Synthesis and Nucleophilic Properties of 4-Aryl-5-triphenylphosphonium-1,2,3-triazole Ylides or 4-Aryl-1,2,3-triazol-5-yltriphenylphosphoranes[1]

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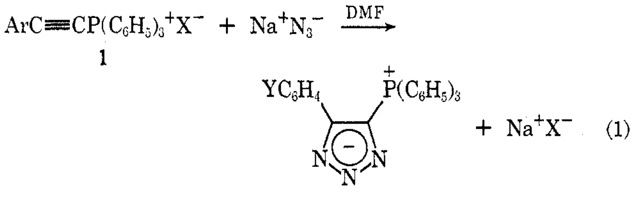
The title heterocyclic compounds have been prepared by the addition of sodium azide to arylethynyltriphenylphosphonium halides in dimethylformamide. In hot basic aqueous solution these ylides hydrolyze to give 4-aryltriazole anion and triphenylphosphine oxide. More notably, the ylides are nucleophilic: displacements of halide from ethyl iodide, benzoyl chloride, ethyl chloroacetate, ethyl β-chloropropionate, 2,4-dinitrobromobenzene, and mercuric chloride and Michael additions to ethyl propiolate have been realized. In all of these examples, the point of attack is exclusively at the 2-nitrogen of the ylide. CNDO calculations on the hypothetical unsubstituted 1,2,3-triazol-4-ylphosphorane indicate a charge density in the molecule which is consistent with a mesoionic or ylide structure.

In exploring the scope of a recently developed approach to the synthesis of *H*-1,2,3-triazoles,[2] we discovered a new family of heterocyclic ylides (**2**). In general, the synthesis involves the addition of azide ion to acetylenes activated by electron-withdrawing groups.[2] Knowing that ethynylphosphonium compounds (**1**) are suitably activated and that nucleophiles add readily to them,[3,4] we carried out process 1 and

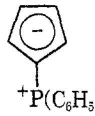


(1)

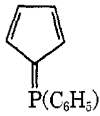
2a, Y = H
b, Y = *p*-Cl

obtained the *H*-1,2,3-triazolyltriphenylphosphoranes (**2**). These ylides or phosphoranes show a pattern of reactivity, particularly as nucleophiles, which often differs markedly from that of typical ylides.[5]

Compounds of type **2** differ from the usual phosphoranes in the same general way that triphenylphosphonium and dimethylsulfonium cyclopentadienylides (**3**, **4**) differ from their respective simpler ylides:



3a (ylide)



3a′ (ylene)

4

they do not undergo the Wittig reaction with carbonyl compounds, they react as nucleophiles rather than as dienes, and they are relatively stable.[5,6] The common structural feature of **2**–**4** is, of course, the delocalization of negative charge (aromaticity) in the five-membered ring. In fact, Yoshida, *et al.*, concluded that the ylide of **3** or **4** is the appropriate (*ca.* 88%) representation in the ground state, while the ylene is more suitable for the excited states.[6b] In this work we describe the first chemistry of **2**, which is quite different from the rather unexceptional properties reported for a number of other heterocyclic systems bearing various phosphorus substituents.[7]

Synthesis of Triazolyl Ylides.—The heterocyclic ylides, 4-aryl-5-triphenylphosphonium-1,2,3-triazoles (**2**), have been prepared by the addition of azide ion to arylethynyltriphenylphosphonium salts in dimethylformamide (DMF). This addition is, in principle, straightforward and similar to some 20 or so other activated additions.[2] A limiting factor would be the availablity of **1**, were it not that the conversions of eq 2

$$\mathrm{ArC{\equiv}CH} \xrightarrow[\mathrm{X\,=\,Br,\,Cl}]{\mathrm{OH^-,OX^-}} \mathrm{ArC{\equiv}CX} \xrightarrow[\mathrm{ether,\,25^\circ}]{\mathrm{(C_6H_5)_3P}} \underset{\mathbf{1}}{\mathrm{ArC{\equiv}CP(C_6H_5)_3{}^+}X^-} \qquad (2)$$

are on record. Admittedly, many acetylenes still have to be prepared in a fairly tedious set of steps,[8] some haloalkynes are still difficult to prepare,[8] our knowledge of ethynylphosphonium salts is still limited,[3] and as yet we have no information on the conversion of alkylethynyl or ethynylphosphonium salts to ylides. However, it does now seem possible to proceed from the stage of the arylhaloalkyne to several ylides (eq 1 and 2) by a one-vessel ("pot") reaction.

By analogy with process 1, we hoped that azide ion would also add to ynamines. Our preliminary results with ethynyltriethylammonium bromide were inconclusive, however.

Reactions of Triazolyl Ylides.—Like many phosphonium salts, the triazolyl ylides (**2**) are soluble in dipolar aprotic solvents such as DMF and alcohol. They are relatively stable, surviving 1 day of heating at reflux in ethanol–water solution; above the melting point, **2a** decomposes at *ca.* 260° while **2b** decomposes at *ca.* 280–300°. In aqueous *basic* solution, the ylides are easily hydrolyzed to afford quantitatively the *H*-1,2,3-triazole and triphenylphosphine oxide (eq 3).

It was of obvious interest to investigate **2** either as a Wittig reagent or as a diene. Heating **2** with benzalde-

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[1] Abstracted from the Ph.D. thesis of Y. T., 1972.

