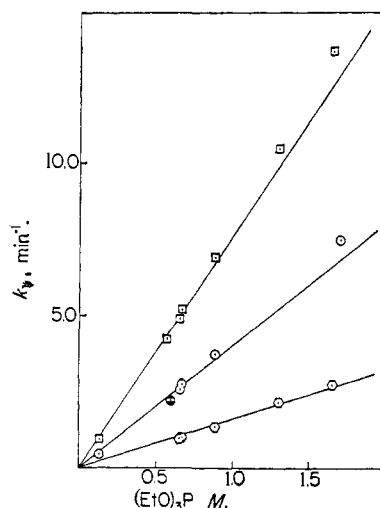


Figure 1. Pseudo-first-order rate constants of phenylbromoacetylene with triethyl phosphite in THF: \circ , 102 $^\circ$, $k_p \times 10^2$; \square , 79 $^\circ$, $k_p \times 10^3$; \odot , 60 $^\circ$, $k_p \times 10^3$; \bullet , Et_3NBr , 8.7×10^{-4} mol/l.

The activation parameters were determined from a least squares treatment of $\log k/T$ vs. $1/T$ according to the standard relation. All of the k 's, the activation parameters, and their probable errors

$$k = (kT/h)e^{\Delta S^\ddagger/R}e^{-\Delta H^\ddagger/RT} \quad (7)$$

(0.845 \times average deviation) are given in Table I.

Decomposition of Diethyl Phenylethynylphosphonate. In THF at 102 $^\circ$, the disappearance of this phosphonate (0.059 M) followed neither first- nor second-order rate laws, and the total decom-

position was 2.2% after 50.5 hr. No product was identified. The decomposition of the phosphonate (0.053 M) in the presence of excess triethyl phosphite (0.53 M) in THF at 102 $^\circ$ had a second-order rate constant of $3.46 \times 10^{-7} M^{-1} \text{sec}^{-1}$, based on one run. The decomposition product was not identified, but may be a mono- or diadduct.²³ In any case, the decomposition of the ethynylphosphonate on the time scale of process 2 is negligible and does not affect our kinetic data on eq 2.

The Reactions of Phenylchloro- and Phenylbromoacetylenes with Triethyl Phosphite in THF-Ethanol. Initially, the product ratio PR was determined at 80-90% reaction. At some ethanol con-

$$PR = [\text{C}_6\text{H}_5\text{C}\equiv\text{CPO}(\text{OC}_2\text{H}_5)_2]/[\text{C}_6\text{H}_5\text{C}\equiv\text{CH}] \quad (8)$$

centrations, we found that the apparent value of PR changed with the degree of conversion of phenylbromoacetylene. This led us to check both reactant and products as a function of time, with the emphasis on low conversion. Unfortunately, the analyses which yield PR are least precise here. On the other hand, enough points were obtained in some runs so that rate constants, based on the disappearance of phenylhaloacetylene, could be estimated. It is emphasized, however, that these k 's are crude values based on only three to five points. (See Table II and the figure in ref 2e.)

When phenylacetylene (0.073 M), triethyl phosphite (0.79 M), and ethanol (9.7 M) were heated at 102 $^\circ$ in THF for 28.2 hr, 3.3% of the acetylene was lost. When diethyl ethynylphosphonate (0.075 M), triethyl phosphite (0.78 M), and ethanol (8.5 M) were heated at 102 $^\circ$ in THF for 3.7 hr, only 4.7% of the phosphonate was lost. Since product analyses were carried out on mixtures which had been heated <40-60 min, the decomposition of the products was not a factor in changing PR or the material balance.

The run at 60 $^\circ$ (Table II) had a reasonably constant PR . As for a variable ratio, we give the case $\text{C}_6\text{H}_5\text{C}\equiv\text{CBr}$, 0.225 M , $(\text{C}_2\text{H}_5\text{O})_3\text{P}$, 1.74 M , $\text{C}_2\text{H}_5\text{OH}$, 1.7 M at 77.23 $^\circ$ in which four PR values, 9.6, 12.1, 14.4, and 16.1 were found; the mean PR is 14 ± 3 and the value extrapolated to zero time is 5.2. Since the material balance was high at $89 \pm 2\%$ and the range of conversion was small at 24-42%, we tentatively ascribe the trends in PR to analytical problems.

