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Negatively Substituted Acetylenes. III.[1] Reverse Wittig Reactions with Triphenylphosphine Oxide and Triphenylarsine Oxide

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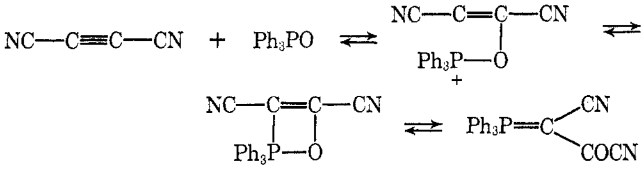
Dicyanoacetylene reacts with triphenylphosphine oxide in a reverse Wittig reaction to give triphenylphosphoranylideneoxalacetonitrile (**1**). The reaction is reversible. The analogous reaction with triphenylarsine oxide proceeds much more readily and is not, as in the case of the phosphine oxide, limited to dicyanoacetylene. Adducts of triphenylarsine oxide with methyl propiolate, dimethyl acetylenedicarboxylate, ethyl phenylpropiolate, and hexafluoro-2-butyne have been obtained.

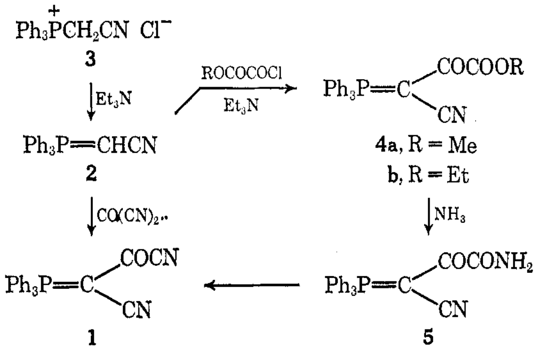
One of the driving forces of the Wittig reaction[2] is the formation of the highly stable phosphorus–oxygen bond.[3] Consequently, reverse Wittig reactions where a P–O bond is broken are rare.[4] We have investigated the reaction of some highly electrophilic acetylenes with triphenylphosphine oxide as well as with triphenylarsine oxide to determine whether reverse Wittig reactions might be observable in these systems. An analogy was available in the reaction of activated acetylenes[5] and benzyne[6] with dimethyl sulfoxide. On the other hand, pyrolysis of a number of acylphosphoranes has been shown to give triphenylphosphine oxide and acetylenes by an intramolecular Wittig reaction.[7]

Results and Discussion

Dicyanoacetylene reacted with triphenylphosphine oxide in benzene at 160° to give triphenylphosphoranylideneoxalacetonitrile (**1**) in 78% yield. The structure of **1** was ascertained by an unambiguous synthesis (Scheme I). Acylation of triphenylphosphoranylideneacetonitrile (**2**) with methyl or ethyl chloroglyoxylate in the presence of triethylamine gave the triphenylphosphoranylidenecyanopyruvates (**4**). Cyanomethyltriphenylphosphonium chloride (**3**) could be used in place of **2**, the latter presumably being formed first by the action of excess triethylamine. Reaction of **4b** with ammonia gave the amide **5**, which on dehydration furnished triphenylphosphoranylideneoxalacetonitrile (**1**). This phosphorane was also obtained, in low yield, by direct cyanoacylation of **2** with carbonyl cyanide.[8]



SCHEME I



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[1] E. Ciganek, *J. Org. Chem.*, **34**, 1923 (1969).

[2] A. Maercker, *Org. React.*, **14**, 270 (1965); A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966.

[3] The dissociation energy of the P–O bond is 130–140 kcal/mol: S. B. Hartley, W. S. Holmes, J. K. Jacques, M. F. Mole, and J. C. McCoubrey, *Quart. Rev. Chem. Soc.*, **17**, 204 (1963).

[4] One such example is the reaction of certain phospholene 1-oxides with isocyanates: T. W. Campbell, J. J. Monagle, and V. S. Foldi, *J. Amer. Chem. Soc.*, **84**, 3673 (1962); J. J. Monagle, T. W. Campbell, and H. F. McShane, Jr., *ibid.*, **84**, 4288 (1962); J. J. Monagle, *J. Org. Chem.*, **27**, 3851 (1962).

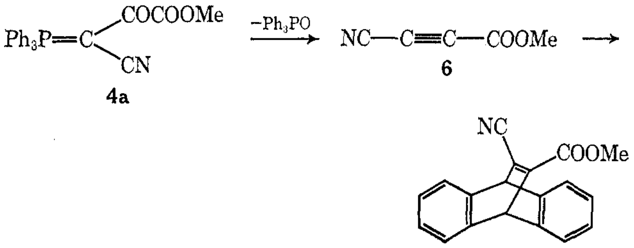
[5] E. Winterfeld, *Chem. Ber.*, **98**, 1518 (1965); E. Winterfeld and H. J. Dillinger, *ibid.*, **99**, 1558 (1966).

[6] R. Kise, T. Asari, N. Furukawa, and S. Oae, *Chem. Ind.* (London), 276 (1967); H. H. Szmant and S. Vazquez, *ibid.*, 1000 (1967); R. Gompper, E. Kutter, and G. Seybold, *Chem. Ber.*, **101**, 2340 (1968).