[2] Y. Tanaka and S. I. Miller, *Tetrahedron*, in press.

[3] J. I. Dickstein and S. I. Miller, *J. Org. Chem.*, **37**, 2168 (1972).

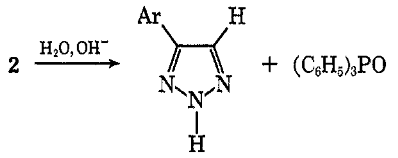
[4] H. Hoffmann and H. Förster, *Tetrahedron Lett.*, 983 (1964).

[5] A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966, (a) Chapters 3–4; (b) Chapter 9.

[6] (a) Z. Yoshida, S. Yoneda, and M. Hazama, *J. Org. Chem.*, **37**, 1364 (1972); (b) Z. Yoshida, K. Iwata, and S. Yoneda, *Tetrahedron Lett.*, 1519 (1971); (c) Z. Yoshida, S. Yoneda, H. Hashimoto, and Y. Murata, *ibid.*, 1523 (1971); (d) Z. Yoshida, S. Yoneda, H. Hashimoto, and Y. Murata, *ibid.*, 1527 (1971).

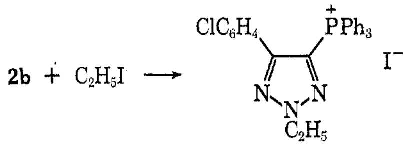
[7] D. Redmore, *Chem. Rev.*, **71**, 315 (1971).

[8] (a) A. Fujii and S. I. Miller, *J. Amer. Chem. Soc.* **93**, 3694 (1971); (b) R.-R. Lii and S. I. Miller, *ibid.*, **95**, 1602 (1973).


(3)

hyde in dimethyl sulfoxide (DMSO) for 48 hr at reflux did not yield the Wittig product. Likewise, treatment of 2 with dienophiles did not give Diels–Alder products but gave Michael adducts (see below).

Triazolyl ylides turn out to be excellent nucleophiles. Heating them with organic halides in chloroform produces stable phosphonium salts (eq 4–7).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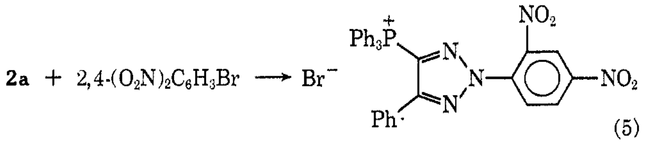
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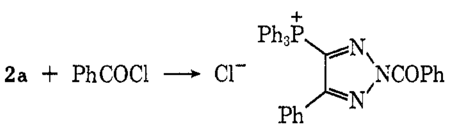
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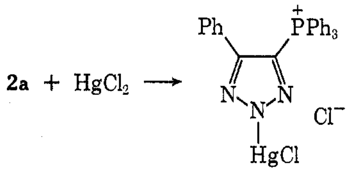
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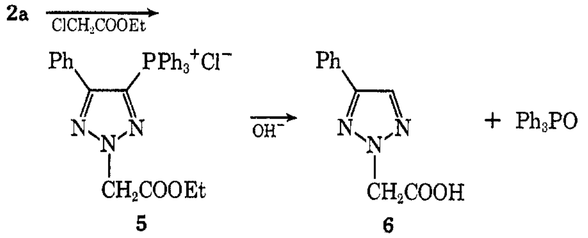
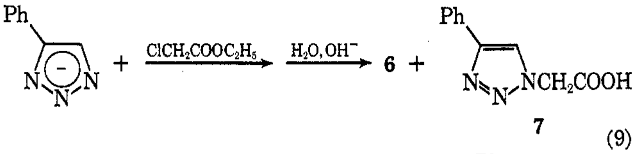
These reactions are analogous to alkylations or acylations of typical phosphoranes, although products of the latter tend to be relatively unstable.[5]

In 2 there are *five* potential sites for attack on the organic halide. This is a general problem in the triazole series which is also treated in a separate paper.[9] To establish that the central nitrogen was the *exclusive* point of attack in 2, we synthesized the possible products in a number of cases. The displacement in eq 8 yields one (**5**) of three plausible products which


(8)