In general, the material recovery in the runs averaged about 90%, but occasionally dropped to 85%. These deficiencies are ascribed to cumulative errors in the analyses of reactant and products. The PR values were of course particularly sensitive to these errors, but the calculated k 's of Table II were based on analyses of the phenylhaloalkynes and no serious errors in their values (>15%) are anticipated. In retrospect, minor improvements in the analytical

(23) C. E. Griffin and T. D. Mitchell, *J. Org. Chem.*, **30**, 1935 (1965); B. C. Saunders and P. Simpson, *J. Chem. Soc.*, 3351 (1963).

Table II. The Reactions of Phenylchloro- or Phenylbromoacetylene with Triethyl Phosphite in Tetrahydrofuran–Ethanol

Temp, °C	[C ₆ H ₅ C≡CX], <i>M</i>	[(C ₂ H ₅ O) ₃ P], <i>M</i>	[C ₂ H ₅ OH], <i>M</i>	Product ratio, <i>PR</i> (<i>PR</i> ₀) ^a	<i>k</i> , <i>M</i> ⁻¹ sec ⁻¹ × 10 ⁴ , ^b (no. of pts) ^c
				C ₆ H ₅ C≡CCl	
77.23			0	>100	1.5 ^d
	0.218	1.95	0.910	>10	1.4 (3)
	0.214	1.98	1.95	>10	1.5 (3)
	0.216	1.97	2.94	>10	1.6 (3)
	0.221	1.95	4.20	>10	1.5 (3)
				C ₆ H ₅ C≡CBr	
60.00			0	>100	0.30 ^d
	0.236	1.97	6.85	0.73 ± 0.03	0.7 (5) ^e
77.23			0	>100	1.4 ^d
	0.194	1.74	0.984	6.9 ± 0.7	1.6 (5) ^{b,f}
	0.225	1.74	1.70	14 ± 3 (5.2)	1.6 (4) ^{b,g}
	0.125	1.14	2.55	6 ± 1 (3.2)	1.5 (4) ^{b,h}
	0.236	1.97	6.85	0.90 ± 0.09	3.4 (5) ^{b,i}
79.4	0.0808 (?)	0.967 (?)	0.685	9.0	
			1.35	4.8	
			8.22	0.9	
			17.2	0.18	
102.25			8.22	1.0	
120.30			8.22	1.2	

^a *PR* = [C₆H₅C≡CPO(OC₂H₅)₂]/[C₆H₅C≡CH]. The average and average deviation are indicated. Values in parentheses (*PR*₀) were obtained by extrapolation to 0% reaction, because of a trend in *PR*. ^b The disappearance of C₆H₅C≡CX was followed. ^c The number of points on which *PR* and the approximate *k*'s are based is indicated in parentheses; otherwise a single determination was made. ^d From Table I. ^e Mean material balance (Mmb) 93%. ^f Mmb 92%. ^g Mmb 89%. ^h Mmb 98%. ⁱ Mmb 93%.

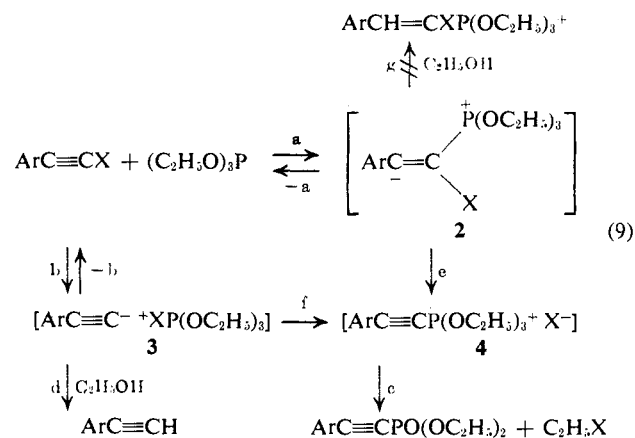
methods and slight changes in the total system, e.g., the solvent or phosphite, should lead to more precise results.

