graphed **5**, mp 62–78 °C, in 20 mL of 95% EtOH was hydrogenated for 20 h at 1 atm over 75 mg of 30% Pd/C. Filtration, distillation of solvent in vacuo, dissolution of the residue in Et_2O, and isolation A (5 N KOH wash) left 110 mg (98%) of **7**: IR 3580, 1715 cm^{-1}; ^1H NMR τ 2.60 (broad s, 1 H), 2.87 (broad s, 2 H), 5.14 (t, J = 8.5 Hz, 1 H), 6.35 (s, 3 H), 8.73 (s, 3 H), 8.73 (s, 3 H), 8.78 (d, J = 7 Hz, 6 H). This crude **7** in 10 mL of 95% EtOH was hydrogenated for 12 h at 1 atm over 50 mg of 30% Pd/C. Filtration, distillation of solvent in vacuo, dissolution of the residue in Et_2O, and isolation A afforded 96 mg (90% based on **5**) of **8** as a colorless oil which was crystallized from EtOH–H_2O to give 85 mg (80%) of pure **8** as colorless needles: mp 70–72 °C (lit. 71.5–73 °C[12]); UV max 268 nm (ϵ 700), 276 (700); IR 1715 cm^{-1}; ^1H NMR τ 2.70–3.15 (m, 3 H), 6.36 (s, 3 H), 8.74 (s, 3 H), 8.79 (d, J = 7 Hz, 6 H), 8.80 (s, 3 H). IR and ^1H NMR spectra were identical with those of the authentic (+) enantiomer prepared by CH_2N_2 esterification of (+)-dehydroabietic acid.

Anal. Calcd for $C_{21}H_{30}O_2$: C, 80.21; H, 9.62. Found: C, 80.45; H, 9.65.

Registry No.—**1**, 16981-49-0; **2**, 62475-60-9; **3**, 62448-50-4; **4**, 62475-61-0; **5**, 62448-51-5; **7**, 62475-62-1; **8**, 10178-27-5; 4α-carbomethoxy-4β,10-dimethyl-8-hydroxymethylene-5α-decalone-7, 62448-52-6; 4α-carbomethoxy-4β,10-dimethyl-8-formyl-5α-Δ^8-octalone-7, 16981-50-3; *tert*-butyl isovalerylacetate, 39140-54-0; 4α-carbomethoxy-4β,10-dimethyl-8-formyl-9-(5-methyl-3-oxohexanoic acid-2-yl)-*tert*-butyl ester, 62448-53-7; 2-chlorobenzoxazole, 615-18-9.

References and Notes

(1) (a) Part 10: W. L. Meyer, T. E. Goodwin, R. J. Hoff, and C. W. Sigel, *J. Org. Chem.*, preceding paper in this issue. (b) Abstracted from the Ph.D. Dissertation of C.W.S., Indiana University, 1967. (c) Supported by Grant AM-10123 from the National Institute of Arthritis and Metabolic Diseases. (d) Preliminary communication: W. L. Meyer and C. W. Sigel, *Tetrahedron Lett.*, 2485 (1967). (e) National Institutes of Health Predoctoral Fellow, 1965–1967.

(2) For position numbering and nomenclature conventions see structures **1** and **2** and footnote 2 of ref 5.

(3) W. L. Meyer, G. B. Clemans, and R. A. Manning, *J. Org. Chem.*, **40**, 3686 (1975).

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(5) W. L. Meyer, R. A. Manning, P. G. Schroeder, and D. C. Shew, *J. Org. Chem.*, accompanying paper in this issue.

(6) The bromo compound has not been isolated in pure form; its formulation is based on two aromatic proton singlets (τ 2.12 and 3.23), a 12.5-Hz doublet at τ 5.02 (–CHBrCO–), and a downfield 16-methyl singlet (τ 8.51) which accompany resonances of **4** in the ^1H NMR spectrum of the mixture; cf. R. C. Cambie, G. R. Clark, D. R. Crump, and T. N. Waters, *Chem. Commun.*, 183 (1968).

(7) Cf. discussion of structures **25–31** in ref 3.

(8) T. E. Goodwin, Ph.D. Dissertation, University of Arkansas, 1974.

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(12) G. Stork and J. W. Schulenberg, *J. Am. Chem. Soc.*, **84**, 284 (1962).

