(from the acetylene and methyllithium) was substituted for the Grignard reagent. This method gives yields of 70%, about 15% lower than the other method: ^{1}H nmr δ 1.20 (s, 9 H), 1.44 (s, 6 H), 2.12 (s, 1 H); ir 3400 (broad), 2255 cm^{-1}.

2-Chloro-2,5,5-trimethyl-3-hexyne (3) was prepared as before[1,2] by passing HCl gas through a pentane solution of **2** at −15° for 6 hr. The yield was 85%:[12] ^{1}H nmr δ 1.21 (s, 9 H), 1.78 (s, 6 H); ir 2260 cm^{-1}.

Reaction of 3 with Methyllithium (Supplied by PCR). A. Addition of 3 to Methyllithium.—To 15.4 ml (37 mmol) of freshly opened 2.4 *M* methyllithium in ether at room temperature under nitrogen was added a solution of 4.00 g (25.2 mmol) of **3** in 5.0 ml of ether over 60 min. The mixture was stirred magnetically throughout the reaction. The solution became cloudy (suspended lithium chloride) about 30 min after addition ceased. After 24.7 hr 20 ml of water-saturated ether was added to the milky suspension, followed by 7 ml of ether-saturated water, and 2 ml of 1 *N* sulfuric acid to partially neutralize the solution. The ether phase was separated and immediately analyzed by glc. The aqueous phase was neutralized and extracted with 3 × 10 ml of ether. The combined ether solutions were washed once with saturated aqueous sodium chloride and dried at room temperature over molecular sieves. Product isolation is described below.

B. Addition of Methyllithium to 3.—To a solution of 1.77 g (11.2 mmol) of **3** in 2.0 ml of ether at room temperature under nitrogen was added 6.26 ml (15 mmol) of 2.6 *M* methyllithium in ether over 60 min. Cloudiness became apparent immediately. After 24.3 hr the mixture was worked up as above and analyzed.

C. Product Isolation.—The ether solutions from A and B, containing the total products from 36.4 mmol of **3**, were combined and found to exhibit the mole ratio of 1:5:4 of 59.8:24.9:15.3. Since 1 mol of **4** derives from 2 mol of **3**, the above mixture should contain (assuming quantitative yield) 2.61 g of **1**, 1.09 g of **5**, and 1.18 g of **4**, totaling 4.88 g. The solution was slowly distilled at 1 atm through a 9-in. Vigreux column until nearly all of the ether had been collected (bp 34°). This ether contained $<10^{-2}$ mol % **1**. The pot residue (4.90 g), containing 5% ether by glc, was flash distilled down to 0.2 mm into a Dry Ice–acetone cooled receiver. The distillate (2.62 g) was redistilled to yield 2.24 g (45%) of ether, **1**, and **5** in the mole ratio 5:69.7:24.1. The boiling point of this mixture was 56–77° (152 mm); earlier fractions were richer in **1**, later fractions in **5**. When run on the mole scale, distillation alone will separate **1** from **5**,[1,2] while at this level preparative glc is preferable.

Di-*tert*-butylacetylene (1)[1-3] had ^{1}H nmr δ 1.17; ir no C≡C discernible.[9]

2,2,3,5-Tetramethyl-3,4-hexadiene (5)[3] had ^{1}H nmr δ 1.01 (s, 9 H), 1.62 (s, 3 H), 1.65 (s, 6 H); ir 1960 cm^{-1}.

Isolation of 4.—The combined semisolid residues from the flash and subsequent distillations were combined (2.6 g) and sublimed at 0.15 mm bulb-to-bulb to give 1.10 g (12%) of crude **4**. The sole contaminant was 5% of a minor product with slightly greater retention time.[17] Acetonitrile recrystallizations gave a high recovery of material with mp 109–110°, still contaminated with 3% of the minor product. Three recrystallizations of the crude material from ethanol gave >99% pure **4**, mp 112.4–112.7°, but the recovery was only 20–30%. The spectral data for **4** are given in the text.