gives 4-phenyltriazol-2-ylacetic acid (**6**) on hydrolysis. This differs from the reaction of 4-phenyltriazole anion with ethyl chloroacetate, in which esters leading to **6** and **7** are produced (eq 9).[9] Both of the isomeric acids (**7**, **8**) were prepared by the alternate route of eq 10. Since the structures of **7** and **8** are predetermined by their mode of synthesis as either 1 or 3 substituted, the remaining isomer (**6**) must be 2 substituted.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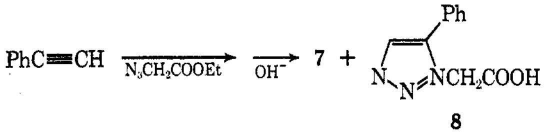
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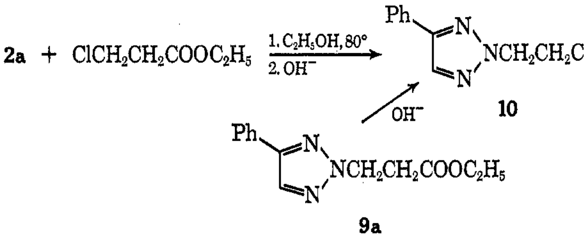
Our general approach of preparing the plausible products by independent routes is also illustrated by the following series of reactions (eq 11–15), among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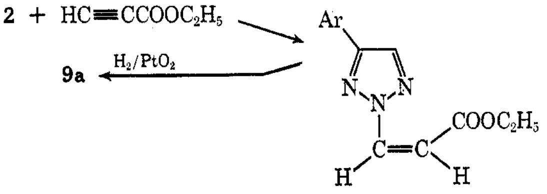
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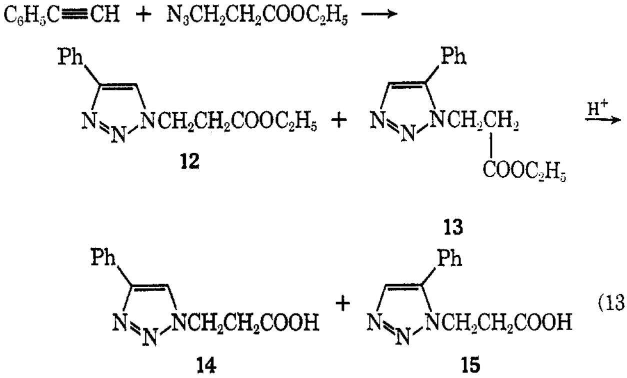
11a, Ar = Ph
b, Ar = p-ClC$_6$H$_4$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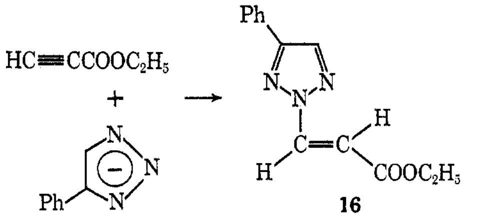
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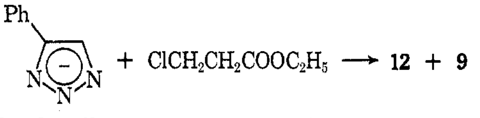
(15)

which the details on eq 13–15 are given in ref 9. Differerences among the propionic esters (**9**, **12**, **13**) would have sufficed to establish the orientation in the displacement process (eq 11), but it was somewhat easier to separate, purify, and identify the acids (**10**, **14**, **15**). Again, the displacement of eq 11 or the Michael addition (eq 12) involve the 2-nitrogen of the ylide. This was established by the sequence outlined in eq 11–15, showing that the final acid product (**9**) was both identical with that of eq 12 and different from the isomeric propionic acids (**14**, **15**).

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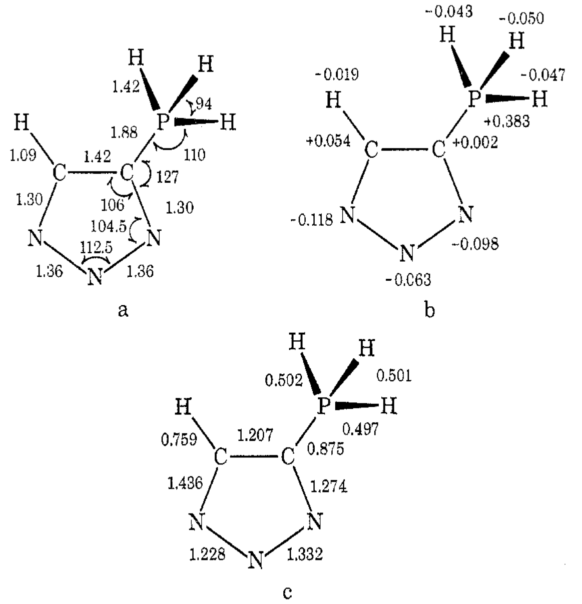
[9] Y. Tanaka and S. I. Miller, *Tetrahedron*, in press.

Incidentally, other workers have shown that the nmr chemical shift of the 5-hydrogen of the triazole may be helpful as an indicator of structure, even with two of the three isomers in hand.[10] When a 4-phenyl is present, we find that $-CH_2COOH$ on 1-, 2-, or 3-nitrogen leads to δ 8.41, 8.16, and 7.81 ppm, respectively, and $-CH_2CH_2COOH$ on 1-, 2-, or 3-nitrogen gives δ 8.31, 8.04, and 7.83 ppm, respectively. The values of δ 8.46 and 7.81 ppm for $-CH_2COOC_2H_5$ on the 1- and 3-nitrogen presumably bracket δ for the 2-substituted compound. Although these data are for acetone-*d* and the chemical shifts will generally be solvent sensitive,[10b,c] their trends could be invaluable in differentiating isomeric triazoles.

Discussion

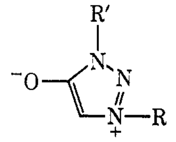
In an attempt to gain some understanding of the properties of *H*-1,2,3-triazoles and their anions, we carried out CNDO calculations on model systems.[9] This CNDO approach has been described[11] and a computer program is available.[12] Our model, given in Chart I, includes our assumed geometry and the calculated atomic charge densities and relative bond energies. Note that our model for the triazolyl ylide or phosphorane is consistent with the ylide representation. That is, there is polarization in the molecule with a net negative charge in the ring (mostly on nitrogen) and a net positive charge outside the ring (mostly on phosphorus). This charge distribution in the ylide is consistent with the nucleophilicity at nitrogen and the susceptibility to basic hydrolysis at phosphorus.