Phosphonic Acid Chemistry. 2. Studies on the Arbuzov Reaction of 1-Bromo-4,4-diethoxy-2-butyne and Rabinowitch Method of Dealkylation of Phosphonate Diesters Using Chloro- and Bromotrimethylsilane[1]

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The Arbuzov reaction of the title compound **2** and trimethyl phosphite [$(MeO)_3P$] was shown to yield a mixture of phosphonate and diphosphonate products, the composition of the reaction mixture being a function of reaction conditions. The phosphonates **1**, **3**, and **11** were identified as products of the reaction. The structure of the unexpected allenylphosphonate **11** was established in the usual manner as well as by conversion to the alkenylphosphonate **12**. The Arbuzov reaction of **2** and triisopropyl phosphite [$(i\text{-}PrO)_3P$] was shown under comparable conditions to yield moderate yields of the 1-alkynylphosphonate **14**. Certain interconversions, **1** → **3** by Al_2O_3 and **1**, **3**, **11** → diphosphonates, were effected. The Rabinowitch method of dealkylating phosphonate diesters [refluxing chlorotrimethylsilane (Me_3SiCl)] was used to convert **3** into **4**. Attempts to convert **1** into **5** were unsuccessful. A side product, the alkadienylphosphonate **17**, was isolated and characterized. The conversion of **1** into **5** and of **3** into **4** using bromotrimethylsilane (Me_3SiBr) was tried unsuccessfully. Reaction mixtures were obtained consistent with the alkadienylphosphonate **26** as being the chief product of these reactions, but work-up yielded no characterizable products.

Arbuzov reactions of propargyl halides have been reported[2–4] to give complex reaction mixtures from which 2-alkynylphosphonates are difficultly isolable in pure form and good yield. As part of our program[5] to prepare new and novel analogues of pyridoxal phosphate (PPal), we undertook the synthesis of the phosphonate **1**, using the Arbuzov reaction

$(CH_3O)_2P(O)CH_2C{\equiv}CCH(OC_2H_5)_2$

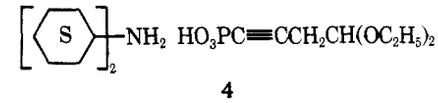
1

$BrCH_2C{\equiv}CCH(OC_2H_5)_2$

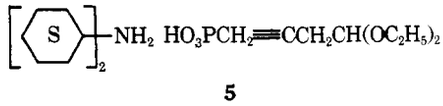
2

$(CH_3O)_2P(O)C{\equiv}CCH_2CH(OC_2H_5)_2$

3



4



5

$HC{\equiv}CCH_2Br$ **6**

$C_2H_5OCH_2C{\equiv}CCH(OC_2H_5)_2$ **7**

of **2** and trimethyl phosphite ($(MeO)_3P$). This communication reports the chemistry of this reaction, the synthesis of **1** and **3**, and the synthesis of the dicyclohexylamine (DCH) salt **4** which was of interest to us.[6] The preparation of the desired

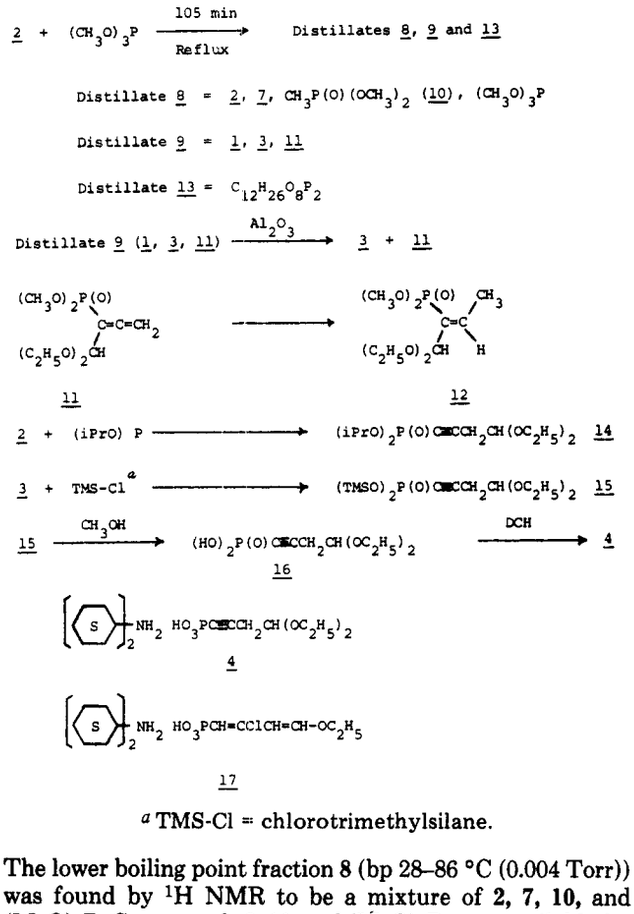
salt **5** was also attempted but could not be achieved by the methods used in this paper.

Arbuzov Reaction

The starting material **2**, prepared from **6** using published procedures,[7] was isolable in the reported yield[8] and was always found to be contaminated with the reported impurity **7**.[9] This impurity did not interfere with the Arbuzov reactions that were carried out (always being isolable from reaction mixtures in unchanged form by distillation) and for this reason a product **2** of 90–95% purity (GLC estimates) was used.

Initial experiments on the Arbuzov reaction of **2** and $(MeO)_3P$ using reaction conditions Ia, outlined in Table I, gave reaction mixtures that were complex and from which pure products were not easily isolable by distillation. Thus, fractional distillation of reaction mixture Ia yielded two broad distillate fractions, **8** and **9**, and a pot residue (see Scheme I).

