were eluted with 0.1 M NH_4OH. After a concentration to dryness the residue was extracted with H_2O and the soluble fraction was applied on a 1.4 × 68 cm column of Dowex 50W (NH_4^+) resin. The derivatives were eluted with 6 l. of a linear gradient from 0 to 0.15 M NH_4OH. Compound **7**, 85 mg, was eluted in fractions 46–71, followed by a mixture of **6**, 57 mg, and 1-(β-aminoethyl-N-β-aminoethyl)uracil[14] (**13**), 56 mg, in fractions 114–140, separable by paper chromatography in solvent A. Fractions 180–190 contained 10 mg of 3-(β-aminoethyl-N-β-aminoethyl)uracil[14] (**14**), followed by 13 mg of **8** in fractions 242–252. Higher alkylated derivatives were identified in fractions 253–300. Thymine derivatives were eluted in the following fractions: **11**, 120 mg, in 85–110; 1-(β-aminoethyl-N-β-aminoethyl)thymine[14] (**15**), 55 mg, in 180–200; **10**, 53 mg, in 206–222, followed by 3-(β-aminoethyl-N-β-aminoethyl)thymine[14] (**16**) and by **12**.

(14) Tentatively identified by uv spectra, chromatographic properties, and correct analysis for N.

Reaction of Alkylated Derivatives with Sodium Hydroxide.—The alkylated derivatives (10 mg) and 0.2 N NaOH (0.5 ml) were heated at 100° for 10 min. The reaction products were chromatographed on paper and the uv spots were examined.

Registry No.—**2**, 66-22-8; **4**, 65-71-4; **5**, 34484-23-6; **6**, 34386-70-4; **6**·HCl, 34386-71-5; **7**, 34386-72-6; **7** HCl, 34386-73-7; **8**·2HCl, 34386-74-8; **9**, 34387-59-2; **10**, 34386-75-9; **10**·HCl, 34386-76-0; **11**, 34386-77-1; **11**·HCl, 34386-78-2; **12**·2HCl, 34386-79-3; ethylenimine, 151-56-4; 2-chloroethylamine, 689-98-5.

Nucleophilic Substitution at an Acetylenic Carbon. A Mechanistic and Synthetic Study of the Reactions of Phosphines with Haloacetylenes[1]

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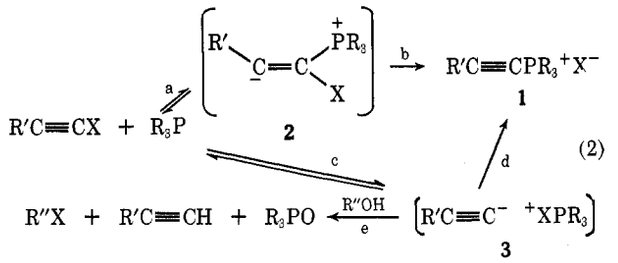
A synthetic route to ethynylphosphonium salts from haloacetylenes, phenylhaloacetylenes, but not alkylhaloacetylenes is described. These salts are electrophiles; when phenylethynyltriphenylphosphonium bromide is treated with tributylphosphine in acetonitrile, the α,β-bis(tributylphosphonium)styrene dibromide is formed. Rate data for the second-order reactions of several systems in DMF are ($\Delta H^{\ddagger}$, kcal/mol; $\Delta S^{\ddagger}$, eu; k, M^{-1} sec^{-1} at 36°): $C_6H_5C{\equiv}CBr$–$(C_6H_5)_3P$ (16.8; 23; 8.45×10^{-5}); $C_6H_5C{\equiv}CCl$–$(C_6H_5)_3P$ (14.5; 29; 1.75×10^{-4}); $C_6H_5C{\equiv}CBr$–$(n\text{-}C_4H_9)_3P$ (5.4; 44; 2.20×10^{-1}); $C_6H_5C{\equiv}CCl$–$(n\text{-}C_4H_9)_3P$ (11.5; 27; 5.92×10^{-2}); CH_3Br–$(C_6H_5)_3P$ (11.8; 31; 2.88×10^{-3}). Both the element effect, $k(Cl) > k(Br)$, and the results of scavenging experiments with methanol provide evidence for mechanistic alternatives. Although tributylphosphine attacks the bromine of phenylbromoacetylene exclusively, attacks on halogen and the terminal carbon atom appear to be competitive in the other systems. The general order of reactivity in substitution at carbon by phosphine nucleophiles is $sp^3 \sim sp > sp^2$.

Nucleophilic displacement at an acetylenic carbon

$$R'C{\equiv}CX + Nuc \longrightarrow R'C{\equiv}C\text{-}Nuc + X \qquad (1)$$

has come of age only within the last few years.[2-7] Substitution attacks on haloalkynes have now been reported for organometallics,[5,7] amines,[2a,e,j,3] phosphites,[2g,3e,6] thiolates,[2b,c,3c] phosphides,[5] alkoxides,[2h,i] etc. Kinetic data in this area are still rare.[2a-c,f-h,j,3e] Our work was undertaken to find out first whether ethynylphosphonium salts could be prepared by process 2, and second to develop a deeper understanding of a still new and relatively unexplored process.



(2)

1a, R′ = R = C_6H_5; X = Br
b, R′ = R = C_6H_5; X = Cl
c, R′ = C_6H_5; R = n-C_4H_9; X = Br
d, R′ = C_6H_5; R = n-C_4H_9; X = Cl
e, R′ = H; R = C_6H_5; X = Cl
f, R′ = H; R = C_6H_5; X = Br
g, R′ = H; R = n-C_4H_9; X = Cl

The first ethynylphosphonium salts were prepared in aprotic solvents.[2b,3d,4] In the presence of a proton donor, the formation of **1** *may* fail, because of diversion of the ion pair **3** along path e. This was found in the system phenylbromoacetylene–triphenylphosphine.[4] For this reason, Hoffmann and Förster suggested that steps c and d in eq 2 were appropriate for this process, and this conclusion has been accepted by workers in the field.[2f] In this paper, we show that all of the options of eq 2 must be retained and describe some of its synthetic applications.

(1) (a) Research supported by National Institutes of Health Grant GM07021. This work was presented in part at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., 1963. (b) Taken from the Ph.D. Thesis of J. I. D., Illinois Institute of Technology, 1970.

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Experimental Section[1b]

Microanalyses were performed by Micro-Tech Laboratories, Skokie, Ill., and A. Bernhardt, Mulheim (Ruhr). Melting points were taken on a Mel-Temp melting point apparatus and are uncorrected. Infrared (ir) spectra were obtained on Perkin-Elmer Model 21 and Infracord Model 137 spectrometers and calibrated against several polystyrene bands. Nuclear magnetic resonance (nmr) spectra were obtained on a Varian A-60 instrument and referred to tetramethylsilane (TMS), which was used as an internal standard. Neat liquids were used for the spectra, except as indicated.

The identities and purities of reactants, products, and solvents were checked routinely by gas chromatography (gc) (Table I).