Reaction of 3 with Pyridine.—To an nmr tube containing 40 mg of **3** and 2 drops of TMS was added 0.4 ml of dry pyridine. The tube was sealed and heated to 88° for 44 hr. Upon cooling the solution deposited crystals of pyridine hydrochloride. The tube was centrifuged and the spectrum of its contents was recorded, showing 100% conversion to **8**: ^{1}H nmr δ 1.24 (s, 9 H), 1.87 (d of d, J = 1.5, 0.9 Hz, 3 H), 5.20 (sym m, 1 H), 5.32 (sym m, 1 H). No attempt was made to isolate **8**, owing to the known proclivity of enynes toward polymerization. **8** seems to be stable indefinitely at −15° in pyridine.

Thermal Stability of 4.—A 20-mg sample of **4** was sealed in a thick-walled tube and immersed in an oil bath heated to 170°; the sample melted immediately. Heating was continued for 23.5 hr, and the sample crystallized quickly after being removed from the bath. Glc analysis indicated no decomposition, and the melting point was undepressed.

Photochemistry of 4.—The exploratory procedure was as follows: 15 mg of **4** and 7 μl of decane (internal standard) were weighed into a quartz tube (i.d. 5 mm) and exactly 6.0 ml of purified solvent was added. After dissolution was complete the contents were analyzed by glc, degassed, and irradiated using a Srinivasen apparatus fitted with mercury vapor lamps (253.7 nm). After the indicated period, the tubes were again analyzed; the results are given in the text.

Reaction of 4 with 9 (Supplied by Alfa Inorganics).—Following the method of King,[15] a solution of 318 mg (1.29 mmol) of **4** and 238 mg (1.32 mmol) of **9** in 5 ml of octane was heated under nitrogen to 133° for 41.4 hr. The pentane-soluble portion of the product mixture was chromatographed on alumina (activity grade II), eluting first with pentane, then with ether. Unreacted **4** (270 mg, 85%) eluted almost immediately, followed by unreacted **9** (16 mg) a minor band (9.8 mg), then the major product (57 mg crude yield, 79% based on consumed **4**). This material was sublimed (87°, 0.05 mm) to yield *ca.* 30 mg of deep red-orange microcrystalline solid: mp 229–233° (without apparent decomposition);[18] ^{1}H nmr (deuteriochloroform, internal TMS) δ 5.09 (s, 5 H), 1.54 (s, 6 H), 1.32 (s, 18 H), 1.27 (s, 6 H); ir (carbon tetrachloride) 2960 (s), 2920 (s), 2865 (m), 1595 (vs), 1484 (m), 1458 (s), 1387 (m), 1369 (m), 1360 (s), 1229 (w), 1190 (w), 1084 (m), 821 (s), 721 cm^{-1} (m); mass spectrum (70 eV) *m/e* 398 (parent and base peak).

Anal. Calcd for $C_{24}H_{35}OCo$: C, 72.34; H, 8.85. Found: C, 72.79; H, 9.17.

Registry No.—**1**, 17530-24-4; **2**, 1522-16-3; **3**, 17553-43-4; **4**, 17553-35-4; **5**, 17530-17-5; **8**, 37439-53-5; **9**, 12078-23-8; **12**, 37584-03-5; methyllithium, 917-54-4; pyridine, 110-86-1.

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(17) The contaminating side product must be chemically and physically quite similar to **4**, as judged from its glc characteristics and the fact that sublimation and recrystallization only inefficiently separate it from **4**. Evidence that it is neither **6** nor **7** comes from the infrared spectrum of impure **4** containing 30% of the contaminant (from concentrated mother liquors), which showed no trace of absorptions in the 1900–2000-cm^{-1} region.

(18) The yield of **12** is unaffected by doubling the amount of dicarbonyl, or by extending the reaction period to 62 hr. Additionally, it is volatile enough to survive passage through an OV-1 glc column at 225°.

Organophosphorus Enamines. VII. Synthesis and Stereochemistry of Enamine Phosphonates

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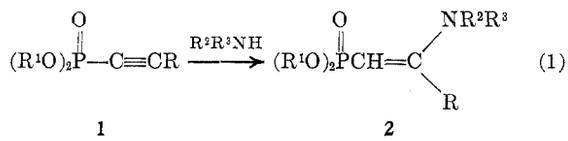
Recently we reported a general synthesis of diphenyl and dialkyl 1-alkynylphosphonates **1**.[2a] The literature contains a very limited amount of information on the nucleophilic addition of amines to the carbon–carbon

(1) The work was initiated at Tulane University, New Orleans, La.