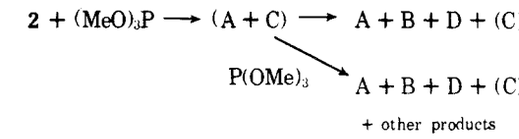
Scheme I



[a] TMS-Cl = chlorotrimethylsilane.

The lower boiling point fraction **8** (bp 28–86 °C (0.004 Torr)) was found by ^1H NMR to be a mixture of **2**, **7**, **10**, and $(MeO)_3P$. Compounds **2**, **10**, and $(MeO)_3P$ were available for comparison. The higher boiling point fraction **9** (bp 103–108 °C (0.004 Torr)) was found by IR and NMR to be a mixture of allenyl- and alkynylphosphonates and showed IR absorptions at 4.43, 5.08, and 6.01 μ and ^1H NMR absorptions at 2.87 ppm (d, J = 22 Hz) and between 5.0 and 5.8 ppm (multiple absorptions, >15 lines). The desired product **1** was discernible in distillate **9** by the propargyl ^1H NMR absorptions at 2.87 ppm (d, J = 22 Hz) which were clearly visible and consistent with published findings.[10] The amount of **1** in **9** (derived from reaction Ia) was estimated by ^1H NMR to be 54%, which was consistent with GLC estimates.

These results, especially the low yield of **1** (11%), prompted a more detailed study of the Arbuzov reaction. This was done by studying the appearance and disappearance of products and reactants by GLC and also by studying the effect of reaction conditions on the yield of **9**. The GLC studies, performed on reactions run at three different temperatures (80, 90, 100 °C) and two **2**:$(MeO)_3P$ ratios using Se-30 and QF-1 columns, showed the Arbuzov reaction to be fast (most of the starting **2** was consumed within the first hour), yielding two inital products, labeled[11] A and C. The product A was stable



throughout the GLC study of this reaction. The product C, on the other hand, underwent a gradual transformation into two new products, B and D. The Arbuzov reactions that were run at lower temperatures showed similar GLC reaction profiles, except that longer reaction times were required to achieve similar product compositions. The reactions run at greater **2**:$(MeO)_3P$ ratios (e.g., 1:4) resulted in GLC profiles that were more complex in nature. Poorly resolvable products having retention times greater than D were observed.

The effect of reaction conditions on the yield of **1**, expressed as distillate **9**,[12] is indicated in Table I. Mild reaction conditions such as short reaction times and a low **2**:$(MeO)_3P$ ratio as in Ic,d were found to favor the formation of **9**. Long reaction times, as Ia or high **2**:$(MeO)_3P$ ratio, as in Ib, favored the formation of pot residues, low yield of **9**, and the formation of **3**. Inverse addition of $(MeO)_3P$ to hot **2** (100 °C) yielded **9** in fair yield (42%) and of similar composition as **9** obtained in Ic.

Since the GLC results presented above were suggestive of transformations other than formation of **1**, i.e., the transformation C → B + D, the thermal stability of Arbuzov reaction mixtures, distillate **9**, and the phosphonate **3** was investigated. It was found that heating Arbuzov reaction mixtures derived under reaction conditions Ia, 100 °C for periods of up to 17 h, produced no changes in product composition as judged by ^1H NMR. Similarly, heating **3** or **9**, neat 105–110 °C, gave similar results. However, heating distillate **9** or phosphonate **3** in $(MeO)_3P$ solution (1:1 mole ratio) resulted in a gradual disappearance of all acetylene–allene IR absorptions and the appearance of strong IR absorptions at 6.11 and 6.18 μ. These new IR absorptions were very similar to those found in IR spectra of pot residues.

The effect of a more hindered phosphite on the Arbuzov reaction of **2** was also investigated. Triisopropyl phosphite ($(i\text{-PrO})_3P$) reacted with **2** (mole ratio, 2:3) to give **14** in 40% yield. The IR spectrum of the crude reaction mixture that was obtained, before distillation, showed a strong IR absorption at 4.52 μ which was consistent with **14** being the major product of the reaction mixture.

Isolation and Characterization of Arbuzov Products

The components of distillate **9** did not lend themselves to separation by fractional distillation. Thus, repeated fractional distillation of **9** (40–60% rich in **1**) was found to give **1** in 5% yield and in 87% purity. Further distillation of this material did not improve the purity and resulted in additional losses of yield. The product **1** was therefore characterized as **1**, 87% pure, using IR, NMR, and mass spectrometry. The IR spectrum of **1** was found to exhibit IR absorptions at 4.44 and 5.07 μ (allene absorption), characteristic ^1H NMR absorptions at 2.87 ppm (d, J = 22 Hz) and 5.3 ppm (2t, J = 1.8 and 4 Hz) (small amounts of allenyl- and alkenylphosphonates were visible by ^1H NMR when the spectrum amplitude was significantly increased), and a mass spectrum only slightly different from that of **3**, suggesting a possible **1** → **3** isomerization in the mass spectrometer.