TABLE I

CONDITIONS EMPLOYED FOR GAS CHROMATOGRAPHIC ANALYSES

Compd	Instrument[a]	Column	Temp, °C[b]
$C_6H_5C{\equiv}CBr$, $C_6H_5C{\equiv}CCl$	BC10	Apiezon L (6 ft × 0.25 in.)[d] Ar (25 psi)	160, 140, 200
$C_6H_5C{\equiv}CH$	A700	20% QF-1 (6 ft × 0.25 in.)[c] He (10 psi)	90, 130, 200
CH_3Br	A350	Apiezon L (6 ft × 0.25 in.) He (5 psi)	0, 25, 25
$(C_6H_5)_3P$ $(C_4H_9)_3P$ $(C_6H_5)_3PO$ $(C_4H_9)_3PO$	BC10	20% Apiezon L (6 ft × 0.25 in)[d] Ar (30 psi)	275, 200, 350
DMF	BC10	Diethylene glycol succinate (DEGS) (6 ft × 0.25 in.) Ar (15 psi)	120, 90, 150

[a] Barber Coleman Model 10; Aerograph Models 350 and 700. [b] Column, detector, inlet. [c] An aluminum column containing 20% by weight QF-1 on 40–60 mesh acid-washed firebrick. [d] A glass column containing 20% Apiezon L on 40–60 mesh acid-washed firebrick.

Materials.—Commercially available compounds were purified, if need be, by distillation or recrystallization. The properties of known compounds that we synthesized will be summarized, while the properties of certain materials, *e.g.*, those used in the kinetic studies, will be given in more detail.

The solvent for our kinetics was dimethylformamide (DMF). Reagent grade material was stored over sodium hydroxide for 1 week and filtered directly into a fractional distillation apparatus. The second of three fractions was used; it had bp 63° (30 mm), $n^{25}D$ 1.4270, and one gc peak [lit.[8] bp 63° (30 mm), $n^{25}D$ 1.4269]; its ir spectrum revealed no trace of water.

Triphenylphosphine was recrystallized from 50% ethanol–ether to mp 80–81° (lit.[9] mp 80°); it had one gc peak. Tributylphosphine was fractionally distilled; the middle fraction had bp 151° (50 mm), $n^{20}D$ 1.4625, one gc peak, and no ir (P=O) band (lit.[10] bp 149.5° (50 mm), $n^{20}D$ 1.4634). Methyl bromide was purified by fractional condensation in U traps at 0, −45, and −78°. The middle fraction had a minimum purity of 99% by gc.

Most of the 1-haloalkynes were prepared by shaking the 1-alkyne, chlorine or bromine, and potassium hydroxide in water. The 1-haloalkynes were purified by fractional distillation and stored under nitrogen in a refrigerator.[11] Phenylbromoacetylene had bp 55–56° (1.5 mm), $n^{25}D$ 1.6102, ir 4.71 μ (C≡C).[11] Phenylchloroacetylene had bp 70–71° (16 mm), $n^{25}D$ 1.5732, ir 4.65 μ (C≡C).[12] 1-Bromo-1-hexyne had bp 41–42° (11 mm), $n^{25}D$ 1.4698, ir 4.62 μ (C≡C).[13] 1-Chloro-1-hexyne, prepared from 1-sodio-1-hexyne and benzenesulfonyl chloride, had bp 45–46° (5 mm), ir 4.51 μ (C≡C).[12] A number of haloacetylenic alcohols and/or their 2′-tetrahydropyranyl ethers were also used: 1-(chloroethynyl)cyclohexanol and ether,[14] 1-(bromoethynyl)-cyclohexanol,[15] 1-chloro-3-methyl-1-pentyn-3-ol and ether,[16] and 2′-(1-chloro-3-methylbutyn-3-oxy)tetrahydropyran.[14]

Chloroacetylene (Hazardous! On contact with air this substance may explode and burn) was generated by refluxing a solution of 1,2-dichloroethylene (48 g, 0.5 mol) and potassium hydroxide (40 g, 0.7 mol) in 1,2-dimethoxyethane (300 ml) under nitrogen. Chloroacetylene was swept out of solution by a nitrogen stream through calcium chloride and phosphorus pentoxide tubes and condensed in a liquid nitrogen cooled trap. High vacuum fractionation through U traps at −94, −120, and −196° yielded material of vapor pressure 416 mm at −45° (lit.[17] 414.7 mm at −44.9°).

Bromoacetylene (Hazardous! On contact with air this substance may explode and burn) was prepared from 1,2-dibromoethene (37.2 g, 0.2 mol) and potassium hydroxide (40 g, 0.7 mol) by the method described for chloroacetylene. Bromoacetylene was passed slowly through a train containing cold baths at −45, −94, and −196°. The center fraction had a vapor pressure of 72 mm at −45° (lit.[17] 74.3 mm at −43.6°).

Preparation of Ethynylphosphonium Salts.—A mixture of the phosphine (0.1 mol) and the haloalkyne (0.1 mol) in 500 ml of ether at *ca.* 25° deposited phosphonium salt in several days. Purification was accomplished by repeated solution of the salt in absolute ethanol followed by slow precipitation with ether. Since some of the phosphonium salts, especially the chlorides, were very hygroscopic, these compounds had to be analyzed as chloroplatinates and tetraphenylborates. We prepared the chloroplatinates from aqueous chloroplatinic acid and the borates from sodium tetraphenylboron in water. The solids were recrystallized from ethanol or acetone–water.

In several cases, *e.g.*, ethynyltributylphosphonium chloride [ir ($CHCl_3$) 3.2 (≡CH) and 4.60 μ (C≡C)] and its derivative (chloroplatinate, mp 224–226°), the expected structures were probably obtained, but the elementary analyses were unsatisfactory. In addition, the alkylhaloalkynes of the preceding section led to products and/or derivatives of uncertain structure. The properties of these unknown materials, *e.g.*, elemental analyses, spectra, melting points, and some speculations concerning their structure, are found in the thesis.[1b]

Phenylethynyltriphenylphosphonium Bromide.—This salt was prepared from phenylbromoethyne (18.1 g, 0.1 mol) and triphenylphosphine (26.2 g, 0.1 mol) in 90% yield, mp 209–211°, ir ($CHCl_3$) 4.55 μ (C≡C) [lit.[4] mp 206°, ir ($CHCl_3$) 4.60 μ (C≡C)].

Anal. Calcd for $C_{26}H_{20}BrP$: C, 70.27; H, 4.50; Br, 17.61. Found: C, 69.87; H, 4.50; Br, 18.02.

The chloroplatinate derivative had mp 208–211°, ir (KBr) 4.67 μ (C≡C).

Anal. Calcd for $C_{52}H_{40}P_2PtCl_6$: C, 55.03; H, 3.52. Found: C, 54.54; H, 3.54.

The bromide (8.8 g) was hydrolyzed in 25% aqueous sodium hydroxide in 2 hr at ~100°; triphenylphosphine oxide (2.7 g), mp 153° from ethanol, and phenylacetylene (0.5 g) were isolated and identified.

Phenylethynyltriphenylphosphonium Chloride.—Phenylchloroacetylene (13.7 g, 0.1 mol) and triphenylphosphine gave a hygroscopic oil in 86% yield, ir ($CHCl_3$) 4.65 μ (C≡C) [lit.[3d] ir ($CHCl_3$) 4.62 μ (C≡C)]. Its ir spectrum was identical with that of phenylethynyltriphenylphosphonium bromide. The chloroplatinate had mp 208–211° and showed no depression in melting point upon admixture with the chloroplatinate of phenylethynyltriphenylphosphonium bromide. The tetraphenylboron derivative had mp 133–136° dec from acetone–water (70:30).

Anal. Calcd for $C_{50}H_{40}BP$: C, 87.97; H, 5.91. Found: C, 87.42; H, 6.27.