Results and Discussion

In this work, we have established the level of reactivity of haloalkynes toward a nucleophile. At one time, it was believed that haloalkynes (and other halo-unsaturates) would resist nucleophilic substitution;^{2,24} if the reactivity toward iodide in acetone at 50° is taken as 1.0 for *n*-butyl chloride, it is 0 for C₆H₅C≡CCl.²⁵ It has been reported that triethyl phosphite and β-bromostyrene do not react at 200°; the reaction with α-methyl-β-bromostyrene does occur at 170°.^{24,26} Here we have shown that most of the reactions covered by eq 2 have *k* (60°) > 2 × 10⁻⁵ M⁻¹ sec⁻¹, which has been reported for triethyl phosphite with ethyl iodide in acetonitrile.¹⁰ Incidentally, we have also shown that ethyl chloride and triethyl phosphite produce little or no product after 24 hr at 102° in THF. In view of the supposed inertness of haloalkynes, it is interesting that the arylhaloacetylenes are more reactive than comparable alkyl, aryl,⁹ or vinyl halides^{24,26} with triethyl phosphite in eq 3.

Much of our discussion will relate to possible mechanisms. The usual Arbuzov reaction (eq 3) is generally thought to consist of a rate-determining S_N2 displacement followed by rapid dealkylation of the quasi-phosphonium salt.⁸ In eq 9, the quasi-salt corresponds to 4. When such salts or their analogs have been prepared by other routes, they have been shown to react readily with weak nucleophiles at low temperatures (<0°).²⁷ It appears to us that ejection of diethylphenylethynylphosphonate (a weaker base) from 4 should be even more favorable and proceed more

rapidly than the loss of diethylethylphosphonate from its quasi-salt (eq 3). In what follows, we shall therefore assume that step c in eq 9 is fast.



Previous work has established, and we have confirmed, that process 2 can be used on the preparative scale.^{4,2a-e} The rate data are consistent with second-order kinetics, first order in haloalkyne and in triethyl phosphite. The derived activation enthalpies and entropies hardly vary (Table I). The similar activation parameters may indicate that no substantial mechanistic change is involved for our arylhaloalkynes. Furthermore, the large negative entropies of activation are consistent with the rate-determining formation of a pair of ions from neutral reagents.²⁸

The effect of high concentration of triethyl phosphite was to increase the rate constant, and the higher the temperature the greater the effect. Thus, *k*₂ for phenylbromoacetylene was linear in [(C₂H₅O)₃P] up to 0.9 *M* at 102°, 1.3 *M* at 79°, and 1.65 *M* at 60° (Figure 1); however, with 1.65 *M* triethyl phosphite at 102°, *k*₂ was ca. 14% high. The highest concentrations given in Table I merely represent runs in which we still found

(24) Y. L. Gefter, "Organophosphorus Monomers and Polymers," Pergamon Press, London, 1962, pp 82–85.

(25) M. J. Murray, *J. Amer. Chem. Soc.*, **60**, 2662 (1938).

(26) B. A. Arbuzov and B. P. Lugovkin, *Zh. Obshch. Khim.*, **21**, 99 (1951).

(27) J. H. Finley, D. Z. Denney, and D. B. Denney, *J. Amer. Chem. Soc.*, **91**, 5826 (1969).

(28) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1965, p 138.