Similar difficulties were encountered in the purification of **3** and the allenylphosphonate present in **9**. It was found that

pure products could not be obtained by fractional distillation of reaction mixtures except in the case of Ib (Table I), where **3** appeared to be the only distillable monophosphonate product of the reaction. The indirect route of Al_2O_3 isomerization of **9** (i.e., of **1**) was therefore used to prepare **3** and **11** in analytical purity. The two products were obtained in 36 and 5% yields, respectively, by distillation of **9** that had been passed through an Al_2O_3 column, basic, Brockman activity No. 1 (Et_2O elution). The phosphonate **3**, derived in this manner, exhibited IR absorptions at 4.53 μ, no allene or other acetylene absorptions, ^1H NMR absorptions at 2.67 (2d, J = 5.5 and 42 Hz) and 4.69 ppm (t, J = 5.5 Hz), and a mass spectrum fragmentation pattern[13] (M → $CH(OEt)_2$ → CH(OH)OEt → $CH(OH)_2$) consistent with structure **3**. The phosphonate analyzed correctly for C, H, P and was the same by IR and NMR as **3** derived from reaction Ib. It was also the same (IR, NMR) as **3** prepared by reacting **2** and $NaP(O)(OMe)_2$ at −65 °C in THF (yield 17%). The allene **11**, obtained from the Al_2O_3 isomerization of **9**, exhibited two allene IR absorptions at 5.09 and 5.14 μ which was consistent with published findings[14] on allenes having the structure $R_2C{=}C{=}CH_2$. This was in contrast to the strong single allene IR absorptions at 5.08 μ observed for crude Arbuzov reaction mixtures and of certain distillate fractions obtained from the fractional distillation of **9**. The allene was also characterized by ^1H NMR, mass spectrometry, and reduction to **12**. The latter product was characterized in the same manner, by IR, NMR, mass spectrometry, and elemental analysis. The stereochemistry of **12** was established by NMR. The vinyl proton–phosphorus coupling constants, J_{PH} = 1, 7, and 48 Hz, were consistent with a trans P/H geometry.[15] The two products, **11** and **3**, were found to have GLC retention times that corresponded to components A and D in gas chromatograms obtained during the study of the Arbuzov reaction of **2** and $(MeO)_3P$.

Pot residues were characterized only partially. Repeated fractional distillation of the pot residue derived under reaction conditions Ic (Table I) yielded a fraction **13**, bp 137–140 °C (0.09 Torr), in 10% yield which analyzed correctly for $C_{12}H_{28}O_8P_2$. The ^1H NMR spectrum of this distillate **13** was complex, showing multiple NMR absorptions between 1.7 and 3.1 ppm and also between 4.6 and 7.6 ppm. The spectrum of distillate **13** appeared to be due to a mixture of compounds.[16] The IR spectrum of **13** showed no acetylene or allene absorptions and strong IR absorptions at 6.14, 12.12, and 13.3 μ, consistent with an alkenyldiphosphonate structure of **13**.

Preparation of Dicyclohexylamine Salts

The Rabinowitch method[17] of dealkylation of dialkylphosphonate esters was used to prepare the DCH salt of **16**. A solution of **3** in Me_3SiCl was refluxed 2 days to effect the complete conversion of **3** into **15**. The conversion was monitored by NMR by observing the gradual disappearance of the phosphonate methoxyl groups. Work-up which consisted of hydrolysis of **15** into **16** and neutralization of **16** with DCH gave **4** in 45% yield. On one occasion the reaction mixture obtained from the reaction of **3** and Me_3SiCl was set aside for 1 week. Work-up of this reaction mixture resulted in the isolation of a small amount of product which by IR and ^1H NMR as well as by elemental analysis was **17**.

The attempt to carry out this same dealkylation using distillate **9** (rich in **1**) for the purpose of obtaining **5** proved to be unsuccessful. Refluxing **9** with an excess of Me_3SiCl resulted in a gradual and complete disappearance of **1** in the reaction mixture. NMR spectra of the crude reaction mixtures could not be analyzed and work-up yielded no characterizable products.

The dealkylation of the phosphonate esters **3** and **9** was also attempted using bromotrimethylsilane (Me_3SiBr).[5] Mixing **3** and **9**, respectively, with Me_3SiBr (available commercially or by synthesis[23]) resulted in an exothermic reaction and the rapid liberation of gas (presumably MeBr). NMR spectra of these reaction mixtures (both from **9** and **3**) had similar spectral absorptions, δ 1.27 (t), 3.85 (q), 5.54 (d), 6.97 (ABq) (CCl_4 solution) ppm. No NMR absorptions characteristic of **3** and **1** were observed. The crude reaction mixtures were also observed to have a minty odor very similar to that observed for Me_3Si ethers of MeOH and EtOH. Work-up of these reaction mixtures (for both **3** and **9**) resulted in the isolation of of DCH salts which proved to be inorganic, mp >300 °C; NMR spectra were indicative of DCH protons only; and the IR spectrum was indicative of DCH and not of phosphorus-containing product (no P–O IR absorptions were observed).