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Phenylethynyltributylphosphonium Bromide.—Phenylbromoethyne (18.1 g, 0.1 mol) and tributylphosphine (20.2 g, 0.1 mol) gave an oil in 92% yield. Repeated solution–precipitation yielded white crystals: mp 57–59°; ir ($CHCl_3$) 4.59 μ (C≡C); nmr ($DCCl_3$) 7.55 (m, 5, ArH), 2.32 (6, CH_2), 1.49 (12, CH_2), and 0.9 ppm (9, CH_3).

Anal. Calcd for $C_{20}H_{32}BrP$: C, 62.66; H, 8.30. Found: C, 62.72; H, 8.26.

The chloroplatinate had mp 149–152°.

Anal. Calcd for $C_{40}H_{64}P_2PtCl_6$: C, 47.34; H, 6.28. Found: C, 47.10; H, 6.29.

Phenylethynyltributylphosphonium Chloride.—Phenylchloroethyne (13.7 g, 0.1 mol) and tributylphosphine (20.2 g, 0.1 mol) produced a viscous oil in 83% yield, ir ($CHCl_3$) 4.65 μ (C≡C). The infrared and nmr spectrum of this salt was identical with that of phenylethynyltributylphosphonium bromide. The chloroplatinate had mp 149–152°, ir (KBr) 4.60 μ (C≡C).

Anal. Calcd for $C_{40}H_{64}P_2PtCl_6$: C, 47.34; H, 6.36. Found: C, 46.94; H, 6.28.

Ethynyltriphenylphosphonium Chloride.—Chloroethyne (3.3 g, 0.055 mol) and triphenylphosphine (13.1 g, 0.05 mol) gave 3.1 g of a hygroscopic solid, ir ($CHCl_3$) 3.23 (≡CH) and 4.55 μ (C≡C) [lit.[3d] ir ($CHCl_3$) 3.02 μ (≡CH)], nmr (D_2O) 7.9–8.3 (ArH) and 4.47 ppm (d, J = 28 Hz, HC≡)]. The chloroplatinate had mp 205–207°, ir (KBr) 3.20 μ (≡CH), and an unsatisfactory analysis. The tetraphenylboron derivative had mp 172° dec.

Anal. Calcd for $C_{44}H_{36}BP$: C, 87.13; H, 5.98. Found: C, 86.92; H, 6.28.

Ethynyltriphenylphosphonium Bromide.—Bromoethyne (5.3 g, 0.05 mol) and triphenylphosphine (13.1 g, 0.05 mol) gave 4.3 g of a hygroscopic solid which had an ir spectrum identical with that of ethynyltriphenylphosphonium chloride.

α-(Triphenylphosphonium)-β-(tributylphosphonium)styrene Dibromide.—The reaction between phenylethynyltributylphosphonium bromide (7.6 g, 0.02 mol) and triphenylphosphine (10.5 g, 0.04 mol) was carried out in boiling acetonitrile. After 24 hr, 3.8 g of product was precipitated by the addition of ether and recrystallized several times from acetonitrile–ether: mp 239–241°; ir ($CHCl_3$) 6.15 μ (C=C); nmr ($CDCl_3$) 7.50–8.28 (20, ArH) and 0.65–3.0 ppm (27, alkyl H).

Anal. Calcd for $C_{38}H_{48}P_2Br_2$: C, 62.80; H, 6.66. Found: C, 62.73; H, 6.29.

α,β-Bis(tributylphosphonium)styrene Dibromide.—By the procedure described in the preceding section, phenylethynyltriphenylphosphonium bromide (8.8 g, 0.02 mol) and tributylphosphine (8.1 g, 0.04 mol) gave 3.1 g of the solid product: mp 211–212°; ir ($CHCl_3$) 6.10 μ (C=C); nmr ($CDCl_3$) 7.50–7.99 (5, ArH) and 1.59–3.15 ppm (54, alkyl H).

Anal. Calcd for $C_{32}H_{60}P_2Br_2$: C, 57.65; H, 9.07. Found: C, 57.71; H, 9.15.

Analytical Procedures.[1b] **Halide Analysis.**—A Precision Scientific Titrometer equipped with glass and silver electrodes was used for potentiometric bromide titrations. The silver nitrate solution, which was standardized potentiometrically, was checked by the eosin (0.1%) adsorption indicator method; the two methods agreed to within 0.3%. The bromide in benzyltriphenylphosphonium bromide, a typical salt, was determined to within 0.2% of the calculated value by potentiometric titration. In the kinetic studies, triphenylphosphine appeared to interfere with the bromide analysis. After removal of triphenylphosphine with two ether extractions, 0.5 ml of concentrated nitric acid was added to the aqueous layer and the bromide was estimated by potentiometric titration. DMF, acetone, and phenylbromoethyne did not interfere with the halide titration. In DMF solutions containing triphenylphosphine or phenylbromoacetylene and phenylethynyltriphenylphosphonium bromide in concentration ranges similar to the kinetic experiments, the bromide ion content could be estimated to ±0.25%.

In the kinetic study of phenylchloroethyne with triphenylphosphine in DMF, the amount of ionic chloride could not be determined potentiometrically because of insensitivity at the end point. After removal of the organic compounds with ether, the chloride in the aqueous layer was determined in a Volhard titration. The accuracy of this procedure was established to be 0.5%.

Kinetic Procedures.—The identity of the products under kinetic and synthetic conditions was established, *e.g.*, by ir and melting point. The disappearance of organic halide or nucleophile was followed by gc and paralleled the production of ionic halide. In the first method, aliquots (5 or 10 ml) at 20–25° were distributed among nitrogen-flushed ampoules, which were capped, cooled at −78°, and sealed. In the case of methyl bromide, aliquots (5 ml) of the reaction mixture were distributed with an automatic overflow pipet, which minimized losses by evaporation. For a kinetic run, an ampoule was brought to *ca.* 25° and then immersed quickly, with vigorous shaking, in a constant-temperature bath. After a known interval, the ampoule was removed from the bath, shaken in Dry Ice–acetone, and stored at −78°. For analysis, the ampoules were washed out with several portions of water and acetone and the halide ion was determined.

Because we corrected for the warm-up period (0.5–2.5 min), the uncertainty in the time was usually <2%. Normally, no significant amounts of halide were formed during preparation of the runs or storage of the ampoules. Methyl bromide did, however, show 3–4% reaction blanks. The concentration of our stock methyl bromide solution was found by treating aliquots of it with excess sodium hydroxide until reaction was complete. The amount of blank reaction was found by analyzing the contents of the first and last ampoules of the set to be used in the kinetic run. The mean concentration of unreacted methyl bromide at $t = 0$ was taken as $[CH_3Br]_0$.

Blank experiments on organic halide and solvent indicated that no ionic halide was formed under the reaction conditions. The presence of *ca.* 1% of water had no effect on the rate constants. In the triphenylphosphine reactions, a few ampoules were analyzed to determine whether oxidation had occurred; no triphenylphosphine oxide was detected by gc.