Chart I
CNDO Calculation of
4-Phosphonium-1,2,3-triazolyl Ylide[a]



[a] a, geometry, bond distances, Å, and angles in degrees; b, atomic charge densities; c, relative bond energies.

Comparisons of **2** with several other species are interesting. Compound **3** is one of the more stable compounds in the ylide series. It is not hydrolyzed with aqueous base and does not react with aldehydes or ketones as in the Wittig reaction. Electrophilic attacks on **3**, however, such as diazotization, bromination, Vilsmeier reaction, and Michael anti addition, do occur.[5,6c,d] Likewise, dimethylsulfonium cyclopentadienylide (**4**) reacts with similar electrophiles.[6a] These are properties we have found or can reasonably expect for **2**. By contrast mesoionic triazoles with the opposite arrangement of charges, positive charge inside and negative charge outside the ring, *e.g.*, **17**,[13] react as electrophiles and as Diels–Alder dienes.



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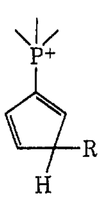

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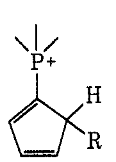

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The directiospecificity of electrophilic attacks on **2**, **3**, and **4** is puzzling. Our tentative conclusions for normal 1,2,3-triazoles are that electronic effects are relatively unimportant in unsubstituted triazoles and that steric effects appear in 4-substituted triazoles.[9] Anions of the former attack at all three nitrogens,[10a] whereas the latter favor the 1 and 2 positions.[9] In **2** we found attachment only to the middle nitrogen, that is, remote from $>P^+$, while in **3** and **4** it has been reported that bond formation is always vicinal to $>P^+$ or $>S^+$.[6] One can suppose that there is a buttressing effect in **2**: the 4-aryl and 5-PPh_3^+ substituents spring apart just enough to partially block the adjacent 1 and 3 positions so that only the middle nitrogen is open for electrophilic attack.

With regard to "explaining" or "predicting" orientation of electrophilic attacks in the species **2**–**4**, the simple quantum methods are still ineffective.[9] In our model for **2** (Chart I), the charge densities (au) on the three nitrogens are, 3-N, −0.118; 1-N, −0.098; and 2-N, −0.063. Of the three nitrogens, the middle one has the lowest electron density, which is not in accord with this being the most nucleophilic site.

With regard to **3**, Yoshida, *et al.*, examined HMO π electron densities and found the order for the 1, 2, and 3 positions to be −1.193, −1.165, and −1.178, respectively.[6b] Because these densities were inconsistent with the observed exclusiveness of 2 attack, Yoshida proposed a one-electron transfer process (16).[6c] Note that electron transfer between reactants is followed by combination of the radical pair. Recently, an addition reaction of **3** was formulated according to an ion pair and Elcb sequence (17).[14] Since we know of no precedent for, or real justification of, scheme 16, we are inclined to be skeptical of it.

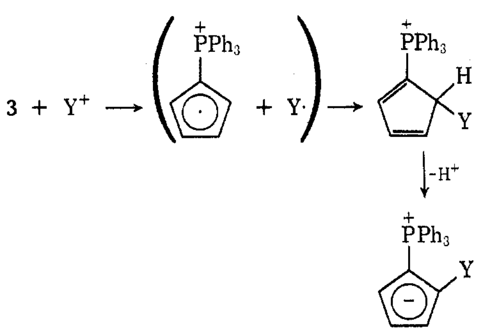
(10) (a) H. Gold, *Justus Liebigs Ann. Chem.*, **688**, 205 (1965); (b) G. Alonso, M. T. Garcia-López, G. Garcia-Muñoz, R. Madroñero, and M. Rico, *J. Heterocycl. Chem.*, **7**, 1269 (1970); (c) G. Garcia-Muñoz, R. Madroñero, M. Rico, and M. C. Saldaña, *ibid.*, **6**, 921 (1969).

(11) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.

(12) Quantum Chemistry Program Exchange, Program 141, P. A. Dobosh, Indiana University, Bloomington, Ind. This program has been modified: A. L. Companion, *Theor. Chim. Acta*, **25**, 268 (1972); *J. Mol. Struct.*, **14**, 117 (1972).

(13) (a) M. Begtrup, *Acta Chem. Scand.*, **26**, 1243 (1972); (b) K. T. Potts and S. Husain, *J. Org. Chem.*, **37**, 2049 (1972), and previous papers.

(14) C. W. Rigby, E. Lord, M. P. Naan, and C. D. Hall, *J. Chem. Soc. B*, 1192 (1971).



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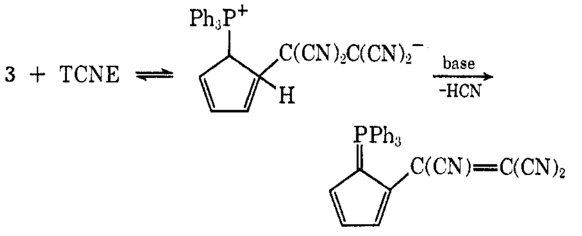

(17)

One can attempt to rationalize the specificities by paying attention to the transition states, or at least to the first intermediates (**18**, **19**) which may be regarded as models for them. Because of the extended rather than branched conjugation, it would seem that, on electronic grounds, **19** would be preferred over **18**, thus explaining the dominance of 2 attack on **3** and **4**. This electronic effect at the 2 position appears to overcome a steric effect which should favor 3 substitutions in **3** and **4**. The validity of this "explanation" could perhaps be decided by further work on the unsubstituted triazolyl ylide.