Table I. The Effect of Reaction Conditions on the Yield of 9 in the Arbuzov Reaction of 2 and $(MeO)_3P$

	2:$(MeO)_3P$	Reaction conditions	Yield of 9, %
Ia	1:1	6 h, 95 °C	20[a]
Ib	1:3	6 h, 105 °C	0[b]
Ic	1:2	105 min, 105 °C	66
Id	1:1	15 min, 100 °C, inverse addition	42[c]

[a] Distillate **8** was isolated in 33% yield. [b] Phosphonate **3** was isolated only in 17% yield. None of the products normally found in distillate **9** were observed. [c] The product was similar to **9** obtained in Ic. The normal products of distillate **8** were also obtained.

Discussion

The results presented in this paper compare favorably with experimental data reported on a closely related reaction, that of **6** and triethyl phosphite. This latter reaction was first reported[18] to give **18** in 5% yield. Later the reported yield[2] of **18**

$CH_3C{\equiv}CP(O)(OC_2H_5)_2$ **18**

$HC{\equiv}CCH_2P(O)(OC_2H_5)_2$ **19**

$CH_2{=}C{=}CHP(O)(OC_2H_5)_2$ **20**

$C_2H_5P(O)(OC_2H_5)_2$ **21**

$(CH_3O)_2P(O)CH{=}C{=}CHCH(OC_2H_5)_2$ **24**

$(TMSO)_2P(O)CH{=}CBr{-}CH{=}CH{-}OC_2H_5$ **26**

$(C_2H_5O)_2P(O)C(CH_3){=}CHP(O)(OC_2H_5)_2$ **22**

$(C_2H_5O)_2P(O)-C(H)-C{=}CH_2$
$(C_2H_5O)_2P(O)-C(H)-C{=}CH$
23

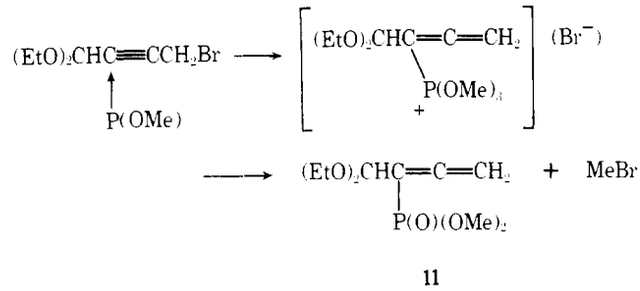
$(CH_3)_2CClC{\equiv}CH$ **25**

was increased to 15%. Griffin[19] reported that dropwise addition of **6** to hot triethyl phosphite (140 °C) yielded **19** and **20** in a combined yield of 38%. More recently, the identity of the various products formed under reaction conditions in which a large excess of **6** was added to hot triethyl phosphite (140 °C) was reported by Pfeiffer and co-workers.[3] These authors reported that the products **18** (2%), **19** (−), **20** (5%), **21** (50%), **22** (10%), and **23** (20%) were formed in the yields indicated. Fractional distillation of the reaction mixture was reported to yield a distillate A composed of **18**, **19**, and **20**, from which the individual components of the mixture could not be obtained in pure form by fractional distillation. These compounds were identified by GLC and by comparison with authentic samples prepared by other synthetic routes. The products, **22** and **23**, were however obtained in pure form by distillation. These results obtained by Pfeiffer for the reaction of **6** and triethyl phosphite are therefore very similar to those reported in the present communication for **2** and $(MeO)_3P$ in that (1) low yields of 1-alkynylphosphonates (**3** and **18**, respectively) were observed in both cases, (2) appreciable yields

of dialkyl alkylphosphonates **10** and **21** were obtained, and (3) the allenylphosphonates **20** and **24** were present in low yield in both cases. An apparent difference in the two reactions is the much better yield of propargylphosphonate (**1**) that was obtained in the reaction of **2** and $(MeO)_3P$ as compared to that observed in the reaction of **6** and $(EtO)_3P$. The product **19** was present in amounts only sufficient for IR detection.

The formation of **11** in the reaction mixture of **2** and $(MeO)_3P$ was unexpected and appears to involve a propargyl rearrangement as illustrated in Scheme II. Such propargyl

Scheme II. The Postulated Mechanism for the Formation of Phosphonate 11



11

rearrangements[4,20] leading to the formation of allenylphosphonates have been observed with sterically hindered propargyl halides such as **25.** The present result is unusual in that a primary halide is displaced in a propargyl manner. The reaction conditions favoring the formation of **11** are unknown. Prior coordination of the phosphite is unlikely, since the dropwise addition of phosphite to hot **2** gave **11** in about the same yield as the batch reaction.