Each kinetic run was followed to at least 75% conversion. The rate constants are defined by the standard second-order expression.[1b] All of the rate constants were corrected for thermal expansion (or contraction). The necessary factors (°C) follow: 0.951 (−25.0), 0.960 (−15.0), 0.970 (−5.0), 0.987 (12.5), 0.974 (0.0), 1.011 (36.3), 1.015 (40.2), 1.021 (46.05), 1.025 (50.0), 1.037 (60.4), 1.037 (60.8), 1.05 (72.2), and 1.065 (86.0).[8] Activation parameters were obtained from Arrhenius plots and the standard expressions

$$\Delta H^{\ddagger} = E_A - RT$$
$$\Delta S^{\ddagger} = 2.303R(\log k - \log kT/h) + \Delta H^{\ddagger}/T \quad (3)$$

In the conductance method, we followed the change in resistance (R) of solutions contained in Freas-type cells by means of a General Radio Impedance Bridge, Model 1650A, operated at 1000 cps. The same results were obtained whether the electrodes were platinized or not. To prevent evaporation of the solutions, the ground stoppers in the cells were greased and held in place by springs. Apiezon N grease was used below 25° and Apiezon T above 25°. We made certain that $1/R$ of the products (salts) were linear functions of their concentrations in the appropriate solvents. Moreover, R of the solutions containing any one reactant or product remained unchanged under the conditions of reaction.

A typical procedure follows. A stock solution (20 ml) of tributylphosphine (10^{-3}–10^{-2} M) was pipetted into a nitrogen-flushed cell. This was immersed to within 0.5 in. of the stopper in a constant-temperature bath. After the solution reached bath temperature, a stock solution (0.1 ml) of the haloalkyne was added to the cell, while it was shaken vigorously. R was followed for at least 3 half-lives. The R's of the reactants in DMF were *ca.* 2–4 × 10^5 Ω; the changes in R during any one run were as low as 18,000 Ω and as high as 120,000 Ω. In all ranges, R could be measured to three significant figures. With a temperature variation of ±0.05°, the accuracy of R was ∼±0.02%.

Since pseudo-first-order conditions were used, the rate law took a simple form (eq 4). R_∞ was determined after 15–20 half-lives. k_ψ was calculated from the slopes of linear plots of log

$$k[\text{Nuc}]t \equiv k_\psi t = 2.303 \log R(R_0 - R_\infty)/(R - R_\infty)R_0 \quad (4)$$

$(R - R_\infty)/RR_\infty$ *vs.* t. Duplicate runs never varied by more than 2% (in k_ψ). The k's were determined from plots of k_ψ *vs.* [Nuc]. Several runs in which the haloalkyne was in large excess led to the same k value. These data are collected in Tables II–VII.

Product Analysis in Some Mechanistically Interesting Systems.—Ampoules containing the phosphine (1.0 M) and the haloalkyne (0.5 M) in 30 ml of methanol–DMF were sealed and placed in constant-temperature baths. At appropriate times the ampoules were removed from the baths, opened, and analyzed. Products

TABLE II

THE REACTION OF PHENYLBROMOETHYNE WITH TRIPHENYLPHOSPHINE IN DMF

Temp, °C	$C_6H_5C{\equiv}CBr$, $M \times 10^3$	$(C_6H_5)_3P$, $M \times 10^3$	$k \times 10^4$,[a] M^{-1} sec^{-1}
86.00 ± 0.03	24.84	55.97	40.8 ± 0.7
	9.033	67.84	41.5 ± 0.8
	90.33	6.784	40.3 ± 0.7
	6.210	69.96	40.7 ± 0.8
			k_{corr} 43.5 ± 0.8
72.20 ± 0.03	24.84	55.97	15.5 ± 0.1
	9.033	67.84	15.5 ± 0.3
	90.33	6.784[b]	15.6 ± 0.3
	6.210	69.96	15.7 ± 0.3
			k_{corr} 16.3 ± 0.3
60.80 ± 0.03	24.84	55.97	6.72 ± 0.08
	9.033	67.84	6.65 ± 0.13
	90.33	6.784	6.60 ± 0.10
	6.210	69.96	6.70 ± 0.12
			k_{corr} 6.91 ± 0.12

[a] k_{corr} is the mean rate constant corrected for solvent expansion. The average deviation of k_{corr} for the four runs is shown while average deviations for the points of an individual run are also given. [b] 0.1% water was added.

TABLE III

THE REACTION OF PHENYLCHLOROETHYNE WITH TRIPHENYLPHOSPHINE IN DMF

Temp, °C	$C_6H_5C{\equiv}CCl$, $M \times 10^2$	$(C_6H_5)_3P$, $M \times 10^2$	$k \times 10^5$,[a] M^{-1} sec^{-1}
60.40 ± 0.05	2.463	7.718	102 ± 2
	7.390	2.573	101 ± 1
	6.569	1.372	104 ± 2
	3.284	6.860	101 ± 2
			k_{corr} 106 ± 2
50.00 ± 0.05	2.463	7.718	50.2 ± 1.8
	7.390	2.573[b]	49.3 ± 0.7
	6.569	1.372	50.7 ± 0.9
	3.284	6.860	48.8 ± 1.3
			k_{corr} 51.0 ± 1.2
40.20 ± 0.03	2.463	7.718	23.8 ± 0.5
	7.390	2.573	23.5 ± 0.8
	6.569	1.372	23.5 ± 0.7
	3.284	6.860	22.3 ± 0.5
			k_{corr} 23.6 ± 0.6

[a] k_{corr} is the mean rate constant corrected for solvent expansion. The average deviation of k_{corr} for the four runs is shown while average deviations for the points of an individual run are also given. [b] 0.1% water was added.

were identified by their ir spectra and their gc retention times (Table I). For quantitative work, samples containing known amounts of *tert*-butylbenzene, an internal standard, and phenylacetylene were made up to 5 ml in DMF–CH_3OH. The accuracy of plots of the ratio of the peak areas of phenylacetylene to *tert*-butylbenzene *vs.* the concentration of phenylacetylene was *ca.* 4–5%. In blank experiments, no phenylacetylene could be detected in solutions of bromo- or chlorophenylacetylene (0.5 *M*) and methanol (12.4 *M*) in DMF which were kept for 4 days at 77°. When phenylethynyltriphenylphosphonium bromide (0.5 *M*) was heated in the same solvent mixture, 3.7% phenylacetylene was produced after 3 days.

The product ratio PR is defined in eq 5. Since we measured $[X^-]$ and $[R'C{\equiv}CH]$, we could only obtain a lower limit to PR

$$PR = \frac{[R'C{\equiv}CPR_3{}^+X^-]}{[R'C{\equiv}CH]} = \frac{[X^-] - [R'C{\equiv}CH] + [CH_3X]}{[R'C{\equiv}CH]} \quad (5)$$

by neglecting $[CH_3X]$ in eq 5. Because of their high reactivity (Table VII), the methyl halides would eventually be consumed and our calculated PR's would approach the true values in long-term ampoules. The expected increase and leveling off of PR can be seen in Tables VIII and IX. For subsequent discussion, we shall use our highest observed values of PR.

Unless a series was run for a certain solution for varying times, all of the single PR values of Tables VIII–X are based on at least two determinations. Where we did have a series we could also estimate crude second-order rate constants based on halide production. The scatter in these k's (and perhaps in PR too) can be ascribed to the fact that, at the high concentrations used, the time for temperature equilibration of the ampoules was comparable to the total reaction time.