Table III. Hammett ρ Values and Nucleophilic Attacks

Reaction	Solvent	Temp, °C	ρ	Ref
4-R-(2-O ₂ NC ₆ H ₃)X + piperidine	Various	25	>4	a
Ar ₂ C=CHX + C ₂ H ₅ O ⁻	C ₂ H ₅ OH	30	2.1	b
ArC≡CCl + (C ₂ H ₅ O) ₃ P	THF	25	Ca. 2.3	c
ArC≡CBr + (C ₂ H ₅ O) ₃ P	THF	25	Ca. 2	c
ArC≡CT + OH ⁻	25% CH ₃ OH-H ₂ O	25	0.77	d
ArC≡CH + OH ⁻ + BrO ⁻	H ₂ O	25	0.76	e

^a J. Miller, "Aromatic Nucleophilic Substitution," Elsevier, Amsterdam, 1968, Chapter 4; X = Br, Cl. ^b P. Beltrame, P. L. Beltrame, and L. Bellotti, *J. Chem. Soc. B*, 932 (1969); P. Beltrame, P. L. Beltrame, M. L. Cereda, and G. Lazzerini, *ibid.*, 1100 (1969); ρ was corrected for the two phenyl groups; X = F, Cl. We judge another value, $\rho \simeq 4.5$, to be unreliable. D. F. Bender, T. Thippeswamy, and W. L. Rellahan, *J. Org. Chem.*, **35**, 939 (1970). ^c This study. ^d C. Eaborn, G. A. Skinner, and D. R. M. Walton, *J. Chem. Soc. B*, 922 (1966). ^e R. R. Lii and S. I. Miller, unpublished results.

a first-order dependence in triethyl phosphite. Since triethyl phosphite is more polarizable ($R = 43 \text{ cm}^3$) and more polar than THF ($R = 20 \text{ cm}^3$, $\mu = 7.4 \text{ D}$), it is probably a better medium than THF; similar observations have been made with other Arbuzov examples.^{8,10a} In this regard, the rates for some runs in the presence of ethanol are mildly enhanced over those in THF (Table II).

Correlations. Our studies had limited objectives— as soon as the structure–reactivity information bearing on mechanism was clear, we turned to other approaches. The Hammett ρ values for the arylchloroacetylenes are 1.98, 2.05, and 2.13 at 102, 77, and 60°, respectively, and ρ for the arylbromoacetylenes is 1.56 at 102°. We have also been able to use eq 10²⁹ to estimate $\rho \simeq 2.2$ at 50° and $\rho \simeq 2.3$ at 25° for the arylchloroacety-

$$\rho = (0.804 \pm 0.097)/T + (439 \pm 34) \quad (10)$$

lenes.

Whenever two independent linear relations, e.g., the Hammett and Arrhenius equations, are obeyed, it can be shown that a single surface, a hyperbolic paraboloid, includes all of the data.²⁹ For the arylchloroacetylenes, we used a fitting program to obtain eq 11 for 12 k 's, where the standard errors are indicated

$$(\log k \pm 0.0201) = (0.858 \pm 1.260)\sigma - (3941 \pm 82.6)/T + (404 \pm 429.7)\sigma/T + (7.420 \pm 0.240) \quad (11)$$

and the variance is 0.00134.³⁰ Judging by the values of k we calculate from eq 11, the fit is excellent. The compact storage of all of our rate data is an advantage; eq 11 can also be used to predict the rate constants of many arylchloroacetylenes at any temperature in process 2, since over 100 σ values are now available.³¹

Interpretations of observed ρ values depend on other ρ values of "model" processes. It may be recalled that for certain related processes, there is a systematic fall-off in ρ as the distance of the reaction site to the aromatic ring increases.^{31,32} In Table III we list the ρ values of systems that seem closely related to ours. Based on these limited data, a clear distinction can be

(29) S. I. Miller, *J. Amer. Chem. Soc.*, **81**, 101 (1959); G. S. Krishnamurthy and S. I. Miller, *ibid.*, **83**, 3961 (1961).

(30) G. Struble, "Non-Linear Least Squares Curve Fitting Program," IBM 1620 Users Group Library, Statistical Laboratory and Computing Center, University of Oregon, Eugene, Ore.

(31) C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, **2**, 323 (1964).