[7] S. Trippett and D. M. Walker, *J. Chem. Soc.*, 3874 (1959); S. T. D. Gough and S. Trippett, *Proc. Chem. Soc.* (London), 302 (1961); G. Märkl, *Chem. Ber.*, **94**, 3005 (1961); R. Filler and E. W. Heffern, *J. Org. Chem.*, **32**, 3249 (1967).

[8] Carbonyl cyanide frequently reacts like an acid halide; for a review see E. Ciganek, W. J. Linn, and O. W. Webster, "Chemistry of the Cyano Group," Z. Rappoport, Ed., Interscience Publishers, London, 1970, Chapter 9.

Acylation of phosphoranes with alkyl chloroglyoxylates does not appear to have been reported before. Although we have demonstrated such an acylation with only two phosphoranes (**2** and ethyl triphenylphosphoranylideneacetate), it probably is a generally applicable reaction. The phosphoranes **1**, **4**, and **5** are "resonance-stabilized" ylides[2] and thus are stable to oxygen and water at room temperature; **1** could not be alkylated with methyl iodide at 160°, nor did it react with benzaldehyde at that temperature. On pyrolysis at 300°, the phosphorane **1** reverted to triphenylphosphine oxide and dicyanoacetylene; the latter was isolated in 40% yield. Under analogous conditions, the phosphorane **4a** gave methyl cyanopropiolate (**6**) in very low yield in addition to methanol and other unidentified products. The ester **6** was identified by its spectral properties and conversion to the anthracene adduct **7**. These reactions are further examples of the formation of acetylenes by pyrolysis of acylphosphoranes.[7]

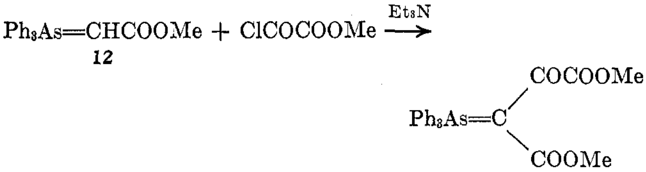


$$Ph_3P{=}C(COCOOMe)(CN) \xrightarrow{-Ph_3PO} NC{-}C{\equiv}C{-}COOMe \longrightarrow$$

4a **6** **7**

The reaction with triphenylphosphine oxide could not be extended to other negatively substituted acetylenes. Thus, no adducts of type **1** could be obtained on treating triphenylphosphine oxide with hexafluoro-2-butyne (160°), cyanoacetylene (160°), and dimethyl acetylenedicarboxylate (120 and 200°). Generation of benzyne in the presence of triphenylphosphine oxide similarly failed to give a 1:1 adduct. However, when triphenylarsine oxide was used instead of the phosphine oxide, methyl propiolate, ethyl phenylpropiolate, dimethyl acetylenedicarboxylate, and hexafluoro-2-butyne, as well as dicyanoacetylene, reacted readily to give the arsenic analogs **10** (Scheme II). The reaction temperatures required ranged from −70° in the case of dicyanoacetylene to +130° in the case of ethyl phenylpropiolate.

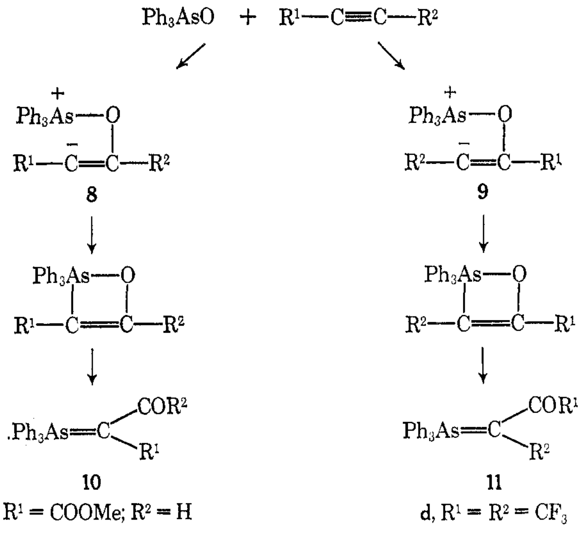
The structure of the dimethyl acetylenedicarboxylate adduct **10c** was proved by independent synthesis from methoxycarbonylmethylenetriphenylarsenic (**12**) and methyl chloroglyoxylate. In principle, two isomeric arsenic ylides could be formed in reactions involving unsymmetrically substituted acetylenes. With both methyl propiolate and ethyl phenylpropiolate, one isomer was formed to the virtual exclusion of the other. The structures of the adducts **10a** and **10b** were assigned on the basis of spectral evidence. The methyl propiolate adduct **10a** shows a one-proton singlet at τ 0.16 due to the aldehyde proton (R^2); the corresponding proton (R^2) in **11a** should absorb at considerably higher field.[9] Furthermore, the infrared spectrum of **10a** shows no band at 1740 cm^{-1}, characteristic of an alkoxycarbonyl group in α position to a keto function. This band is present in **10c** as well as in the related phosphoranes **4a** and **4b**. The ketone band in the ylides **10** occurred at 1530–1600 cm^{-1}, depending on the substituents. In the infrared spectrum of the ethyl phenylpropiolate adduct **10b**, the band at 1740 cm^{-1} again is absent. The observed selectivity is readily rationalized on the basis of the mechanism shown in Scheme II. The alkoxycarbonyl group in the initially formed zwitterion **8** provides better stabilization for the negative charge than does hydrogen and phenyl, respectively, in the alternate intermediate **9**.