TABLE IV

THE REACTION OF PHENYLBROMOETHYNE (8.016×10^{-4} *M*) WITH TRIBUTYLPHOSPHINE IN DMF

Temp, °C	$(C_4H_9)_3P$, $M \times 10^3$	$k\psi \times 10^4$, sec^{-1}	$k \times 10^2$,[a] M^{-1} sec^{-1}
−25.00 ± 0.05	8.115	1.82	2.23
	17.58	3.87	2.20
	26.38[b]	5.73	2.17
	47.48	10.22	2.15
			k_{corr} 2.03 ± 0.03
−15.00 ± 0.05	10.55	3.87	3.67
	20.57	7.02	3.42
	28.49	9.77	3.43
	37.67	12.92	3.43
			k_{corr} 3.23 ± 0.09
−5.00 ± 0.05	8.245	4.43	5.38
	17.11	9.07	5.30
	23.98	12.62	5.27
	32.98	17.00	5.15
			k_{corr} 5.00 ± 0.06

[a] k_{corr}, which is corrected for solvent contraction, is based on a graph of k_ψ *vs.* $[(C_4H_9)_3P]$. The average deviation is from the precision of a mean k for the four runs. The corrected k_{mean} values for the three temperatures are 2.08, 3.35, and 5.12 × 10^{-2}, respectively. [b] 0.1% water was added.

TABLE V

THE REACTION OF PHENYLCHLOROETHYNE (7.785×10^{-4} *M*) WITH TRIBUTYLPHOSPHINE IN DMF

Temp, °C	$(C_4H_9)_3P$, $M \times 10^3$	$k\psi \times 10^5$, sec^{-1}	$k \times 10^3$,[a] M^{-1} sec^{-1}
0.00 ± 0.03	6.24	2.90	4.65
	11.32	5.00	4.42
	24.51	10.82	4.42
	50.88	23.00	4.52
			k_{corr} 4.42 ± 0.08
12.50 ± 0.03	67.36	7.65	11.4
	11.75	13.58	11.6
	24.90	29.00	11.7
	50.49	58.83	11.7
			k_{corr} 11.5 ± 0.1
25.00 ± 0.03	7.215[b]	20.83	28.8
	12.29	34.33	28.0
	25.11	71.83	28.7
	36.78	105.50	28.7
			k_{corr} 28.6 ± 0.3

[a] k_{corr}, which is corrected for solvent contraction, is based on a graph of k_ψ *vs.* $[(C_4H_9)_3P]$. The average deviation is derived from the precision of a mean k for the four runs. The corrected k_{mean} values for the three temperatures are 4.38, 11.4, and 28.6 × 10^{-3}, respectively. [b] 0.1% water was added.

Results and Discussion

Syntheses.—Most alkynylphosphonium compounds have been prepared from a phosphorus halide and an acetylide.[5,18,19] The syntheses of ethynylphosphonium

(18) H. Hartmann, C. Beerman, and H. Czempik, *Z. Anorg. Allg. Chem.*, **287**, 261 (1956).

(19) P. Cadiot and W. Chodkiewicz in "Chemistry of Acetylenes," H. G. Viehe, Ed., Marcel Dekker, New York, N. Y., 1969, Chapter 13.

TABLE VI

THE REACTION OF METHYL BROMIDE WITH TRIPHENYLPHOSPHINE IN DMF

Temp, °C	CH_3Br, $M \times 10^3$	$(C_6H_5)_3P$, $M \times 10^2$	$k \times 10^3$,[a] M^{-1} sec^{-1}
46.05 ± 0.03	32.38	4.523	5.43 ± 0.10
	9.338	6.167	5.22 ± 0.20
	83.00	1.131	5.43 ± 0.15
	66.00	2.035	5.40 ± 0.12
			k_{corr} 5.48 ± 0.15
36.30 ± 0.03	32.38	4.523	2.82 ± 0.15
	9.338	6.167	2.82 ± 0.12
	83.00	1.131	2.88 ± 0.11
	66.00	2.035	2.92 ± 0.15
			k_{corr} 2.89 ± 0.13
25.03 ± 0.03	32.38	4.523	1.38 ± 0.01
	9.338	6.167	1.38 ± 0,01
	83.00	1.131	1.38 ± 0.01
	66.00	2.035	1.36 ± 0.01
			k_{corr} 1.38 ± 0.01

[a] k_{corr} is the mean rate constant corrected for solvent expansion. The average deviation of k_{corr} for the four runs is shown, while average deviations for the points of an individual run are also given.

TABLE VII

RATE DATA FOR PHOSPHINE DISPLACEMENT REACTIONS

Reaction	k, M^{-1} sec^{-1} at 36°	$\Delta H^{\neq}$,[a] kcal/mol	$-\Delta S^{\neq}$,[b] eu
$C_6H_5C{\equiv}CBr$-$(C_6H_5)_3P$	8.45×10^{-5}	16.8[c]	23[c]
$C_6H_5C{\equiv}CCl$-$(C_6H_5)_3P$	1.75×10^{-4}	14.5[d]	29[d]
$C_6H_5C{\equiv}CBr$-$(n\text{-}C_4H_9)_3P$	2.20×10^{-1}	5.4[e]	44[e]
$C_6H_5C{\equiv}CCl$-$(n\text{-}C_4H_9)_3P$	5.92×10^{-2}	11.5[f]	27[f]
CH_3Br-$(C_6H_5)_3P$	2.88×10^{-3}	11.8[g]	31[g]
$n\text{-}C_3H_7Br$-$(n\text{-}C_4H_9)_3P$	6.0×10^{-5} [h]		
$n\text{-}C_3H_7Cl$-$(n\text{-}C_4H_9)_3P$	2.4×10^{-7} [h]		

[a] Uncertainty <1 kcal/mol. [b] Uncertainty <3 eu. [c] At 72.20°. [d] At 60.40°. [e] At −15.00°. [f] At 12.50°. [g] At 36.30°. [h] Reference 24. k was determined at 34.97°. The solvent was acetone.

salts from 1-haloalkynes, as in eq 2, is at least as direct and convenient. The first reports mention fluoroacetylene, chloroacetylene, phenylbromo- and phenylchloroacetylene.[2b,3d,4] In our work, high yields of **1a–d** were obtained in 2–3 days in ether at 25° according to eq 2. For salts **1e–g**, longer reaction times were required and lower yields were obtained.

Like typical phosphonium compounds, the bromides were generally solids while the chlorides were obtained as oils. These could be converted into solid chloroplatinate and tetraphenylboron derivatives which were used for elemental analysis. These salts exhibit a moderately strong ir C≡C stretching band at 2150–2200 cm^{-1} and the ethynylphosphonium compounds also show the characteristic CH band at *ca.* 3200 cm^{-1}. The nmr spectrum of **1b** shows an H–P coupling constant of 28 Hz. Compounds **1** are relatively stable toward heat and oxygen: salts kept for 1 year in contact with atmosphere showed no change in their ir spectra; only at temperatures above 250° is there any appreciable decomposition. In the presence of aqueous refluxing base, however, **1a** decomposed to triphenylphosphine oxide and phenylacetylene. Other nucleophiles, *e.g.*, amines and alkoxides, attack the carbon β to phosphorus, giving vinylphosphonium salts;[4] for example, when **1a** is heated in water, phenacyltriphenylphosphonium bromide is obtained.[4]

Unlike the haloacetylenes and phenylhaloacetylenes, the applicability of process 1 to the alkylhaloacetylenes has not yet been established. This is not because the latter are inert to triphenyl- or tributylphosphine, for we have been able to obtain products (or derivatives) from several of them. At present, we tentatively ascribe the unsatisfactory elementary analyses of these products to the fact that they consisted of mixtures deriving from nucleophilic attack at halogen, at carbon α and at carbon β, as well as from further conversion of the initial products (see below). Judging by our difficulties with the ethynylphosphonium salts, we suggest that the mere observation of salt formation and an ir peak in the C≡C region[3d] is not really a structure proof for **1**.