The rather facile displacement of Br^- in a propargyl manner points up the ease with which this reaction occurs and also suggests that some of the allenylphosphonate **20** formed in the reaction of **6** and $(EtO)_3P$ probably results from such a propargyl displacement of Br^- from **6.** This would be in addition to the expected isomerization of **19** → **20** and provides an explanation for the poor yield of **19** observed in this reaction.

In a previous publication[5] it was reported that the dealkylation of phosphonate diesters proceeded more readily with Me_3SiBr. The results presented in this communication substantiate these initial observations. The dealkylation of distillate **9** or of **3** did proceed at room temperature (even exothermically) to give dealkylated products (confirmed by NMR). The products of the reaction were, however, not **4** or **5** as expected. The ^1H NMR spectra of crude reaction mixtures were consistent with **26**[21] being the major product. These results would appear to suggest that the trace amounts of HBr (usually present in Me_3SiBr) effect the transformation **1, 3** → **26,** a process which once started could be expected to be autocatalytic. Although it is not entirely clear why **26** could not be converted into a crystalline DCH salt, the above-mentioned NMR results clearly indicate the unsuitability of Me_3SiBr for the preparation of **4** and **5** from **3** and **9.**

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 237 grating spectrophotometer and on an IR-8 Beckman spectrophotometer. The NMR spectra were obtained on Varian A60A, and T-60 spectrophotometers and on a Perkin-Elmer Model R-24B spectrophotometer. All chemical shifts are reported in parts per million. The mass spectra were obtained on an Hitachi Perkin-Elmer RMV-6D mass spectrometer. Elemental analyses were performed by Galbraith Laboratories, Nashville, Tenn., and by Daessle Laboratory, Montreal. The melting points were taken on a Fisher-Johns melting block and are uncorrected. Gas chromatographic analyses were done on an Aerograph Hi Fi gas chromatograph using 3 and 15% Se-30 analytical columns (⅛ in. × 5 ft) and a 5% QF-1 analytical column (⅛ in. × 5 ft), under the conditions specified, and the retention times are reported in min.

4-Bromo-1,1-diethoxy-2-butyne (2). The compound was prepared in the reported yield (65%) according to the method of Epsztein and Marszak[7] by reacting propargyl bromide with triethyl orthoformate[8] using zinc iodide as the catalyst: bp 117–121 °C (14 Torr) (lit.[7] yield 65%, bp 113–115 °C (13 Torr)); NMR (CCl_4) δ 1.2 (t, J = 7 Hz, CH_3CH_2O), 3.58 (ABq, CH_2O),[22] 3.9 (d, J = ~1.5 Hz, CH_2C), 5.23 (t, J = ~1.5 Hz, CH). The impurity **7,** first observed by Epsztein and Marszak,[7] had NMR absorptions ($CHCl_3$) δ 1.23 (t, J = 7 Hz, CH_3CH_2), 3.65 (ABq, CH_2O), 4.23 (d, J = ~1.5 Hz, $CH_2OC_2H_5$), 5.33 (t, J = ~1.5 Hz, CH).

Arbuzov Reaction of 4-Bromo-1,1-diethoxy-2-butyne (2) and Trimethyl Phosphite. (A) 2:Trimethyl Phosphite Ratio = 1:1. A solution of 13.26 g (0.06 M) of **2** and 7.44 g (0.06 M) of $(MeO)_3P$ was heated 95 °C for 6 h. Distillation of the reaction mixture yielded three distillate fractions. Fraction A (distillate **8**): 5 g, bp 28–86 °C (0.004 Torr); NMR (CCl_4) δ 1.19 (t, J = 7 Hz), 1.45 (d, J = 18 Hz), 3.5 (ABq, J = 7 Hz), 3.76 (d, J = 11 Hz), 4.07 (d, J = ~1.5 Hz), 4.18 (d, J = 1.5 Hz), 5.22 (t, J = ~1.5 Hz), 5.26 (t, J = ~1.5 Hz), these NMR abosrptions being consistent with the presence of **10, 7,** and **2** in the distillate. Fraction B: bp 87–101 °C (0.004 Torr); 1.2 g (8%); NMR (CCl_4) δ 1.21 (t, J = 7 Hz), 2.85 (2d, J = 1.8, 22 Hz), 3.73 (d, J = 11 Hz), 3.77 (d, J = 7 Hz), 3.8 (d, J = ~1.5 Hz), 5.0, 5.03, 5.07, 5.12, 5.15, 5.33, 5.23, 5.27, 5.3, 5.35, 5.4, 5.47, 5.5, 5.55, 5.62 (olefin-acetal H). Fraction C (distillate **9**): 3.0 g, NMR (CCl_4) δ 1.17 (t, J = 7 Hz), 2.87 (2d, J = 1.8, 22 Hz), ca. 3.63 (ABq, J = 7 Hz), 3.73 (d, J = 11 Hz), 3.79 (d, J = 11 Hz), 5.05, 5.08, 5.12, 5.15, 5.19, 5.22, 5.27, 5.3, 5.38, 5.47, 5.55, 5.62 (olefin-acetal H); IR (neat) 4.43, 5.08, 6.1, 7.95, 9.45, 9.65, 11.95 μ. The IR and NMR absorptions were consistent with the presence of **1** and the allenylphosphonate **11.**