(2) (a) M. S. Chattha and A. M. Aguiar, *J. Org. Chem.*, **36**, 2719 (1971); (b) B. C. Saunders and P. Simpson, *J. Chem. Soc.*, 3351 (1963).

triple bond in **1**.[2b,3,4] We now wish to describe in detail that the addition of primary and secondary aliphatic amines to the triple bond in **1** is rather facile, giving enamine phosphonates **2** in fair to good yields (eq 1).



(1)

1 **2**

R = alkyl, phenyl; R^1 = ethyl, phenyl; R^2 = alkyl; R^3 = alkyl, H

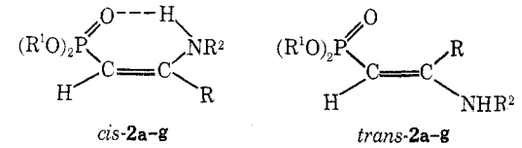
Enamine phosphonates **2** produced in this manner are listed in Table I together with their boiling points and yields.

TABLE I
ENAMINE PHOSPHONATES 2[a]

Compd	R	R^1	R^2	R^3	Bp, °C (mm)	Yield, %
2a	*n*-C_4H_9	C_2H_5	*n*-C_4H_9	H	126–127 (0.07)	81
2b	*n*-C_6H_{13}	C_2H_5	*n*-C_4H_9	H	136–138 (0.07)	82
2c	C_6H_5	C_2H_5	*n*-C_4H_9	H	135–136 (0.05)	72
2d	*n*-C_4H_9	C_2H_5	*t*-C_4H_9	H	108–109 (0.05)	73
2e	*n*-C_6H_{13}	C_2H_5	*t*-C_4H_9	H	134–136 (0.08)	90
2f	C_6H_5	C_2H_5	*t*-C_4H_9	H	129 (0.08)	76
2g	CH_3	C_6H_5	*t*-C_4H_9	H	192–193 (0.06)	65
2h	*n*-C_4H_9	C_2H_5	C_2H_5	C_2H_5	121 (0.06)	80
2i	$C_6H_5CH_2CH_2$	C_2H_5	C_2H_5	C_2H_5	163–164 (0.04)	79

[a] Satisfactory analytical data (C, H, N, P) were reported for all new compounds listed in the table; exceptions were **2c** (P 0.68% high) and **2g** (H 0.82% low).

The ir spectra of all of the compounds **2a–i** show strong absorption in the region of 6.25–6.46 μ (C=C). The nmr spectra of enamines **2a–g** (R^2 = alkyl, R^3 = H) display the amino proton signal at two different chemical shifts (Table II), which indicates that **2a–g** (R^2 = alkyl, R^3 = H) exist as cis–trans mixtures as shown below.



cis-**2a–g** *trans*-**2a–g**

Considering the deshielding effect of the phosphonate group, the lower field amino proton signal has been assigned to the cis isomer and the higher field signal to the trans isomer. Similar differences in chemical shifts for various protons are used as the basis for assignment of configuration. For example, in the nmr spectrum of compounds **2g** (R = CH_3, R^1 = C_6H_5, R^2 = *t*-C_4H_9, R^3 = H), the doublet (J = 2 Hz) at δ 2.17 has been assigned to the propenyl methyl protons when this methyl group lies cis to the phosphonate group (*trans*-**2g**), and the doublet (J = 2 Hz) at δ 2.08 is assigned to the propenyl methyl protons when the methyl group is trans to the phosphonate group (*cis*-**2g**). Similarly the *tert*-butyl group in **2g** displayed resonances at two different chemical shifts (δ 1.26, 1.28); the lower field signal has been assigned to the cis isomer and the higher field signal to the trans isomer. The chemical shifts of the α-vinyl protons can also be used to assign configurations and provide supporting evidence for the configurational assignments based on the amino proton shifts.[5–7]