We have examined the reactions of phenylethynyltributylphosphonium bromide with triphenylphosphine and phenylethynyltriphenylphosphonium bromide with tributylphosphine in acetonitrile. Nmr and elemental analysis indicated that α,β-diphosphonium salts **4** and **5** were formed in 20–25% yield. The overall processes given by eq 6 and 7 do not specify the

$$C_6H_5C{\equiv}\overset{+}{C}P(C_4H_9)_3Br^- + (C_6H_5)_3P \xrightarrow{CH_3CN} C_6H_5C{=}CH\overset{+}{P}(C_4H_9)_3Br^- \quad (6)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (C_6H_5)_3P^+Br^-$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \mathbf{4}$$

$$C_6H_5C{\equiv}\overset{+}{C}P(C_6H_5)_3Br^- + (C_4H_9)_3P \xrightarrow{CH_3CN} C_6H_5C{=}CH\overset{+}{P}(C_4H_9)_3Br^- \quad (7)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (C_4H_9)_3P^+Br^-$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \mathbf{5}$$

origin(s) of the "extra" hydrogen and bromine atoms, but these presumably derive from the reactants and the medium. Since ethynylphosphonium salts (**1**) are activated acetylenes, initial attack by bromine ion or phosphine on **1** is plausible and has precedent.[4,20] The following observations provide support for this idea: triphenylphosphine hydrobromide adds to **1a** in acetonitrile to yield the α,β-bis[triphenylphosphonium]-styrene dibromide[4] or to other alkynes to give vinylphosphonium salts;[21,22] triphenylphosphine reacts with β-bromoacrylic acid in benzene to give α,β-bis[triphenylphosphonium]ethylene dibromide. The formation of **5** involves the substitution of tributylphosphine for triphenylphosphine, the weaker base and nucleophile;[23,24] whether phosphine exchange precedes or follows addition is not determined by our data.

The reactions of phenylbromoethyne with other Group V nucleophiles, triphenylantimony, triphenylbismuth, and triphenylarsenic in boiling xylene (10 hr), failed to produce salts analogous to **1**, although such compounds are known.[19] Since trialkylamines do react,[2a] it appears that basicity may be an important

(20) (a) S. I. Miller and R. Tanaka in "Selective Organic Transformations," B. S. Thyagaragan, Ed., Wiley, New York, N. Y., 1970, p 143; (b) G. Borkent and W. Drenth, *Recl. Trav. Chim. Pays-Bas*, **89**, 1057 (1970).

(21) H. Hoffmann and H. J. Diehr, *Chem. Ber.*, **98**, 363 (1965).

(22) G. Pattenden and B. J. Walker, *J. Chem. Soc. C*, 531 (1969).

(23) W. A. Henderson, Jr., and C. A. Streuli, *J. Amer. Chem. Soc.*, **82**, 5791 (1960); K. Issleib and H. Bruchlos, *Z. Anorg. Allg. Chem.*, **316**, 1 (1962).

(24) W. A. Henderson, Jr., and S. A. Buckler, *J. Amer. Chem. Soc.*, **82**, 5794 (1960).

TABLE VIII

THE REACTION OF $C_6H_5C{\equiv}CBr$ WITH $(C_6H_5)_3P$ (1.0 M) IN DMF AND VARYING CONCENTRATIONS OF METHANOL AT 77°

$[CH_3OH]$, M	$[C_6H_5C{\equiv}CBr]$, $M \times 10$	Time, min	$[C_6H_5C{\equiv}CH]$, $M \times 10^2$	$[Br^-]$,[a] $M \times 10$	PR′[b]	$k \times 10^3$,[c] M^{-1} sec^{-1}
0	3.98	2880	0	3.975		2.2
1.00	5.0	2.0	1.23	0.9915	7.1	2.0
		5.0	1.62	2.439	14	2.7
		15.0	1.59	3.827	23	2.2
		27.0	1.99	3.996	19	1.3
2.47	5.0	25.0	3.92	4.422	10.3	2.1
4.94	5.0	3.0	2.75	1.011	2.7	1.3
		7.0	3.93	2.121	4.4	1.5
		13.5	4.49	4.283	8.5	3.5
		60.0	4.91	4.898	9.0	1.8
6.20[d]	4.02	2880	6.35	4.015	5.3	
8.65	5.0	2.6	6.18	2.115	2.4	4.0
		3.0	6.11	1.983	2.3	3.2
		7.1	8.43	3.351	3.0	3.3
		13.0	9.61	4.402	3.6	4.0
12.4[d]	3.95	2880	13.2	3.950	2.0	
19.8[d]	4.5	2880	29.1	4.470	0.54	

[a] $[Br^-] = [C_6H_5C{\equiv}CP(C_6H_5)_3^+] + [CH_3P(C_6H_5)_3^+]$. [b] PR′ = $([Br^-] - [C_6H_5C{\equiv}CH])/[C_6H_5C{\equiv}CH]$; this ratio is a lower limit to PR; see eq 7. [c] These k's are based on the bromide analyses. They are crude values (see text). [d] Run at 70°.

TABLE IX

THE REACTION OF $C_6H_5C{\equiv}CCl$ (0.5 M) WITH $(C_6H_5)_3P$ (1.0 M) IN DMF AND VARYING CONCENTRATIONS OF METHANOL AT 77°

$[CH_3OH]$, M	Time, min	$[C_6H_5C{\equiv}CH]$, $M \times 10^2$	$[Cl^-]$,[a] $M \times 10$	PR′[b]	$k \times 10^1$,[c] M^{-1} sec^{-1}
0	2880	0	5.0		3.1
2.47	5.0	2.98	3.143	9.5	4.1
	9.0	2.30	3.907	16	3.8
	22.5	3.33	4.670	13	3.2
7.41	3.0	1.48	1.210	7.2	1.7
	8.0	2.43	2.717	10.2	1.9
	13.5	3.78	4.343	10.5	3.6
12.4	3.0	0.843	0.7139	7.4	0.9
	6.0	2.26	2.320	9.3	2.0
	13.0	2.93	3.966	12.5	2.7
	16.2	3.02	3.708	11.3	1.8

[a] $[Cl^-] = [C_6H_5C{\equiv}CP(C_6H_5)_3^+] + [CH_3P(C_6H_5)_3^+]$. [b] PR′ = $([Cl^-] - [C_6H_5C{\equiv}CH])/[C_6H_5C{\equiv}CH]$; this is a lower limit to PR; see eq 7. [c] These k's are based on chloride analyses. They are crude values (see text).

TABLE X

THE PHOSPHINE–PHENYLHALOACETYLENE (R_3P–$R'X$) REACTIONS IN 12.4 M METHANOL IN DIMETHYLFORMAMIDE AT 70°

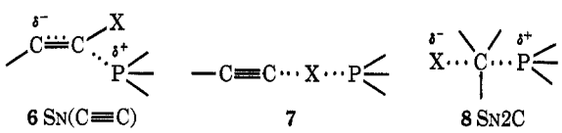
R[a]	X	$[R'X]$, $M \times 10$	$[C_6H_5C{\equiv}CH]$, $M \times 10^2$	PR′[b]	$R'R_3P^+X^-$[c]
n-C_4H_9	Br	4.030	27.1	~0	−
C_6H_5	Br	3.825	11.7	2.3	+
n-C_4H_9	Cl	4.300	22.5	0.91	+
C_6H_5	Cl	4.195	6.0	6.0	+

[a] $[(C_4H_9)_3P] = [(C_6H_5)_3P] = 1.0\ M$. [b] PR′ = $([C_6H_5C{\equiv}CP(C_6H_5)_3{}^+X^-] + [CH_3P(CH_3)_3{}^+X^-] - [C_6H_5C{\equiv}CH])/[C_6H_5C{\equiv}CH]$. Reactions were allowed to proceed to 100% completion. [c] Ethynylphosphonium salts were isolated as chloroplatinates. Analysis by gc showed that R_3PO was also produced in these reactions. At low conversion CH_3X was found by gc.

factor in determining the reactivity of nucleophiles with haloalkynes.