(32) (a) W. K. Kwok, R. A. More O'Ferrall, and S. I. Miller, *Tetrahedron*, **20**, 1913 (1964); (b) R. A. More O'Ferrall and S. I. Miller, *J. Amer. Chem. Soc.*, **85**, 2440 (1963).

made between α -carbon attack and group abstraction from an alkyne: the ρ value for the former is ca. 2 and for the latter ca. 0.8 at 25°. Therefore our observed ρ values are consistent with α -carbon attack in process 3.

With respect to attack at carbon or halogen, the pattern is also plausible: the two products are $\text{ArC}\equiv\text{CXNuc}$ and $\text{ArC}\equiv\text{C}$, and chain lengthening by one atom often introduces a fall-off factor of ca. $0.8/2 = 0.4$.^{31,32} As between halobenzenes and vinyllogs, a factor of ca. 2 in ρ values for nucleophilic substitution also seems to hold.

The Phenylhaloacetylene–Triethyl Phosphite Reaction in the Presence of Ethanol. These trapping experiments were extensive enough to yield rough rate constants (Table II) and product ratios, PR (eq 8). The rate constants were the same, within experimental uncertainty, whether the disappearance of phenylhaloacetylene or appearance of product(s) was followed. Likewise, material recovery was normally >90%. For this reason, and because vinyl phosphonates, if formed, should be stable under our reaction conditions,^{23,24} we discount step g as a significant diversion in eq 9.

Except for the Russian group⁴ and ours,² most workers believe that the rate-determining step of eq 2 generally involves attack on halogen.^{3a,c,d,6,33} (β -Carbon attack, which has been found with analogous alkylhaloalkynes, and some nucleophiles^{6,7} is improbable in our system, because of the directive influence of phenyl.) Subject to the "observations" that $k_g \simeq 0$ and k_c is large (eq 9), in the presence of ethanol, the acetylide intermediate if formed may be diverted to phenylacetylene: likewise, the phosphonium species may be hydrolyzed. Note that the appearance of phenylacetylene is compelling evidence for attack on halogen, while its absence is mechanistically inconclusive, unless information on the rate constant for step f is available.

When phenylchloroacetylene was treated with triethyl phosphite at 77° in THF with added ethanol (0–4.2 M), no phenylacetylene was detected at 10–40% conversion to diethyl phenylethynylphosphate. Since both phenylacetylene and this phosphonate are stable under these reaction conditions, we can conclude that step d did not occur. Surprisingly, the rate constants for the process are not appreciably altered by the addition of ethanol: this is consistent with the notion that there is no change in mechanism between pure THF and THF–ethanol. Nevertheless, the choice of paths a and e vs. b and f cannot be decided by looking

(33) B. Miller, *Top. Phosphorus Chem.*, **2**, 133 (1965).

Table IV. Comparative Reactivities of Haloacetylenes with Triethyl Phosphite or Sodium Diethyl Phosphite in Tetrahydrofuran

Nucleophile	Haloethyne	X	Reactivity $k(\text{Cl})/k(\text{Br})$	Temp, °C	Products
(EtO) ₃ P	C ₆ H ₅ C≡CX ^a	Br ^b	1.2	60–120	C ₆ H ₅ C≡CP(O)(OEt) ₂
	(CH ₃) ₂ C(OH)C≡CX ^b	Cl ^a	?	75–94	(EtO) ₂ P(O)H HC≡CP(O)(OEt) ₂ , (CH ₃) ₂ C(OH)C≡CP(O)(OEt) ₂ ^c
(EtO) ₂ P(O)Na	C ₆ H ₅ C≡CX	Br ^d	≪1	–70	C ₆ H ₅ (C≡CPO)(OEt) ₂
	(CH ₃) ₂ C(OH)C≡CX	Cl ^a	≪1	0	
	(CH ₃) ₂ C(OPy)C≡CX ^e	Br ^d	≪1	–70	(CH ₃) ₂ C(C≡CH)OPO(OEt) ₂ (CH ₃) ₂ C(OPy)C≡CP(O)(OEt) ₂ 45% recovery of starting material
		Cl ^a	≪1	94	

^a This work. ^b Reference 4a. ^c Products uncertain. ^d Reference 5a. ^e Py = 2-tetrahydropyrynyl.

at these results in isolation; we shall return to this point.