$$Ph_3As{=}CHCOOMe + ClCOCOOMe \xrightarrow{Et_3N} Ph_3As{=}C(COCOOMe)(COOMe)$$

12 **10c**

SCHEME II

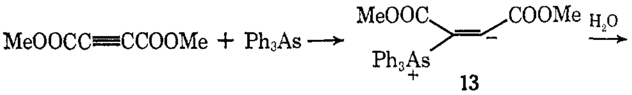


8 **9** **10** **11**

a, R^1 = COOMe; R^2 = H
b, R^1 = COOEt; R^2 = Ph
c, R^1 = R^2 = COOMe
d, R^1 = R^2 = CF_3
e, R^1 = R^2 = CN

Only triphenylarsine (42% yield) was isolated from the reaction of triphenylarsine oxide with cyanoacetylene at 60°. Similarly, no adduct could be isolated when benzyne was generated in the presence of triphenylarsine oxide.

The ylide **10c**, in addition to dimethyl fumarate, has previously been obtained from the reaction of triphenylarsine with dimethyl acetylenedicarboxylate,[10] and a mechanism involving fragmentation of an intermediate 1:2 adduct was proposed. In view of our results it is likely that **10c** arose instead from reaction of the diester with triphenylarsine oxide, the latter having been formed by hydrolysis of the 1:1 adduct **13**. The presence of water was reported[10] to be essential for the success of the reaction.



$$MeOOCC{\equiv}CCOOMe + Ph_3As \longrightarrow \underset{\overset{+}{Ph_3As}}{MeOOC}C{=}\overset{-}{C}COOMe \xrightarrow{H_2O} Ph_3AsO + MeOOCCH{=}CHCOOMe$$

13

The observation that triphenylarsine oxide reacts much more readily with activated acetylenes than does

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(9) The singlet due to the methylene proton in methoxycarbonylmethylenetriphenylarsenic (**12**) occurs at τ 6.8 (in $CDCl_3$).

(10) J. B. Hendrickson, R. E. Spenger, and J. J. Sims, *Tetrahedron*, **19**, 707 (1963).

its phosphorus analog is probably a consequence of the lower bond dissociation energy of the arsenic–oxygen bond[11] compared with that of the phosphorus–oxygen bond, although the relative stabilities of the phosphorus ylides **1** and **4** and of their arsenic analogs **10** may also play a part. A pertinent observation is that triphenylarsine oxide transfers its oxygen to triphenylphosphine.[12] On the other hand, no reaction occurred

$$\mathrm{Ph_3AsO + Ph_3P \xrightarrow[CH_2Cl_2]{105^\circ} Ph_3As + Ph_3PO}$$

between triphenylphosphine and the arsenic ylide **10e** at 110°, nor between triphenylarsine oxide and the phosphorus ylide **1** under similar conditions.

Triphenylstibine oxide reacted at room temperature with dicyanoacetylene, but no pure products could be isolated. Reaction with methyl propiolate at 115° gave methyl phenylpropiolate in 40% yield; the other products were not identified. Elucidation of the mechanism of this curious phenyl transfer reaction awaits further study.

Experimental Section

Triphenylphosphoranylideneoxalacetonitrile (1) from Dicyanoacetylene and Triphenylphosphine Oxide.—A mixture of 5.73 g (20.6 mmol) of triphenylphosphine oxide, 1.974 g (20.6 mmol) of dicyanoacetylene,[13] and 30 ml of benzene, contained in a sealed Carius tube, was heated to 160° for 12 hr. The product was passed through 120 g of Florisil. Elution with 1000 ml of methylene chloride–tetrahydrofuran (98:2) gave 6.09 g of yellow crystals which on crystallization from 30 ml of acetonitrile gave 4.69 g of triphenylphosphoranylideneoxalacetonitrile (1) as yellow crystals, mp 222–223°. Removal of the solvent from the mother liquor and crystallization of the residue from 8 ml of acetonitrile gave an additional 0.97 g of product. The combined yield was 5.66 g (78%): uv max (MeCN) 300 mμ (ε 7900), 275 (7800), 268 (7400), and 225 (sh, 26,000); ir (KBr) 3070, 2190, 1600 (vs), 760 (doublet), and 690 $\mathrm{cm^{-1}}$, among others.

Anal. Calcd for $C_{22}H_{15}N_2OP$: C, 74.58; H, 4.27; N, 7.90; P, 8.74. Found: C, 74.75; H, 4.22; N, 8.05; P, 8.72.