(B) 2:Trimethyl Phosphite Ratio = 1:3. A solution of 44.2 g (0.2 M) of **2** and 74.4 g (0.6 M) of $(MeO)_3P$ was heated to ca. 100 °C with stirring. A violent exothermic reaction occurred and cooling was required. After the exothermicity of the reaction had subsided, the solution was heated at reflux for 6 h. Distillation yielded five fractions: fraction 1, bp 32–65 °C (0.05 Torr); fraction 2, 2.6 g, bp 92–106 °C (0.01 Torr); fraction 3, 3.0 g, (bp 106–145 °C (0.01 Torr); fraction 4, 7.0 g, bp 140–145 °C (0.015 Torr), fraction 5, 8.1 g, bp 160–175 °C (0.01 Torr). The fractions 2–5 were examined by NMR. Fractions 3 and 4 were rich in **3,** exhibiting NMR abosrptions (CCl_4) δ 1.20 (t, J = 7 Hz), 2.68 (2d, J = 5.5 and 4.0 Hz, CH_2CH), 3.61 (Abq, J = 7 Hz), 3.75 (d, J = 12 Hz, CH_3OP), 4.71 (t, J = 5.5 Hz, $CH(OC_2H_5)_2$). The other fractions contained products that were not easily identifiable by NMR. Fractions **3** and **4** were redistilled to give 8.5 g (17%) of **3,** bp 120–126 °C (0.02 Torr). Preperative TLC using Silica Gel G plates, 0.75-mm thickness and benzene–acetone (6/4) as the developing solvent yielded **3** free of impurities. The IR and NMR spectra of **3,** obtained in this way, were the same as **3** prepared by Al_2O_3 isomerization of distillate **9** and by reaction of **2** with $NaPO(OCH_3)_2$ (see below).

(C) 2: Trimethyl Phosphite Ratio = 1:1. Addition of Trimethyl Phosphite to Hot 2 (100–110 °C). Trimethyl phosphite, 16.12 g (0.13 M) was added dropwise over a period of 40 min to hot **2** and heated 100–110 °C. The reaction mixture was heated an additional 15 min and then distilled to give 3.0 g of distillate, bp 50–88 °C (0.45 Torr), composed of unreacted **2, 7,** and some **10.** A second distillate fraction was also obtained, bp 106–130 °C (0.5 Torr), 13.5 g. This fraction was redistilled to give 10.6 g (42.4%) of **9,** bp 95–106 °C (0.125 Torr), rich in **1** and **11.** The pot residues (0.96 g) were examined by IR and were found to exhibit weak IR absorptions at 4.5, 5.09, and 5.14 and strong IR absorptions at 6.17 μ. These same IR absorptions were also present in the IR spectrum of the crude Arbuzov reaction mixture before distillation.

(D) 2: Trimethyl Phosphite Ratio = 1:2. A solution of 99.2 g (0.8 M) of trimethyl phosphite and 88.4 g (0.4 M) of **2** was heated 105 °C. An exothermic reaction occurred. The heating was stopped, the reaction stirred rapidly, and occasional cooling applied so as to maintain a gentle reflux. When the exothermic reaction had subsided, heating was resumed so that the total reflux time was 105 min. Rapid distillation yielded 66.6 g (67%) of material (distillate **9**): bp 77–100 °C (0.05 Torr); IR (neat) 4.5, 5.08, 5.15, 7.9 μ; NMR (CCl_4) δ 1.11 (t, J = 7 Hz, CH_3CH_2O), 2.81 (2d, J = ~1.8, 22 Hz, CH_2PO), 3.57 (ABq, J = 7 Hz, CH_2O), 3.7 (d, J = 11 Hz, CH_3OP), 3.8 (d, J = 11 Hz, CH_3OP), 4.97–5.5 (two groups of multiplets, one centered at 5.15, the other at 5.5 ppm, integrating for 1.5 and 0.5 protons, acetal–allene protons); GLC retention times (15% Se-30 column, 165 °C) for **9** was 0.7, 7.7, 9.9, 12.0 (allene **11,** i.e., peak A), 16.4, 20.8 (B/C) min; GLC retention times on a 5% QF-1 column, run 165 °C; 0.4, 3.6 (A, allene **11**), 5.8 (B/C) min.