When phenylbromoacetylene is treated with triethyl phosphite in THF–ethanol (Table II), the *PR* is high when $[\text{C}_2\text{H}_5\text{OH}] \rightarrow 0$ and low when $1/[\text{C}_2\text{H}_5\text{OH}] \rightarrow 0$. At 77°, the overall rate constant is sensibly constant in 0–3 *M* ethanol and then doubles in 6.85 *M* ethanol. As the temperature rises, the formation of the ethynyl phosphonate is favored over that of phenylacetylene. An estimate for the temperature coefficient of *PR* at either 6.85 or 8.2 *M* ethanol in THF yields $\Delta\Delta H^\ddagger \simeq 3.9$ kcal/mol (Table II).

The changes in the course of the trapping reaction between phenylchloro- and phenylbromoacetylene differ. The fact that phenylacetylene is a product of the phenylbromoacetylene reactions indicates that step b of eq 9 does occur. Is b exclusive and does a compete? We find it difficult to believe that a mere change in halogen could give rise to such differences in partitioning of **3**. Therefore, we shall argue that phenylchloroacetylene follows step a and phenylbromoacetylene follows step b, at least in part.

Now consider how *PR* can be related to eq 9. Provided that the steady-state assumption applies to the intermediates **2–4**, the partitioning relation 12 holds exactly for a given solvent composition. A linear plot of *PR* vs. $1/[\text{C}_2\text{H}_5\text{OH}]$ based on data at 77 or 79° extrapolates to

$$PR = \frac{k_f}{k_d[\text{C}_2\text{H}_5\text{OH}]} + \frac{k_a k_e}{k_b(k_{-a} + k_e)} \left(\frac{k_{-b} + k_f}{k_d[\text{C}_2\text{H}_5\text{OH}]} + 1 \right) \quad (12)$$

olates to $PR \leq 0.25$ at $1/[\text{C}_2\text{H}_5\text{OH}] = 0$, with a slope of ca. 6 (Figure 2). (This extrapolation gives us a hypothetical limit which is, however, valid in the region to which eq 12 applies.) On the other hand, a linear plot (not shown) of $1/PR$ vs. $[\text{C}_2\text{H}_5\text{OH}]$ extrapolates to $PR = 0$ at $[\text{C}_2\text{H}_5\text{OH}] = 0$, with a slope of ca. 0.1. Whether $k_e \gg k_{-a}$ or $k_e \ll k_{-a}$ does not affect the immediate argument—we use the former assumption and discuss it later. (1) Suppose that $k_f \ll k_d \sim k_{-b}$. Then eq 12 yields $k_a k_{-b}/k_b k_d \approx 6$ –10 for both limiting slopes. Since $k_a/k_b \leq 0.25$ at $1/[\text{C}_2\text{H}_5\text{OH}] = 0$, $k_{-b}/k_d \geq 25$. (2) Suppose that eq 12 has a zero intercept; k_a (or k_e) = 0 and the limiting slopes yield $k_f/k_d \approx 6$ –10.

While the analysis which connects eq 9 with eq 12 is unequivocal, the mechanistic choices have to be evaluated in chemical rather than in purely kinetic

terms. A key point concerns the partitioning of **3**. Step d involves proton transfer to a carbanion and should be very fast.³⁴ Step f could involve rearrangement within the ion pair **3** followed by S_N2 backside attack, or collapse of **3** to form a pentacovalent species followed by dissociation or rearrangement, etc.; either of these processes is probably slower than proton