Methyl Triphenylphosphoranylidenecyanopyruvate (4a).—To a mixture of 100 g (0.30 mol) of cyanomethyltriphenylphosphonium chloride,[14] 100 g (1.00 mol) of triethylamine, and 800 ml of methylene chloride was added, with mechanical stirring, during 30 min, a solution of 37 g (0.30 mol) of methyl chloroglyoxylate,[15] the temperature was kept at −60°. The mixture was allowed to warm to 0°, ice and water were added, the layers were separated, and the organic phase was washed with water and concentrated sodium chloride solution and dried ($MgSO_4$). Removal of the solvent and crystallization of the residue from 200 ml of acetonitrile gave 69.5 g (60%) of methyl triphenylphosphoranylidenecyanopyruvate (**4a**), mp 210–211°, as pale yellow crystals. An analytical sample (MeCN) had mp 211–212°: uv max (MeCN) 295 mμ (sh, ε 450), 274 (7000), 268 (3700), and 222 (sh, 27,500); ir (KBr) 2200, 1740, and 1600 (vs) $\mathrm{cm^{-1}}$, among others; nmr ($CDCl_3$) τ 2.2–2.6 (m, 15, Ph) and 6.2 (s, 3, COOMe).

Anal. Calcd for $C_{23}H_{18}NO_3P$: C, 71.31; H, 4.69; N, 3.62. Found: C, 70.86; H, 4.64; N, 3.70.

Ethyl Triphenylphosphoranylidenecyanopyruvate (4b).—To a stirred suspension of 25.62 g (85 mmol) of triphenylphosphoranylideneacetonitrile[16] in a mixture of 13.0 g (0.13 mol) of triethylamine and 200 ml of acetonitrile was added, at 5°, over a period of 30 min, a solution of ethyl chloroglyoxylate (Eastman White Label) in 50 ml of acetonitrile. The mixture was stirred at room temperature for 1 hr, the solvent was removed, and the residue was washed well with water and dried. Crystallization from 70 ml of acetonitrile gave 22.25 g (66%) of ethyl triphenylphosphoranylidenecyanopyruvate (**4b**) as pale yellow crystals. An analytical sample was prepared by recrystallization from acetonitrile. The melting point of both samples was 192° in one determination and 215–216° in a second determination. When a fairly large sample was introduced into the bath at 205°, it melted immediately and then resolidified. The infrared spectrum of the resolidified product, taken immediately, was essentially that of the product before heating, with small differences in the C–H out-of-plane vibration region: nmr ($CDCl_3$) 2.2–2.6 (m, 15), 5.67 (q, 2, *J* = 7 Hz), and 8.65 (t, 3, *J* = 7 Hz); uv max (MeCN) 300 mμ (sh, ε 3900), 274 (7000), 268 (7400), and 225 (26,000); ir (KBr) 2190, 1730, and 1590 $\mathrm{cm^{-1}}$, among others.

Anal. Calcd for $C_{24}H_{20}NO_3P$: C, 71.81; H, 5.02; N, 3.49; P, 7.72. Found: C, 71.57; H, 5.15; N, 3.64; P, 7.79.

Diethyl Triphenylphosphoranylideneoxalacetate.—A solution of 5.40 g (39.6 mmol) of ethyl chloroglyoxylate (Eastman White Label) in 20 ml of acetonitrile was added to a suspension of 15.12 g (39.8 mmol) of ethyl triphenylphosphoranylideneacetate (Aldrich Chemical Co.) in 5.30 g (52.7 mmol) of triethylamine and 100 ml of acetonitrile, and the product was isolated as described for the preparation of ethyl triphenylphosphoranylidenecyanopyruvate. There was obtained 19.20 g of a viscous oil which crystallized partially on standing at room temperature for 2 days. Part of this material (18.11 g) was dissolved in 50 ml of hot ethyl acetate; the cooled solution, after being seeded with a crystal of the product, was allowed to stand at room temperature for 3 days. The crystals were collected by filtration and washed with ethyl acetate, giving 12.50 g (66% yield) of diethyl triphenylphosphoranylideneoxalacetate, mp 135–136°. An analytical sample, prepared by two recrystallizations from ethyl acetate, had mp 136.5–137°: nmr ($CDCl_3$) τ 2.1–2.7 (m, 15), 5.70 (q, 2, *J* = 7 Hz), 6.16 (q, 2, *J* = 7 Hz), 8.67 (t, 3, *J* = 7 Hz), and 9.23 (t, 3, *J* = 7 Hz); uv max (MeCN) 256 mμ (ε 11,000), and 225 (sh, 29,000).

Anal. Calcd for $C_{26}H_{25}O_5P$: C, 69.64; H, 5.62; P, 6.91. Found: C, 69.45; H, 5.65; P, 7.15.

Triphenylphosphoranylidenecyanopyruvamide (5).—In a 400-ml shaker tube were placed 10.15 g (25.3 mmol) of ethyl triphenylphosphoranylidenecyanopyruvate (**4b**) and 100 ml of tetrahydrofuran. Ammonia (28 g, 1.65 mol) was added, and the tube was heated to 90° for 6 hr. The solvent was removed, the residue was dissolved in 150 ml of boiling acetonitrile, and the hot solution was filtered. On cooling, 5.87 g of triphenylphosphoranylidenecyanopyruvamide (**5**) was obtained as tan crystals, mp 264° dec. The mother liquor, on standing for 3 days, deposited another 0.30 g of product. The combined yield was 6.17 g (66%). Two crystallizations from acetonitrile gave an almost colorless analytical sample, mp 266° dec: uv max (MeCN) 304 mμ (ε 6100), 275 (5700), 268 (5400), and 225 (sh, 28,000); ir (KBr) 3410, 3280, 3160, 2180, 1695, 1600, and 1550 $\mathrm{cm^{-1}}$, among others.