This method also permits configurational assignments in the absence of amino protons. In compounds **2a–g**, a cis relationship between the amino group and the vinyl proton is indicated by a larger chemical shift of the vinyl proton (see Table II). In compounds **2c–f**, the vinyl proton signals of the trans isomers were found to be obscured by the methylene proton signals from the *O*-ethyl groups. With the application of a strong field (100 MHz), both the vinyl proton signals in **2d,e** could be identified but, in the spectra of **2c** and **2f**, only the higher field proton signal could be seen clearly. However, in **2f**, the *tert*-butyl group signals due to both the isomers could be seen distinctly (δ 1.10, 1.43) in the 60-MHz nmr spectrum; all the chemical shifts listed in Table II represent 60-MHz spectra.

Compounds **2h,i**, resulting from the addition of diethylamine to 1-alkynylphosphonates **1**, seem to exist only in one stereochemical form, as indicated by the presence of only one doublet (J = 8.5 Hz) due to the vinyl proton. These two compounds, **2h,i**, were assigned the trans configuration, since in the most stable configuration the electron-releasing and the electron-withdrawing groups should lie trans to each other.[6,8] In enamines **2a–g**, the cis isomer also exists because of the stability gained by it through hydrogen bonding between the amino proton and the oxygen atom (P=O). The presence of hydrogen bonding was demonstrated by taking ^1H nmr ($CDCl_3$) spectra of **2g** at different concentrations. The higher field chemical shift due to the amino proton (trans isomer) was found to be concentration dependent, while the lower field signal (cis isomer) had a constant chemical shift. This is because, in the cis isomer, the amino proton is already hydrogen bonded and is not significantly affected by the change in concentration, while, in the trans isomer, the increasing dilution with deuteriochloroform shifts the amino proton signal toward the lower field. Further support for the presence of the two isomers, one of which has the amino proton involved in the intramolecular hydrogen bonding, comes from the observation of two weak bands at 2.95 and 2.31 μ in the infrared spectra of **2a–g**.

The trans addition of amines to carbon–carbon triple bonds activated by the phosphoryl group has been described.[5] Through nmr studies it has also been demonstrated that, on raising the temperature, the cis

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(5) W. Hagens, H. J. T. Bos, W. Voskuil, and J. R. Arens, *Recl. Trav. Chim. Pays-Bas*, **88**, 71 (1969).
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TABLE II
DISTRIBUTION OF ISOMERS[a] AND NMR[b] DATA FOR ENAMINE PHOSPHONATES 2a–i

Compd	Isomer % cis	Isomer % trans	Cis PCH δ	Cis PCH J, Hz	Trans PCH δ	Trans PCH J, Hz	NH, δ cis	NH, δ trans	CH_2OP, δ, qn (J = 7.5, 15 Hz)	Other proton chemical shifts, δ
2a	50	50	3.60	13	3.76	10.5	7.32	5.59	4.05	3.08 (m, NCH_2), 2.55 (m, allyl), 1.34 (m, containing t, J = 7 Hz, 20 H)
2b	55	45	3.50	13	3.72	10.5	7.28	5.12	4.03	3.04 (m, NCH_2), 2.45 (m, allyl), 1.28 (m containing t, J = 7 Hz, 24 H)
2c	80	20	3.82	13			7.51	5.22	4.08	7.42 (C_6H_5), 2.92 (m, NCH_2), 1.30 (m, 13 H)
2d	15	85	3.62	13	3.75	11	7.36	4.46	4.02	2.42 (m, allyl), 1.32 (m containing t, J = 7 Hz, 22 H)
2e	10	90	3.67	13	3.74	11	7.42	4.36	4.05	2.43 (m, allyl), 1.36 (m containing t, J = 7.5 Hz, 26 H)
2f	15	85	3.79	13			7.23	4.54	4.11	7.42 (C_6H_5), 1.32 (t, J = 7.5 Hz, CH_3CO), 1.43 and 1.10 (two s, *tert*-butyl)
2g	30	70	3.63	13	4.15	11	7.12	4.39		7.35 (C_6H_5), 2.15 and 2.08 (two d, J = 2 Hz, allyl), 1.28 and 1.26 (two s, *tert*-butyl)
2h		100			3.75	8.5			4.05	3.25 (q, J = 7.5 Hz, NCH_2), 2.65 (m, allyl), 1.31 (m containing two t, J = 7, 7.5 Hz, 19 H)
2i		100			3.87	8.5			4.10	7.32 (C_6H_5), 3.25 (q, J = 7.5 Hz, NCH_2), 2.90 (s, allyl and benzyl), 1.25 (t, J = 7 Hz, CH_3CO), 1.15 (t, J = 7 Hz, CH_3CN)