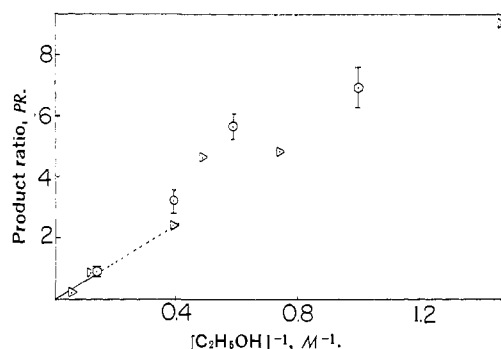


Figure 2. Ethanol effect on product ratio, $[\text{C}_6\text{H}_5\text{C}\equiv\text{CP}(\text{O})(\text{OC}_2\text{H}_5)_2]/[\text{C}_6\text{H}_5\text{C}\equiv\text{CH}]$ at 79° in phenylbromoacetylene–triethyl phosphite reaction in THF: \odot , extrapolated value; \circ , constant value; \triangleright , single measurement.

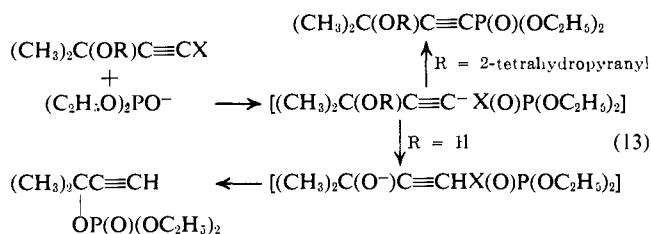
transfer, e.g., d.²⁷ Therefore, we would predict $k_f < k_d$, which is contrary to what is required by k_a (or k_e) $\simeq 0$. Second, $\Delta\Delta H^\ddagger \simeq 3.9$ kcal/mol seems large for product partitioning steps d and f, since these are presumably fast and of low activation energy. On the other hand, such a figure is consistent with a dependence of k_a/k_b which is derived when k_f is negligible. Both of these lines of argument favor the group of mechanisms which have both a and b as competitive and rate determining.

Reactivity Comparisons. By using 1-halo-3-methylbutyn-3-ol and its 2-pyrynyl ether, we were able to complement work reported by French workers.^{5a} The results for paired systems are summarized in Table IV. The reactivity of phenylchloro- and phenylbromoacetylene toward triethyl phosphite is $k(\text{Cl})/k(\text{Br}) \simeq 1.3$ –1.1 at 60–100°, and toward sodium diethyl phosphite is $k(\text{Br}) \gg k(\text{Cl})$. Judging from the reaction conditions, sodium diethyl phosphite is a much more powerful nucleophile than triethyl phosphite (Table IV).

(34) We estimate $k \simeq 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ for the reaction of phenylacetylene with water from the data of E. A. Halevi and F. A. Long, *J. Amer. Chem. Soc.*, **83**, 2809 (1961). Since **3** is an ion pair, this is an upper limit for k_d .

The usual reactivity order for nucleophilic substitution (S_N2C) is found for triethyl phosphite and haloethane, $k(\text{Br}) > k(\text{Cl})$. Likewise, for halogen abstraction by a nucleophile (S_N2Hal) the order $k(\text{Br}) \gg k(\text{Cl})$ has been reported for sodium diethyl phosphite or trialkyl phosphite with α -halo ketones, bromotrichloromethane, etc.^{8, 33, 35} For attacks at unsaturated carbon, e.g., alkene or aryl, in which the rate-determining step involves bond making (C-Nuc), the range of reactivity is often relatively small, and inversions of the S_N2C order, e.g., $k(\text{Cl}) > k(\text{Br})$, are frequently observed.^{36, 37a} Our own reactivities with sodium diethyl phosphite parallel those of S_N2Hal processes and the reactivities of triethyl phosphite are very much like those at other unsaturated carbon sites.

French workers have proposed plausible mechanisms for the reactions of the bromobutynols and their pyranil ethers with sodium diethyl phosphite (eq 13).^{5a} The



fact that $k(\text{Cl}) \ll k(\text{Br})$ is consistent with their trapping experiments and with their proposal that halogen abstraction is followed by fast steps to the product. Qualitatively, at least, we now have a fair measure of the halogen effect to be expected for two nucleophiles when step b of eq 9 occurs. Our tentative generalization for nucleophilic attacks on haloalkynes is that α -halogen abstraction shows a large element effect, $k(\text{Br}) \gg k(\text{Cl})$, while α -carbon attack shows a small element effect, $k(\text{Br}) < k(\text{Cl})$.