Anal. Calcd for $C_{22}H_{17}N_2O_2P$: C, 70.96; H, 4.60. Found: C, 71.00; H, 4.83.

Dehydration of Triphenylphosphoranylidenecyanopyruvamide.—A mixture of 575 mg of triphenylphosphoranylidenecyanopyruvamide, 890 mg of phosphorus pentoxide, and 20 ml of acetonitrile was heated under reflux for 2 hr, cooled, and poured into 50 ml of 10% sodium bicarbonate solution. The product was extracted with methylene chloride; the extracts were washed with water and dried. Removal of the solvent and chromatography of the residue over Florisil gave 78 mg (14%) of triphenylphosphoranylideneoxalacetonitrile (**1**), eluted with methylene chloride–tetrahydrofuran (98:2) and identified by comparison of its infrared spectrum with that of the product obtained in the reaction of dicyanoacetylene with triphenylphosphine oxide.

Reaction of Triphenylphosphoranylideneacetonitrile with Carbonyl Cyanide.—A solution of 705 mg (8.8 mmol) of carbonyl cyanide[17] in 10 ml of acetic acid was added, over 30 min, to a solution of 2.675 g (8.9 mmol) of triphenylphosphoranylideneacetonitrile[16] in 35 ml of acetic acid. The temperature was kept below 20°. The solution was concentrated to dryness at room temperature, giving 3.52 g of a black viscous oil. Chromatography of 1.036 g of this product over 30 g of Florisil gave 35 mg

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[11] F. S. Dainton, *Trans. Faraday Soc.*, **43**, 244 (1947).

[12] A carbon analog of this reaction has been observed in the interaction of methylenetrimethylarsenic with trimethylphosphine to give trimethylarsine and trimethylphosphinemethylene: H. Schmidbauer and W. Tronich, *Inorg. Chem.*, **7**, 168 (1968).

[13] E. Ciganek and C. G. Krespan, *J. Org. Chem.*, **33**, 541 (1968).

[14] G. Wittig and H. Pommer, German Patent 943,648; *Chem. Abstr.*, **52**, 16292 (1958).

[15] S. J. Rhoads and R. E. Michel, *J. Amer. Chem. Soc.*, **85**, 585 (1963).

[16] G. P. Schiemenz and H. Engelhard, *Chem. Ber.*, **94**, 578 (1961).

[17] W. J. Linn, R. E. Benson, and O. W. Webster, *J. Amer. Chem. Soc.*, **87**, 3651 (1965).

(4% yield) of triphenylphosphoranylideneoxalacetonitrile (1), eluted with methylene chloride–tetrahydrofuran (98:2) and identified by its infrared spectrum.

Pyrolysis of Triphenylphosphoranylideneoxalacetonitrile (1).—A flask containing 943 mg of triphenylphosphoranylideneoxalacetonitrile (1) and 13 g of sand was connected to a vertical quartz tube, filled with pieces of quartz tube, 0.5 cm in diameter and 0.5 cm in length. The upper end of the tube was connected to a trap cooled with liquid nitrogen. The tube was heated to 300°. The flask was immersed in an air bath, evacuated to 0.1-mm pressure, and heated slowly, over 5.5 hr, to 280°. The trap contained 83 mg (40% yield) of dicyanoacetylene, identified by its infrared spectrum. The sublimate at the top of the column weighed 669 mg; its infrared spectrum was mostly that of triphenylphosphine oxide with additional bands due to unreacted starting material.

Pyrolysis of methyl triphenylphosphoranylidenecyanopyruvate (**4a**) (30 g, mixed with 30 g of sand) was carried out as described for the pyrolysis of triphenylphosphoranylideneoxalacetonitrile (above). The nmr spectrum of the contents of the liquid nitrogen trap (0.95 g) showed the presence of methanol and other compounds in addition to methyl cyanopropiolate (COOMe at τ 6.1, neat); ir (neat) 2180 and 1740 cm^{-1}, among others. A mixture of 0.68 g of the pyrolysate, 2.20 g of anthracene, and 8 ml of methylene chloride, contained in a sealed Carius tube, was heated to 110° for 6 hr. The solvent was removed from the cooled, filtered solution, and the residue (1.21 g) was chromatographed on 30 g of Florisil. Unreacted anthracene was eluted with hexane–benzene (4:1); the fraction eluted with methylene chloride was crystallized from acetonitrile to give 560 mg (3% based on methyl triphenylphosphoranylidenecyanopyruvate) of methyl 12-cyano-9,10-dihydro-9,10-ethenoanthracene-11-carboxylate, mp 229–230°, unchanged on further recrystallization: uv max (MeCN) 310 mμ (sh, 600), 228 (9400), and 213 (46,500); ir (KBr) 2220, 1710, and 1610 cm^{-1}, among others; nmr τ 2.5–3.0 (m, 8, aromatic H), 4.2 (s, 1, bridgehead), 4.6 (s, 1, bridgehead), and 6.2 (s, 3, COOMe).