Kinetics.—All of the reactions of haloalkynes and phosphines in DMF proceeded according to eq 1 and produced **1**, as in eq 2. The processes were first order in each reagent. The rate data are given in Tables II–V and VII. Two features of the activation parameters stand out. The negative entropies of activation are comparable to others found for reactions of molecules which produce ions.[25] The $\Delta H^{\ddagger} = 5.4$ kcal/mol and $\Delta S^{\ddagger} = -44$ eu are unusually low for substitution of an organic halide and may indicate a mechanistic discontinuity, a point to which we shall return shortly.

In order to compare reactivities at different carbon sites, we included methyl bromide[26] in our work (Tables VI, VII). At 36°, k (CH_3Br)/k ($C_6H_5C{\equiv}CBr$) = 34 for triphenylphosphine. If, however, we compare Henderson and Buckler's kinetic data for tributylphosphine and the 1-propyl bromide or chloride in acetone[24] with the corresponding data for the phenylhaloacetylenes, the rate ratio k (sp) > k (sp^3). (DMF and acetone are similar solvents for molecule–molecule reactions.[27]) Such comparisons are given here to dispel a general impression about the inertness of haloalkynes in process 1 but they can be misleading for two reasons. The "standard" n-alkyl halide presumably reacts by concerted displacement, while halounsaturates react by stepwise processes. As between halounsaturates and haloalkanes the transition states to be compared are different (**6** or **7** *vs.* **8**). Secondly, broad generaliza-



6 SN(C≡C) **7** **8** SN2C

tions based on specific unreactive systems, *e.g.*, haloalkyne–nucleophile in proton solvents or phenylchloroacetylene–iodide in acetone,[28] simply do not stand up.

To compare reactivities at an unsaturated carbon, we ran the reaction of tributylphosphine with β-bromo-p-nitrostyrene (0.1 mol) in benzene at *ca.* 80°. No ionic bromide (<5%) was found after several days. Pattenden and Walker recently found that activated

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

(26) The first standard we tried was n-butyl bromide, triphenylphosphine in DMF, but elimination rather than displacement occurred.

(27) (a) M. H. Abraham, *Chem. Commun.*, 1307 (1969); (b) A. J. Parker, *Chem. Rev.*, **69**, 1 (1969).

(28) (a) J. A. Nieuwland and R. R. Vogt, "The Chemistry of Acetylene," Reinhold, New York, N. Y., 1945, p 71; (b) M. J. Murray, *J. Amer. Chem. Soc.*, **60**, 2662 (1938).

haloalkenes, *e.g.*, β-haloacrylic acids, reacted readily with tributyl- or triphenylphosphine in benzene but that α- or β-alkyl-β-haloacrylic acids or β-chlorovinyl ketones did not react under forcing conditions.[22] With 1-bromo- and 1-chloro-2,4-dinitrobenzene and phosphines, facile displacement has been found.[1b] Taking into account the activation by substituents, we can set up the following tentative rate sequence for phosphine nucleophiles at an unsaturated carbon site in DMF: k (sp) $\gg$ k (sp^2) $\sim$ k (sp$^{2.5}$).

The effect of methanol in phenylhaloacetylene–triphenylphosphine systems may seem puzzling at first glance (Tables VIII, IX). For phenylchloroacetylene, both the rate constants and the PR are roughly constant, *i.e.*, PR $\cong$ 12.5 $\pm$ 1.5 in 2.5–12.4 M methanol; for phenylbromoacetylene, the rate constant does not vary much, but the PR changes markedly, *i.e.*, PR = 0.54–19 in 1–19.8 M methanol. In the next section, we shall argue that if a single process were involved, one might expect roughly parallel effects, but if two competing processes, a and c of eq 2, are involved and their weights are different for the two substrates, one could expect to find a differentiating medium effect.

Mechanisms.—Detailed mechanisms for *two* alternatives in eq 2, namely attack on the terminal carbon (a) *vs.* attack on halogen (c), will be considered here. Both steps may be rate determining and reversible. Second-order kinetics do not distinguish between them. We must resort, therefore, to other means to establish the competitive nature of process 1.

Consider our "element" effect. It will be recalled that in substitution reactions of organic halides, k (Cl) $\ll$ k (Br), when carbon–halogen bond breaking *is* involved; but k (Cl) $\gtrsim$ k (Br), when carbon–halogen bond breaking *is not* involved in the rate-determining step. The former reactivity order is found in the SN2C reaction of the tributylphosphine and propyl halides (Table VII)[24] and the SN2Hal reaction of triethyl phosphite and 1-halo-3-methylbut-1-yn-3-ols;[2g] the latter reactivity order is found in substitutions at aryl and vinyl carbons.[29] Both orders are found in the phenylhaloacetylenes: with triphenylphosphine k (Cl) > k (Br) and with tributylphosphine k (Cl) < k (Br) (see Table VII). On this basis, we would favor step a for triphenylphosphine and step c for tributylphosphine. Another plausible "arrangement," in which the pattern of activation parameters is taken into account, would assign only the system phenylbromoacetylene–tributylphosphine to path c in eq 2. An interesting situation involves the syntheses triphenylphosphine with fluoro- or chloroacetylene to give **1**;[3d] the fact that fluoroacetylene reacts much more rapidly indicates a strong preference for path a in eq 2.

More direct insight into the mechanism is afforded by those systems in which a trapping agent such as methanol is present. The appearance of parent acetylene with or without product **1** is compelling evidence for the existence of steps c and e in eq 2. The product ratio as defined in eq 5 may now be used to set limits on the competition in eq 2, *i.e.*, PR $\leq$ k_a/k_c. Although such an approach is probably oversimplified here, it appears to apply to the reaction of phenylbromoacetylene with methoxide[2b] and it does convey the essential notion that the substitution process 1 may be more complex than it seems.

If the steady-state assumption is applied to the intermediates **2** and **3** of eq 2, one can derive the product ratio expression eq 8 for a given concentration of methanol. The steady-state assumption would appear to

$$\mathrm{PR} = \frac{k_a k_b (k_c + k_d + k_e[\mathrm{CH_3OH}])}{k_c k_e (k_{-a} + k_b)[\mathrm{CH_3OH}]} + \frac{k_d}{k_e[\mathrm{CH_3OH}]} \qquad (8)$$

be sound, but the possible medium dependence of each k limits the utility of eq 8 to limited regions of solvent composition. For our purposes, it will suffice to outline two of the numerous mechanistic variations following from the kinetic analysis.