There is an enormous range in reactivity from the "slow" combination of alkylhaloalkyne and triethyl phosphite to the "fast" system of arylhaloalkyne and sodium diethyl phosphite. In this reactivity spectrum, alkylhaloacetylene or diethyl phosphite as reagents appear to ensure attack on halogen, but the arylhaloacetylenes or triethyl phosphite react by two mechanisms. By way of rationalization, it is obvious that bromine is more susceptible to abstraction by a nucleophile

than chlorine.³³ Compared to arylhaloalkynes, the alkylhaloalkynes are weak electrophiles. This is understandable, whether we are looking at attacks at α -carbon or halogen. In either case, the aryl group can stabilize the incipient anion; the β -alkyl group would be deactivating here and would tend to direct nucleophilic attack to the β -carbon (see 1). We find it difficult, however, to find a satisfactory rationale for the behavior of the nucleophiles: though diethyl phosphite anion is more basic and more nucleophilic (toward halogen, sulfur, and carbon sites) than triethyl phosphite,⁸ this does not clarify their preferences in one- vs. two-site attacks.

Mechanistic Conclusions. The activation parameters, solvent effects, and trapping results with ethanol are merely consistent with a as the rate-determining step for phenylchloroacetylene and both a and b as parallel rate-determining steps for phenylbromoacetylene in eq 9. But the Hammett ρ values for process 2 and the halogen effects in THF for both alkyl- and arylhaloalkynes provide strong support for our mechanistic suggestions. That a particular mechanistic choice has been made seems less important than the fact that the changes and alternatives in mechanism with both nucleophile and electrophile have been recognized.

Equation 9 includes a number of reaction steps and intermediates of general interest. Species 2 may be regarded as the intermediate in an E1cb reaction in which syn elimination *via* e, anti elimination *via* a, or proton uptake on step g are formal possibilities.³⁸ The competition of syn departure of halide, a good leaving group, with proton uptake, *i.e.*, $k_e \geq k_g$ has been discussed.³⁸ No evidence relevant to the loss of triethyl phosphite from 2 seems to be available, but triethyl phosphite is generally considered to be a poor leaving group.⁸ Charge delocalization, in 2, e.g., $\text{Ar}\ddot{\text{C}}-\text{CX}=\text{P}(\text{OC}_2\text{H}_5)_3$, does in fact provide a rationale for retardation of steps - a and g and facilitation of step e by anti elimination; that is, $k_e > k_{-a} \sim k_g$. Concerning species 4, halide attack on 4 can conceivably lead to 2 or 3, but we considered these steps improbable in this system. It would, however, be amusing to find a system which went to both products *via* step a ($k_b = 0$)!

Acknowledgments. We wish to acknowledge the exploratory work at I.I.T. of Dr. A. Dondoni (Bologna, Italy) on process 2 in 1963-1964, when the work of ref 4 was still unknown to us. Samples of triethyl phosphite from Mobil Chemical and of the butynols from Airco Chemical Co. were appreciated.

(38) S. I. Miller and W. G. Lee, *J. Amer. Chem. Soc.*, **81**, 6313 (1959); W. K. Kwok, W. G. Lee, and S. I. Miller, *ibid.*, **91**, 468 (1969).

(35) R. E. Atkinson, J. I. G. Cadogan, and J. T. Sharp, *J. Chem. Soc. C*, 138 (1969).

(36) Z. Rappoport, *Advan. Phys. Org. Chem.*, **7**, 1 (1969).

(37) (a) J. Miller, "Aromatic Nucleophilic Substitution," Elsevier, Amsterdam, 1968, Chapter 5; (b) S. D. Ross, *Progr. Phys. Org. Chem.*, **1**, 31 (1963).