Anal. Calcd for $C_{19}H_{13}NO_2$: C, 79.43; H, 4.56; N, 4.88. Found: C, 79.19; H, 4.50; N, 5.13.

Triphenylarsine Oxide.—To remove the water (present as a hydrate or crystal water) in commercial triphenylarsine oxide, a 100-g sample was heated under reflux with 500 ml of benzene under a Dean–Stark trap until no more water distilled (*ca.* 5 hr); 4 ml of water was collected. The arsine oxide initially went into solution and then precipitated out. The cooled mixture was filtered and the solid was dried at 135° (0.1 mm). The sample so prepared no longer showed any OH absorption in the infrared spectrum; in addition, bands at 1660, 870, 755, and 750 cm^{-1}, present in the original sample, had disappeared. All bands reappeared in a sample allowed to stand exposed to the atmosphere overnight.

Reaction of Triphenylarsine Oxide with Methyl Propiolate.—A mixture of 3.47 g of triphenylarsine oxide, 2.67 g of methyl propiolate (Columbia Organic Chemicals Co.), and 20 ml of ethyl acetate was heated under reflux for 65 hr. Removal of the solvent gave 5.00 g of a brown oil. It was redissolved in hot ethyl acetate, the solution was cooled, and the precipitate which formed on scratching was collected by filtration, washed with ethyl acetate, and dried to give 2.00 g (46% yield) of [(formyl)(methoxycarbonyl)methylene]triphenylarsenic (**10a**), mp 148–149°. A sample recrystallized from ethyl acetate had mp 147–148°: uv max (MeCN) 252 mμ (ϵ 13,500); ir (KBr) 2810, 2750, 1650, and 1605 cm^{-1} among others; nmr ($CDCl_3$) τ 0.16 (s, 1, CHO), 2.3–2.7 (m, 15, Ph), and 6.5 (s, 3, COOMe).

Anal. Calcd for $C_{22}H_{19}AsO_3$: C, 65.04; H, 4.72. Found: C, 65.18; H, 4.50.

The nmr spectrum of the mother liquors showed ethyl acetate, [(formyl)(methoxycarbonyl)methylene]triphenylarsenic, as well as a singlet at τ 1.8 which may have been due to [(methoxyoxalyl)-methylene]triphenylarsenic.

Reaction of Triphenylarsine Oxide with Dimethyl Acetylenedicarboxylate.—A mixture of 3.27 g of triphenylarsine oxide, 3.11 g of dimethyl acetylenedicarboxylate, 20 ml of ethyl acetate, and 7 ml of methylene chloride was heated under reflux for 5 min. The solvent was then distilled until the boiling point reached 75°. The precipitate obtained on cooling was collected by filtration, washed with ethyl acetate, and dried to give 2.95 g (62% yield) of [(methoxycarbonyl)(methoxyoxalyl) methylene]triphenylarsenic (**10c**), mp 213–214° dec (lit.[10] mp 214°), unchanged by crystallization from ethyl acetate: uv max (MeCN) 262 mμ (ϵ 10,000) and 220 (30,000); ir (KBr) 1740, 1675, and 1550 cm^{-1}, among others; nmr ($CDCl_3$) τ 2.2–2.7 (m, 15, Ph), 6.1 (s, 3, COOMe), and 6.7 (s, 3, COOMe).

Anal. Calcd for $C_{24}H_{21}AsO_5$: C, 62.08; H, 4.56. Found: C, 62.38; H, 4.63.

Preparation of [(Methoxycarbonyl)(methoxyoxalyl)methylene]-triphenylarsenic (10c) from (Methoxycarbonylmethylene)triphenylarsenic and Methyl Chloroglyoxylate.—A solution of 0.69 g of methyl chloroglyoxylate[15] in 3 ml of anhydrous acetonitrile was added, over 10 min, to a stirred, cooled (ice bath) suspension of 2.00 g of (methoxycarbonylmethylene)triphenylarsenic[18] in 15 ml of acetonitrile and 4 ml of triethylamine. The mixture was stirred at room temperature for 1 hr and then concentrated to dryness. The residue was taken up in methylene chloride–water, the layers were separated, and the aqueous phase was extracted with methylene chloride. The combined organic phases were washed with water and concentrated sodium chloride solution and dried. Removal of the solvent gave 2.05 g of a tan solid. Crystallization from acetonitrile gave 1.60 g (65% yield) of [(methoxycarbonyl)(methoxyoxalyl)methylene]triphenylarsenic (**10c**), identical in melting point and infrared spectrum with the sample prepared from triphenylarsine oxide and dimethyl acetylenedicarboxylate (see above).