[a] Configuration cis and trans refer to the amino and the phosphonate groups being cis or trans to each other. [b] In the nmr description, s, d, t, q, qn, and m represent a singlet, doublet, triplet, quartet, quintet, and multiplet, respectively.

isomer rapidly isomerized to the trans product.[6] Conceivably, the trans addition of amines to 1-alkynylphosphonates **1** results in the cis isomers, which, on heating, isomerize to the trans products. Under the reflux conditions employed in this investigation, a different mode of addition may also be taking place.[5,6]

The isomerization of the cis to the trans isomers is in accordance with the concept that the electron-withdrawing substituents on one end and electron-releasing substituents on the other end of the double bond favor cis–trans isomerization.[5,6,8] The excess of amine in the reaction mixture may also be playing some role in the cis–trans isomerization.

A comparison of the amounts of cis and trans isomers in adducts **2a–c** (N-*n*-C_4H_9) and **2d–g** (N-*t*-C_4H_9) shows that the greater steric requirements of the *N*-alkyl group result in the increasing amount of the trans product. In compound **2c** (R = C_6H_5), the cis isomer predominates because the phenyl ring is probably in conjugation with the ring formed through hydrogen bonding of the amino proton to the oxygen atom of the phosphonate group. However, in adduct **2f** (R = C_6H_5), resulting from the addition of *tert*-butylamine to **1** (R = C_6H_5), this effect is found to be offset by the bulkiness of the *tert*-butyl group and the trans isomer predominates.

Experimental Section

The amines were dried over potassium hydroxide pellets and the starting 1-alkynylphosphonates **1** were redistilled before use. The nmr spectra were determined on a Varian A-60 and 100 MHz spectrometer using deuteriochloroform as solvent and tetramethylsilane as an internal standard. Chemical analyses were performed by Geller Microanalytical Laboratories, Saddle River, N. J.

Preparation of Enamine Phosphonates 2a–i. General Procedure.—The 1-alkynylphosphonates **1** were refluxed with a 10–12 molar excess of the amines. The reflux was continued for 3–6 days until the ir spectra of a test portion of the reaction mixture showed almost complete disappearance of the absorption band in the region of 4.5–4.6 μ (C≡C). The excess amines were evaporated *in vacuo* at aspirator pressure. The resulting adducts were short path distilled at reduced pressure from anhydrous potassium carbonate.

Registry No.—**1a**, 3450-61-1; **1b**, 3450-66-6; **1c**, 3450-67-7; **1g**, 3095-09-8; **1i**, 30238-19-8; *cis*-**2a**, 37692-17-4; *trans*-**2a**, 37692-18-5; *cis*-**2b**, 37692-19-6; *trans*-**2b**, 37692-20-9; *cis*-**2c**, 37692-21-0; *trans*-**2c**, 37692-22-1; *cis*-**2d**, 37692-23-2; *trans*-**2d**, 37692-24-3; *cis*-**2e**, 37692-25-4; *trans*-**2e**, 37692-26-5; *cis*-**2f**, 37692-27-6; *trans*-**2f**, 37692-28-7; *cis*-**2g**, 37692-29-8; *trans*-**2g**, 37692-30-1; *trans*-**2h**, 37755-04-7; *trans*-**2i**, 37692-31-2; butylamine, 109-73-9; diethylamine, 109-89-7; *tert*-butylamine, 109-73-9.

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Reductive Cleavage of Phenylhydrazones of α-Keto Acids to Amino Acids

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Reductive cleavage of phenylhydrazones of α-keto acids is an important method for the synthesis of α-amino acids, because of the easy availability of these phenylhydrazones by the Japp–Klingemann reaction.[1] This reaction, which takes place between a phenyl-

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