Experimental Section

All melting points were uncorrected. Infrared spectra were taken on a Beckman IR-8 spectrometer. Nuclear magnetic resonance spectra were obtained on a Varian A-60 instrument using tetramethylsilane as an internal standard. Microanalyses were made by M-H-W Laboratories, Garden City, Mich.

4-Phenyl-5-triphenylphosphonium-1,2,3-triazolyl Ylide (2a).—Phenylethynyltriphenylphosphonium bromide was prepared in 72% yield by Dickstein's procedure given below for the para chloro salt.[3] It had mp 207–209° (lit.[3] mp 206°). To a stirred suspension of sodium azide (1.42 g, 2.8 mmol) in DMF (80 ml), phenylethynyltriphenylphosphonium bromide (9.2 g, 20.8 mmol) in DMF (70 ml) was gradually added at 60° for 30 min. It was kept at 60° for another 2.5 hr. Evaporation of the solvent under reduced pressure gave a white solid, which was taken up in chloroform. After removal of sodium bromide by filtration, the filtrate was evaporated to dryness. The white residue was washed with ether–methylene chloride (1:1) and recrystallized from ether–methylene chloride (2:3) (7.95 g, 93%): mp 240–241°; nmr (CDCl$_3$) δ 7.6 (m, 20 H); ir (CHCl$_3$) 2988, 1485, 1441, 1337, 1110 cm^{-1}; no NH peak.

Anal. Calcd for $C_{26}H_{20}N_3P$: C, 77.02; H, 4.97. Found: C, 76.78; H, 4.74.

p-Chlorophenylethynyltriphenylphosphonium Bromide.—A solution of *p*-chlorophenylbromoethyne[8a] (2.45 g, 11.4 mmol) and triphenylphosphine (2.98 g, 11.4 mmol) in ether (90 ml) was put aside for 6 days. The precipitate was filtered off, washed with ether, and dried thoroughly *in vacuo* (2 mm) (5.04 g, 93%): mp 188–190°; nmr (CDCl$_3$) δ 8.1–7.4 (m, 19 H); ir (CHCl$_3$) 2195, 1590, 1489, 1442, 1113 cm^{-1}.

Anal. Calcd for $C_{26}H_{19}BrClP$: C, 64.02; H, 3.93. Found: C, 64.27; H, 3.85.

4-(p-Chlorophenyl)-5-triphenylphosphonium-1,2,3-triazolyl Ylide (2b).—Although both freshly prepared or aged samples of arylethynyltriphenylphosphonium salts may be used to prepare the ylide, the immediate consumption of these salts is recommended because of their hygroscopic character. *p*-Chlorophenylchloroethyne[8a] (3.61 g, 21.1 mmol) and triphenylphosphine (5.55 g, 21.1 mmol) were left for 5 days in ether at *ca.* 25°. The salt was filtered and its solution in DMF (70 ml) was added dropwise with stirring to a suspension of sodium azide (1.25 g, 19.3 mmol) in DMF (80 ml) at 60° over 20 min and then kept at 60° for 2 hr more. The work-up of compound **2b** was used to obtain a white solid (7.30 g, 86%): mp 278–280° dec; nmr (CDCl$_3$) δ 3.1–2.1 (m, 19 H); ir (CHCl$_3$) 2988, 1487, 1444, 1330, 1112 cm^{-1}. This triazole (4.24 g, 94%) was also prepared from *p*-chlorophenylethynyltriphenylphosphonium bromide (4.89 g, 10.2 mmol) and sodium azide (0.665 g, 10.2 mmol), as described above, mp 276–279° dec.

Anal. Calcd: C, 70.99; H, 4.35. Found: C, 70.88; H, 4.43.

Hydrolyses of 4-Aryl-5-phenyltriphenylphosphonium-1,2,3-triazolyl Ylides (2).—A solution of **2a** (0.350 g, 0.865 mmol), sodium hydroxide (0.100 g, 2.5 mmol), ethanol (5 ml), and water (10 ml) was heated at reflux for 2 hr, cooled, and extracted twice with chloroform. The organic extract gave the phosphine oxide, mp 152–153°, from ether–methylene chloride–hexane (2:1:1) (0.207 g, 86%). The aqueous portion was acidified with hydrochloric acid to give a white precipitate, which was recrystallized from water. The product, 4-phenyl-1,2,3-triazole, was identical with the product we made from phenylacetylene and trimethylsilyl azide[2] and had mp 147–148°. In an analogous experiment, **2b** (0.450 g, 1.01 mmol) gave triphenylphosphine oxide (0.290 g, 89%) and 4-*p*-chlorophenyl 1,2,3-triazole (0.101 g, 72%), mp 162–162.5°. The triazole was identified by comparison with an authentic sample we prepared from *p*-chlorophenylacetylene and trimethylsilyl azide.[2]

When **2b** was heated at reflux in aqueous ethanol or in 10% acetic acid for 1 day, hydrolysis did not take place.