In our trapping experiments with methanol (Tables VIII–X), we found that one system was unique; *i.e.*, tributylphosphine and phenylbromoacetylene gave methyl halide, tributylphosphine oxide, phenylacetylene, and none of **1** (Table X). On this basis, we can say that $k_a \simeq 0$ and $k_d \ll k_e[\mathrm{CH_3OH}]$; only the second term on the right hand side of eq 8 survives! By way of contrast, tributylphosphine and phenylchloroacetylene gave these products as well as **1** (Table X). We do not believe that the relatively rapid partitioning of **3** in eq 2 should be highly sensitive to structure. (The possibility that the chloro ion pair is diverted to the substitution product **1** more readily than the ion pair formed from the bromoalkyne is unlikely; phosphorochloridates, for example, undergo nucleophilic displacement at a faster rate than the corresponding fluoridates.[30]) We can conclude that k_d and the second term of eq 8 can be neglected, except when [CH$_3$OH] $\rightarrow$ 0. It thus appears that the reaction of tributylphosphine with phenylbromoacetylene follows step c and with phenylchloroacetylene follows both steps a and c.

We turn to the three remaining systems in which both **1** and phenylacetylene are produced in methanol–DMF. If nucleophilic attack on halogen were exclusive or $k_a \simeq 0$, a plot (eq 8) of PR *vs.* 1/[CH$_3$OH] should be linear, have a slope of k_d/k_e, and pass through the origin. Unfortunately, there is sufficient uncertainty both in the estimated PR values and in the long extrapolation to 1/[CH$_3$OH] = 0 to leave open the question of the limiting slope and intercept. As we have indicated above, it does not appear necessary to include step d in any of our systems when [CH$_3$OH] is moderate or high; thus, we *must* accept a contribution from step a. Further support of the notion of competition between steps a and c comes from the high PR values in 0–8 M methanol. Finally, if the data for phenylchloroacetylene–triphenylphosphine (Table IX) are plotted to test eq 8,[1b] one obtains results which are quite decisive: the intercept of a linear plot is substantial at *ca.* 12 and the slope is zero or negative. We take this as strong evidence for the operation of both steps a and c.

Based on the preceding interpretation, the rate constant for the formation of product **1** in the absence of proton donor would have the form of eq 9. In the case

$$k_{\mathrm{obsd}} = \frac{k_a k_b}{k_b + k_{-a}} + \frac{k_c k_d}{k_d + k_{-c}} \qquad (9)$$

(29) (a) Z. Rappoport, *Advan. Phys. Org. Chem.*, **7**, 1 (1969); (b) J. Miller, "Aromatic Nucleophilic Substitution," Elsevier, Amsterdam, 1968, Chapter 5; (c) S. D. Ross, *Progr. Phys. Org. Chem.*, **1**, 31 (1963).

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of tributylphosphine–phenylbromoacetylene, the first term is small, if not negligible; in the three other phosphine–haloalkyne systems, both terms contribute, the first being more important than the second. Equation 9 does not lend itself to facile interpretation of rate data, *e.g.*, activation parameters, element effects, solvent variations, etc. With some plausible, but *ad hoc*, assumptions, we can obtain the more tractable form, eq 10, and refine our rationalizations: the "abnormal"

$$k_{obsd} \simeq k_a + k_c k_d / k_{-c} \quad (10)$$

activation energy and entropy for tributylphosphine–phenylbromoacetylene (Table VII) is associated with a composite rate constant $k_c k_d / k_{-c}$; the element effect and the activation parameters for the reactions of triphenylphosphine and the phenylhaloacetylenes appear to derive from different mixes of the two terms in eq 10 (or eq 9); the rates of formation of **2**, a dipole, and **3**, an ion pair, in eq 2 have different susceptibilities to added methanol, hence the different behavior of the phenylhaloacetylenes (Tables VIII, IX), etc.

In summary, we have suggested that phenylbromoacetylene tends to favor step c of eq 2 and phenylchloroacetylene takes both branches a and c. The methanol scavenging results, the element effect, and perhaps the activation parameters support this approach. Certainly, the rejection of step a by some chemists was premature. It is clear, however, that careful kinetic and product studies over the whole DMF–CH_3OH solvent range will be necessary before eq 8 can be fully exploited and the mechanistic details filled in. Variations on the mechanisms of process 1 appear in the companion paper.[2a]

Registry No.—Phenylbromoacetylene, 932-87-6; phenylchloroacetylene, 1483-82-5; 1-bromo-1-hexyne, 1119-64-8; 1-chloro-1-hexyne, 1119-66-0; ethynyltributylphosphonium chloroplatinate, 34384-16-2; phenylethynyltriphenylphosphonium bromide, 34387-64-9; phenylethynyltriphenylphosphonium chloroplatinate, 34384-17-3; triphenylphosphine oxide, 791-28-6; phenylethynyltriphenylphosphonium tetraphenylboron, 34384-18-4; phenylethynyltributylphosphonium bromide, 34387-65-0; phenylethynyltributylphosphonium chloroplatinate, 34384-20-8; ethynyltriphenylphosphonium chloroplatinate, 34384-19-5; ethynyltriphenylphosphonium tetraphenylboron, 34384-21-9; α-(triphenylphosphonium)-β-(tributylphosphonium)styrene bromide, 34387-66-1; α,β-bis(tributylphosphonium)styrene dibromide, 34387-67-2; triphenylphosphine, 603-35-0; tributylphosphine, 998-40-3; methyl bromide, 74-83-9.

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Nucleophilic Substitution at an Acetylenic Carbon. Kinetics, Mechanism, and Syntheses with Tertiary Amines[1]

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Haloalkynes cleave one bond at the amine bridgehead to produce ynamines **9** or amides **10**. A number of new substitution products have been obtained with phenylbromo- or phenylchloroacetylene and 1,4-diazobicyclo[2.2.2]octane (Dabco), brucine, dihydrobrucine, quinuclidine, as well as with 2′-(3-chloro-1,1-dimethyl-2-propynyloxy)tetrahydropyran and Dabco. Rate data for the second-order reactions of several halides with Dabco in acetonitrile are ($\Delta H^{\pm}$, kcal/mol; $-\Delta S^{\pm}$, eu; $10^4 k$, M^{-1} sec^{-1} at 60°): $C_6H_5C{\equiv}CBr$ (14.2, 30, 7.95); $C_6H_5C{\equiv}CCl$ (10.7, 40, 10.6); n-C_4H_9Cl (13.8, 34, 1.82). Toward Dabco, the electrophilic order of carbon sites is k (sp) $\geq$ k (sp^2) > k (sp$^{2.5}$). Although Dabco does appear to abstract halogen from the phenylhaloacetylenes, this appears to be far less important than attack on the terminal carbon, which leads to ynamines **2**.

As a part of our interest in nucleophilic displacement reactions at the triple bond, we studied both the synthetic and mechanistic aspects of process 1.[2] When this work was begun, the sp carbon to nitrogen bond system, $-C{\equiv}CN<$, was essentially unknown. In

$$R'C{\equiv}CX + R_3N \longrightarrow (R'C{\equiv}CNR_3{}^+X^-) \quad (1)$$

the meantime, alkynylamines or ynamines have been prepared by several routes and shown to be interesting and useful synthetic intermediates.[3,4] Our present contribution emphasizes the kinetics, mechanism, and some synthetic applications of bridgehead amines in process 1.

Certain complications in reaction 1 are worth attention.[3a] A haloalkyne may form charge transfer complexes, *e.g.*, $C_6H_5C{\equiv}CI \cdot H_2NC_6H_5$.[5] Alternatively, the "positive" halogen may be abstracted by the nu-

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