Reaction of Triphenylarsine Oxide with Dicyanoacetylene.—To a suspension of 2.23 g of triphenylarsine oxide in 30 ml of toluene was added, with stirring, at −70°, under nitrogen, during 15 min, a solution of 0.57 g of dicyanoacetylene[13] in 5 ml of toluene. The mixture was stirred at −70° for 4 hr and then allowed to come to room temperature overnight. The solid obtained on removal of the solvent was chromatographed on 80 g of Florisil. Elution with benzene–hexane (1:1) gave 33 mg of triphenylarsine. Elution with methylene chloride–tetrahydrofuran (9:1) gave 1.69 g of a solid which on crystallization from methyl ethyl ketone gave 1.08 g of [(cyano)(cyanocarbonyl)methylene]triphenylarsenic (**10e**), mp 216–217°. Another 0.40 g of the product, mp 216–217°, was obtained by removal of the solvent from the mother liquors and crystallization of the residue from methyl ethyl ketone: combined yield 1.48 g, 54%; uv max (MeCN) 297 mμ (ϵ 7900), 270 (6400), 264 (5900), and 220 (sh, 28,400); ir (KBr) 2190, 1590, and 1575 cm^{-1}, among others.

Anal. Calcd for $C_{22}H_{15}AsN_2O$: C, 66.34; H, 3.80; N, 7.03. Found: C, 66.34; H, 3.94; N, 7.17.

Reaction of Triphenylarsine Oxide with Ethyl Phenylpropiolate.—A mixture of 6.86 g of triphenylarsine oxide and 21.16 g of ethyl phenylpropiolate (Columbia Organic Chemicals Co.) was placed in a Carius tube which was sealed and heated to 130° for 21 hr. The excess ethyl phenylpropiolate was removed by shortpath distillation (100° bath temperature, 0.1-μ pressure). The residue was dissolved in 14 ml of hot benzene, 14 ml of cyclohexane was added, and the mixture was allowed to cool slowly. The pale yellow crystals were collected by filtration and washed with cyclohexane–benzene (1:1) to give 9.57 g of [(benzoyl)(ethoxycarbonyl)methylene]triphenylarsenic (**10b**), 90% yield), mp 118–125°. Crystallization of 9.09 g of the crude product from 16 ml of ethyl acetate gave 6.70 g of product, mp 144–145°. An analytical sample, obtained by crystallization from ethyl acetate, had mp 145–146°: uv max (MeCN) 285 (sh, ϵ 6400), 270 (7600), 265 (7700), and 220 (35,400); nmr ($CDCl_3$) τ 2.1–3.0 (m, 20, Ph), 6.3 (q, 2, CH_2), and 9.4 (t, 3, CH_3); ir (KBr) 1670 and 1530 cm^{-1}, among others.

Anal. Calcd for $C_{29}H_{25}AsO_3$: C, 70.16; H, 5.08. Found: C, 70.39; H, 5.07.

Reaction of Triphenylarsine Oxide with Hexafluoro-2-butyne.—In a Carius tube were placed 10 g of triphenylarsine oxide, 20 ml of methylene chloride, and 5 ml of hexafluoro-2-butyne (Columbia Organic Chemicals Co). The tube was sealed under vacuum and heated to 50° for 16 hr. Removal of the solvent and crystallization of the residue from 55 ml of isopropyl alcohol gave 11.18 g (75% yield) of [(trifluoromethyl)(trifluoroacetyl)-methylene]triphenylarsenic (**10d**), mp 157–159°, unchanged by crystallization from isopropyl alcohol: uv max (MeCN) 270 mμ (ϵ 6000), 263 (7200), 258 (7100), 220 (sh, 27,600); ir (KBr) 1570 cm^{-1}, among others; ^{19}F nmr, two quartets of equal intensities at +2395 and +3995 cps from external Freon-11, J = 11.5 cps.

Anal. Calcd for $C_{22}H_{15}AsF_6O$: C, 54.57; H, 3.12. Found: C, 54.86; H, 3.20.

Reaction of Triphenylphosphine with Triphenylarsine Oxide.—A mixture of 1.04 g (32.4 mmol) of triphenylarsine oxide, 0.85 g

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(18) N. A. Nesmeyanov, V. V. Pravdina, and O. A. Reutov, *Dokl. Akad. Nauk SSSR*, **155**, 1364 (1964).

(32.4 mmol) of triphenylphosphine, and 2 ml of anhydrous methylene chloride was placed in a Carius tube which was then sealed under nitrogen and heated to 105° for 4.5 hr (no reaction occurred at room temperature over a period of 3 weeks). The infrared spectrum of the crude product indicated the absence of triphenylarsine oxide (within detectability by this method). Chromatography over Florisil and elution with benzene gave 0.92 g (93%) of triphenylarsine, mp 60–61°, undepressed by admixture of an authentic sample; the product was also identified by its infrared spectrum. Elution with methylene chloride-tetrahydrofuran (7:3) gave 0.81 g (86%) of triphenylphosphine oxide which was identified by comparison of its infrared spectrum with that of an authentic sample. Elution with tetrahydrofuran-methanol (9:1) gave 0.05 g of triphenylarsine oxide hydrate as indicated by its infrared spectrum.

Registry No.—Triphenylphosphine oxide, 791-28-6; triphenylarsine oxide, 1153-05-5; **1**, 23853-23-8; **4a**, 23853-24-9; **4b**, 23853-25-0; **5**, 23853-26-1; **10a**, 23853-27-2; **10b**, 23853-28-3; **10c**, 23853-29-4; **10d**, 23853-30-7; **10e**, 23853-31-8; methyl 12-cyano-9,10-dihydro-9,10-ethenoanthracene-11-carboxylate, 23853-32-9.