2-Ethyl-4-p-chlorophenyl-5-triphenylphosphonium-1,2,3-triazole Iodide.—A solution of **2b** (0.418 g, 0.947 mmol) and iodoethane (0.155 g, 0.994 mmol) in chloroform (10 ml) was refluxed for 10 hr. Evaporation of the solvent deposited a white solid (0.402 g, 71%) which was recrystallized from methylene chloride–ether (1:1): mp 219–222°; nmr (CDCl$_3$) δ 1.73 (t, J = 7.2 Hz, 3 H), 4.71 (q, J = 7.2 Hz, 2 H), 8.1–7.1 (m, 20 H); ir (KBr) 1604, 1586, 1485, 1442, 1112 cm^{-1}.

Anal. Calcd for $C_{28}H_{24}ClIN_3P$: C, 56.44; H, 4.06. Found: C, 56.14; H, 3.96.

2-Benzoyl-4-phenyl-5-triphenylphosphonium-1,2,3-triazole Chloride.—A solution of **2a** (0.490 g, 1.31 mmol) and benzoyl chloride (0.193 g, 1.38 mmol) in chloroform (10 ml) was refluxed for 20 hr. A white solid which gradually precipitated was filtered off. The filtrate was evaporated to give a residue which was combined with the precipitate obtained above and then recrystallized from methylene chloride–ether (3:1): yield 0.635 g (94%); mp 299–305° dec; nmr (CDCl$_3$) δ 2.9–1.7; ir (Nujol) 2200–2400 (broad), 1544, 1184, 1111, 980 cm^{-1}.

Anal. Calcd for $C_{33}H_{25}ClN_3OP$: C, 72.59; H, 4.62. Found: C, 72.76; H, 4.55.

2-o,p-Dinitrophenyl-4-phenyl-5-triphenylphosphonium-1,2,3-triazole Bromide.—A solution of **2a** (0.439 g, 1.08 mmol) and 2,4-dinitrobromobenzene (0.268 g, 1.08 mmol) in chloroform (10 ml) was heated at reflux for 22 hr. Removal of the solvent gave a yellow solid, which was washed with ether (3 × 5 ml). After drying under vacuum, it was recrystallized from methylene chloride–benzene (1:4) to give yellow crystals (0.470 g, 67%): mp 95–96°; ir (Nujol) 1604, 1540, 1111, 980 cm^{-1}.

Anal. Calcd for $C_{32}H_{23}BrN_5O_4P$: C, 58.91; H, 355. Found: C, 58.79; H, 3.68.

2-Chloromercuric 4-Phenyl-5-triphenylphosphonium-1,2,3-triazole Chloride.—Compound **2a** (0.106 g, 0.261 mmol) in methanol (2 ml) was mixed with mercuric chloride (0.065 g, 0.240 mmol) in methanol (1 ml). The mixture was kept at 20° for 2 hr, while a white solid deposited gradually. The solid was filtered off and well washed with methanol (113 mg, 70%), mp 231–234°, ir (Nujol) 1112 cm^{-1}.

Anal. Calcd for $C_{26}H_{20}Cl_2HgN_3P$: C, 46.13; H, 2.98. Found: C, 45.76; H, 3.03.

4-Phenyl-1,2,3-triazol-2-ylacetic Acid (6).—A solution of 4-phenyl-5-triphenylphosphonium-1,2,3-triazolyl ylide (0.518 g, 1.28 mmol) and ethyl chloroacetate (0.173 g, 1.40 mmol) in chloroform (5 ml) was refluxed for 20 hr and then evaporated. The nmr spectrum of the first product, a phosphonium salt, had δ 5.66 (-$C_2N_3CH_2COO$-). This hygroscopic residue was treated with 10 ml of 5% sodium hydroxide in methanol–water (1:4), heated at reflux for 3 hr, and evaporated under vacuum. The remaining aqueous solution was extracted with ether (10 ml) from which triphenylphosphine oxide (0.250 g, 70%) was eventually obtained. The aqueous layer was acidified to give a white solid which was crystallized from benzene (0.160 g, 79%): mp 199–200°; nmr (acetone) δ 5.37 (s, 2 H), 6.90 (broad, 1 H), 7.45 (m, 3 H), 7.90 (m, 2 H), 8.16 (s, 1 H).

Anal. Calcd for $C_{10}H_9O_2N_3$: C, 59.11; H, 4.46. Found: C, 58.78; H, 4.67.

We also traced this reaction by nmr. A solution of 4-phenyl-5-triphenylphosphonium-1,2,3-triazolyl ylide (0.06 g, 0.15 mmol) and ethyl chloroacetate (0.024 g, 0.20 mmol) in chloroform-*d* (0.800 ml) was heated at 60° and the nmr spectrum of the solution was checked after 1 and 2 days. After 2 days this solution was worked up as described above and again the product was checked by nmr; only **6** was observed.