Adducts of Acetylenes and Sulfur Dichloride

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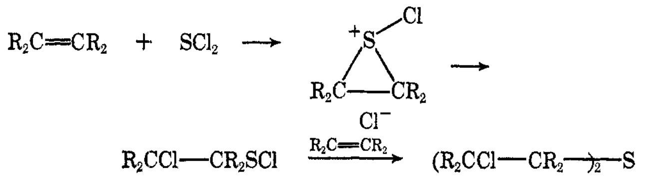
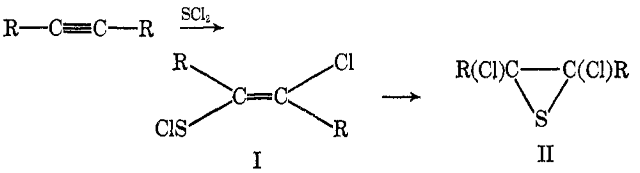
Reactions of selected acetylenes with sulfur dichloride have been studied. Dialkylacetylenes afford the corresponding divinyl sulfides (III) in quantitative yield. Diphenylacetylene provides either 3-chloro-2-phenylbenzo[*b*]thiophene (IV) or the divinyl sulfide VIII, depending upon the reaction conditions. In certain cases it is possible to isolate in good yield the intermediate vinylsulfenyl chloride, which can be utilized in a variety of synthetic schemes. The stereochemistry of the acetylene adducts is *trans*. Orientation of addition to unsymmetrical acetylenes is largely anti-Markovnikov. This orientation has been found to be relatively insensitive to the nature of the solvent. The relative reactivity of sulfur dichloride to olefins and acetylenes follows the usual order of electrophiles except with *trans*-stilbene, which was always the least reactive member in competition experiments.

Interest in the organic chemistry of sulfur dichloride has recently been revived and has led to the syntheses of a number of novel sulfur-containing heterocycles.[1–5] However, the investigations of interactions with multiple bonds to date have been largely limited to reactions of sulfur dichloride and olefins. Surprisingly, no report of a reaction of sulfur dichloride with an acetylene has appeared in the literature. We present here the results of the addition of this versatile reagent to diaryl-, arylalkyl-, and dialkylacetylenes.

From the products (and most importantly their stereochemistry) resulting from reaction of sulfur dichloride and olefinic systems, it has been concluded[1–5] that the mechanistic course of this reaction is the initial formation of an episulfonium ion, which is then opened to an alkylsulfenyl chloride. This latter species may then proceed to products by reaction with another olefinic bond.

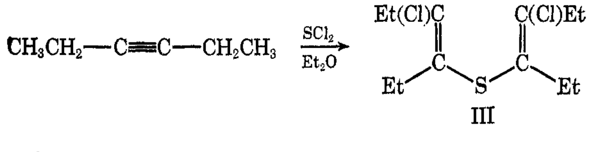


The analogous reaction with alkynes is more difficult to predict, especially in view of the uncertainty of the stereochemistry of electrophilic addition to triply bonded species.[6] However, it has been shown by a number of workers that the addition of sulfenyl halides to alkynes proceeds so as to afford *trans* products almost exclusively.[7–9] Initially it was hoped by us that the final product of this reaction would be a thiirane, thus providing a simple route to this sometimes elusive ring system. By analogy to the reactions of sulfur dichloride with olefins and the reactions of other electrophiles, such as bromine, with acetylenes the initial adduct would be expected to be a vinylsulfenyl chloride (I). Ring closure resulting from internal attack of the sulfenyl chloride upon the adjacent double bond could then provide the thiirane (II).



Results and Discussion

The first acetylene examined in our study was the readily available 3-hexyne. Addition of freshly distilled sulfur dichloride to an ethereal solution of 3-hexyne afforded the divinyl sulfide (III) as a colorless liquid in 95% yield. The structure assigned was founded on the mass spectrum (base and parent peak *m/e* 266), elemental analysis, the nmr spectrum (showing only two nonequivalent ethyl groups), and conversion



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(1) E. J. Corey and E. Block, *J. Org. Chem.*, **31**, 1663 (1966).

(2) E. D. Weil, K. J. Smith, and R. J. Gruber, *ibid.*, **31**, 1669 (1966).

(3) F. Lautenschlaeger, *ibid.*, **31**, 1679 (1966).

(4) F. Lautenschlaeger, *Can. J. Chem.*, **44**, 2813 (1966).

(5) F. Lautenschlaeger, *J. Org. Chem.*, **33**, 2620, 2627 (1968).

(6) T. C. Fahey and D. J. Lee, *J. Amer. Chem. Soc.*, **88**, 5555 (1966), and references cited therein.

(7) A. Dondoni, G. Modena, and G. Scorrano, *Boll. Sci. Fac. Chim. Ind. Bologna*, **22**, 26 (1964).

(8) V. Caló, G. Melloni, G. Modena, and G. Scorrano, *Tetrahedron Lett.*, No. 49, 4399 (1965).

(9) L. DiNunno, G. Gelloni, G. Modena, and G. Scorrano, *ibid.*, No. 49, 4405 (1965).