Ethyl *cis*-(4-Phenyl-1,2,3-triazol-2-yl)acrylate (11a).—A solution of 4 phenyl-5-triphenylphosphonium-1,2,3-triazolyl ylide (0.798 g, 1.97 mmol) and ethyl propiolate (0.196 g, 2.0 mmol) in ethanol (10 ml) was heated at reflux. After 2 hr, water (0.1 ml) was added, and the solution was refluxed for another 20 hr and then evaporated. The oily residue was taken up in ether and washed with water, dried, and chromatographed on silica gel with ether. A white solid (0.35 g, 73%) was obtained: mp 54–56°; nmr (CCl_4) δ 7.87 (s, 1 H), 7.75 (m, 2 H), 7.35 (m, 3 H), 7.17 (d, J = 10.1 Hz, 1 H), 5.64 (d, J = 10.1 Hz, 1 H), 4.24 (q, J = 7.1 Hz, 2 H), 1.25 (t, J = 7.1 Hz, 3 H); ir (CCl_4) 2980, 1734, 1666, 1613, 1481, 1462, 1422, 1200, 1092, 1033, 982 cm^{-1}. The assignment of the cis rather than the trans structure to this ester was made on the basis of nmr (J_{HH} = 10.1 Hz) and ir (1637 cm^{-1}) and by analogies to similar additions.[9] The other isomer was assigned the trans structure in the same way.

Anal. Calcd for $C_{13}H_{13}N_3O_2$: C, 64.18; H, 5.39. Found: C, 63.99; H, 5.46.

Ethyl β-(4-Phenyl-1,2,3-triazol-2-yl)propionate (9a).—To a suspension of platinum oxide (0.04 g) in ethyl acetate (5 ml) was added 0.125 g (0.51 mmol) of **11a**. The hydrogenation was carried out with a pressure of hydrogen of 3–4 atm for 1 hr; the solution was then treated with ethanol (10 ml) and water (2 ml) and filtered to remove the catalyst. The filtrate was extracted with dichloromethane and washed with water. Removal of the solvent yielded the ester **9a** (0.110 g, 89%): nmr (CCl_4) δ 7.73 (s, 1 H), 7.65 (m, 2 H), 7.30 (m, 3 H), 4.67 (t, J = 7.1 Hz, 2 H), 4.09 (q, J = 7.1 Hz, 2 H), 2.95 (t, J = 7.1 Hz, 2 H), 1.20 (t, J = 7.1 Hz, 3 H); ir (CCl_4) 1738, 1192, 1095, 1026, 982 cm^{-1}. This nmr spectrum is similar to the one obtained on the same compound prepared by eq 15.[9]

β-(4-Phenyl-1,2,3-triazol-2-yl)propionic Acid (10).—A solution of 4-phenyl-5-phenylphosphonium-1,2,3-triazolyl ylide (0.620 g, 1.43 mmol) and ethyl 3-chloropropionate (0.220 g, 1.61 mmol) in ethanol (10 ml) was heated at reflux for 2 days and then evaporated. The residue was dissolved in aqueous sodium hydroxide and heated at *ca.* 100° for 15 min. On cooling, the solution, which deposited triphenylphosphine oxide (0.380 g, 93%), was filtered. The filtrate was washed twice with ether and then acidified with 10% hydrochloric acid to give a white solid. This acid was recrystallized from water–methanol (4:1) to give **10**: yield 0.190 g (58%); mp 145–146°; nmr (acetone) δ 8.04 (s, 1 H), 7.90 (m, 2 H), 7.42 (m, 3 H), 4.74 (t, J = 7.1 Hz, 2 H), 3.09 (t, J = 7.1 Hz, 2 H); ir (Nujol) 3120, 1730, 1408, 1214, 1181, 1100, 983 cm^{-1}.

Anal. Calcd for $C_{11}H_{11}N_3O_2$: C, 60.82; H, 5.11. Found: C, 61.24; H, 5.04.

In an alternate synthesis of **10**, **9a** (0.058 g) was heated in aqueous sodium hydroxide (5 ml) and neutralized with 10% hydrochloric acid. The white solid (100% yield) had mp 143–144°; the nmr spectra (acetone) was identical with that obtained above.

β-(4-Phenyl-1,2,3-triazol-1-yl)propionic Acid (14) and β-(5-Phenyl-1,2,3-triazol-1-yl)propionic Acid (15).—Ethyl β-azidopropionate was prepared by heating ethyl β-chloropropionate (13.5 g, 0.092 mol) and sodium azide (7.5 g, 0.115 mol) in 1:1 water–ethanol (20 ml) for 24 hr. Work-up and distillation gave ethyl β-azidopropionate (1.95 g, 15%): bp 47–48° (0.8 mm) [lit.[15] bp 62° (5 mm)]; nmr (CCl_4) δ 4.15 (q, J = 7.2 Hz, 2 H), 3.54 (t, J = 6.7 Hz, 2 H), 2.51 (t, J = 6.7 Hz, 2 H), 1.25 (t, J = 7.2 Hz, 3 H); ir (film) 2980, 1733, 1480, 1185, 1030 cm^{-1}. A solution of phenylacetylene (1.40 g, 13.9 mmol) and azido ester (1.79 g, 12.5 mmol) in toluene (9 ml) was heated at reflux for 3 days and evaporated. The liquid residue consisted of roughly equal amounts of **14** and **15** according to its nmr spectrum: δ (CCl_4) 8.11 (1,4 isomer) and 7.58 (1,5 isomer). An attempted separation of the isomers by chromatography on silica gel failed. The mixture was then hydrolyzed in aqueous sodium hydroxide at *ca.* 100° for 10 min and worked up. Repeated recrystallization from water–methanol (v/v 1:1) yielded **14** in the first fractions: mp 177–179°; nmr (acetone) δ 8.31 (s, 1 H), 7.85 (m, 2 H), 7.34 (m, 3 H), 4.72 (t, J = 7.0 Hz, 2 H), 3.06 (t, J = 7.0 Hz, 2 H); ir (Nujol) 1695, 1223, 1080, 980, 914, 842 cm^{-1}. The later fractions yielded **15**: mp 120–121°; nmr (acetone) δ 7.73 (s, 1 H), 7.56 (s, 5 H), 4.46 (t, J = 7.0 Hz, 2 H), 3.04 (t, J = 7.0 Hz, 2 H); ir (Nujol) 1710, 1408, 1223, 1151, 1121, 983, 944, 845 cm^{-1}.

Anal. Calcd for $C_{11}H_{11}N_3O_2$: C, 60.82; H, 5.11. Found for **14**: C, 61.07; H, 5.08; Found for **15**: C, 60.98; H, 5.15.

Ethyl *cis*-(4-*p*-Chlorophenyl)-1,2,3-triazol-2-ylacrylate (11b).—A solution of 4-(*p*-chlorophenyl)-5-triphenylphosphonium-1,2,3-triazolyl ylide (0.600 g, 1.36 mmol) and ethyl propiolate (0.140 g, 1.43 mmol) in ethanol (20 ml) was heated at reflux for 10 hr. Water (0.1 ml) was added, and the solution was refluxed for 10 hr and evaporated. The oily residue was taken up in ether (8 ml), and hexane (1 ml) was added. A precipitate appeared which was filtered off; the filtrate was chromatographed on alumina with ether. The first eluate included **11b**, which separated on removal of ether (0.195 g, 52%): nmr (CCl_4) δ 1.26 (t, J = 7.2 Hz, 3 H), 4.25 (q, J = 7.2 Hz, 2 H), 5.71 (d, J = 9.9 Hz, 1 H), 7.11 (d, J = 9.9 Hz, 1 H), 7.85–7.25 (m, 4 H), 7.90 (s, 1 H); ir (film) 1729, 1664, 982 cm^{-1}.

Anal. Calcd for $C_{13}H_{12}ClN_3O_2$: C, 56.22; H, 4.36. Found: C, 55.96; H, 4.37.

The next eluate gave triphenylphosphine oxide (0.26 g, 69%).

The possibility of syn *vs.* anti addition was investigated briefly. A solution of *p*-chlorophenyltriphenylphosphonium triazoyl ylide (0.035 g, 0.08 mmol), ethyl propiolate (9 μl), and a drop of water in dimethylacetamide (0.40 ml) was charged into an nmr tube and kept at −25° for 5 days. The nmr spectrum indicated 70% of the cis product (anti addition) and 30% of the trans product (syn addition): δ of $-CH{=}CHCO_2C_2H_5$ 5.60 (trans, J = 14.0 Hz), 5.13 (cis, J = 9.8 Hz).

Reaction of Ethynyltriethylammonium Bromide with Sodium Azide.—Ethynylammonium bromide was prepared in 37% yield, as described by Tanaka.[16] Several attempted additions of sodium azide to this ynamine in DMF (1 hr at *ca.* 25°), THF (1 hr at reflux), or triethylamine (1 hr at reflux) were attempted. Although reactions occurred, the products could not be isolated.

Registry No.—**1** (Ar = Ph; X = Br), 34387-64-9; **1** (Ar = *p*-ClC_6H_4; X = Br), 40139-22-8; **2a** ylide form, 40330-41-4; **2a** ylene form, 40139-23-9; **2b** ylide form, 40110-56-3; **2b** ylene form, 40139-42-2; **6**, 40139-43-3; **9a**, 40139-44-4; **10**, 40139-45-5; **11a**, 40132-84-1; *trans*-**11a**, 40132-85-2; **11b**, 40132-86-3; *trans*-**11b**, 40132-87-4; **14**, 40139-46-6; **15**, 40139-47-7; *p*-chlorophenylchloroethyne, 33491-02-0; triphenylphosphine, 603-35-0; 4-phenyl-1,2,3-triazole, 15965-35-2; 4-*p*-chlorophenyl-1,2,-3-triazole, 34108-73-1; 2-ethyl-4-*p*-chlorophenyl-5-triphenylphosphonium-1,2,3-triazole iodide, 40139-51-3; iodoethane, 75-03-6; 2-benzoyl-4-phenyl-5-triphenylphosphonium-1,2,3-triazole chloride, 40139-52-4; benzoyl chloride, 98-88-4; 2-*o*,*p*-dinitrophenyl-4-phenyl-5-triphenylphosphonium-1,2,3-triazole chloride, 40139-53-5; 2,4-dinitrobromobenzene, 584-48-5; 2-chloromercuric 4-phenyl-5-triphenylphosphonium-1,2,3-triazole chloride, 40139-54-6; mercuric chloride, 7487-94-7; ethyl chloroacetate, 105-39-5; ethyl propiolate, 623-47-2; ethyl 3-chloropropionate, 623-71-2; ethyl β-azidopropionate, 40139-55-7; sodium azide, 12136-89-9.

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