Fractional Distillation of Distillate 9:Dimethyl 4,4-Diethoxy-2-butyn-1-ylphosphonate (1). Fifty grams of distillate **9**, which by GLC (5% QF-1 column, ⅛ in. × 5 ft) was composed of **3** (D), **11** (A), and 60% **1** (confirmed by NMR), was fractionally distilled using a vacuum-jacketed Vigreux column to yield eight fractions. The initial fractions (1–4), 22.4 g, bp 90–120 °C (0.25 Torr), were mixtures of A, B, and C. Fractions 5 and 6, 12.1 g, were still mixtures of A, B, and C, but significantly richer in C than fractions 1–4. Fraction 7, 2.7 g, bp 125–128 °C (0.3 Torr), was 82% C. It contained ca. 11% D and 7% B. No A was observed in this fraction. The IR spectrum of this fraction showed a weak allene IR absorption at 5.07 μ. The remaining fraction **8**, 2.2 g, was a mixture of B, C, and D.

Fractions 1–4, 22.4 g, were fractionally distilled to yield 15 g of A, 72% pure as indicated by GLC, and 5 g of product rich in B, C, and D.

All the fractions rich in C were pooled (23.0 g) and distilled to give 7.8 g (5% yield based on **2**, 16% yield based on **9**) of **1**, bp 108–113 °C (0.3 Torr), which by NMR was 87% pure **1**: IR (neat) 3.37, 3.42, 3.48, 4.44 (w), 5.07 (w), 6.8, 7.15, 7.25, 7.35, 7.5, 7.9, 8.1, 8.7, 9.5, 9.7, 10.9, 11.65, 12.3, 12.65 μ; NMR ($CDCl_3$) δ 1.25, (t, J = 7 Hz, CH_3), 2.85 (2d, J = ~1.8, 21.8, Hz, CH_2P), 3.77 (ABq, J = 7 Hz, CH_2O), 3.88 (d, J = 11 Hz, CH_3OP), 5.3 (2t, J = 1.8, 3.8 Hz, $CH(OR)_2$).

The allene-rich fractions obtained from the distillation of **1** were pooled, redistilled 97–101 °C (0.25 Torr), and examined by IR. It was found to have the IR spectrum (neat) 3.36, 3.48, 4.4, 4.51, 4.6 (w), 5.08 (strong single abosrption), 6.9, 7.18, 7.28, 7.5, 7.62, 7.9, 8.2, 8.95, 9.5, 9.7, 10.92, 12., 12.33, 12.72, 13.22, 13.9 μ.

Fractional Distillation of the Pot Residue of Distillate 9. The pot residue (ca. 40 g) obtained from the Arbuzov reaction of **2** (1 equiv) and $(MeO)_3P$ (2 equiv) was flash distilled to give 20 g of distillate, bp 162–183 °C (0.2 Torr) (superheating required to distill product). Two successive fractional distillations of this material gave 12 g of product (distillate **13**): bp 137–140 °C (0.1 Torr); IR (neat) 3.36, 3.38, 3.45, 3.50, 6.12, 6.9, 7.94, 8.40, 9.43, 9.71, 12.05, 12.5 μ; NMR (C_6D_6) δ 1.0 (t, J = 7 Hz, CH_3), 1.7, 1.9, 2.1, 2.35, 2.7, 3.0, 3.1, 3.3, 3.5 (d, J = 11 Hz, CH_3OP), 3.9 (ABq, J = 7 Hz, CH_2O), 4.6, 4.8, 4.85, 4.9, 5.0, 5.24, 5.65 (2t, J = ~3 and ~6 Hz), 5.95, 6.05 (t, J = ~1.5 Hz), 6.28, 6.35 (t, J = ~1.5 Hz), 6.6 (t, J = 6 Hz), 7.0 (t, J = 6 Hz), 7.08, 7.18, 7.25.

Anal. Calcd for $C_{12}H_{26}O_8P_2$: C, 40.01; H, 7.28; P, 17.18. Found: C, 40.15; H, 7.65; P, 17.12.

Gas Chromatographic Study of the Arbuzov Reaction of 2 and Trimethyl Phosphite. The GLC studies were performed on a Varian Hi Fi gas chromatograph using a 15% Se-30 column (⅛ in. × 5 ft), an isothermal temperature of 175 °C, and a 60 mL/min flow rate of N_2. A solution of 3.31 g (0.015 mM) of **2** and 3.5 g (0.026 M) of $(MeO)_3P$ was heated 100 °C under N_2 atmosphere for a period of 4 h. Samples were withdrawn at regular intervals (20, 60, 90, 120, 180, 210, and 240 min) and analyzed by GLC under the above indicated conditions. The retention times for the products **7**, **2**, **A**, **B**, **C**, and **D** were found to be 2.4, 3.0, 8.2, 12, 13, and 14.6 min.

These experiments were repeated at 80 and 90 °C using the same concentrations and conditions. The results were similar to those obtained for the reaction run at 100 °C. An experiment was also run using a **2**: $(MeO)_3P$ concentration of 1:4 in which the presence of products with retention times greater than D was detected. These products were poorly resolved by 15% Se-30 columns and the experiment was not pursued further.

Dimethyl 1,1-Diethoxy-2,3-butadien-2-ylphosphonate (11) and Dimethyl 4,4-Diethoxy-1-butyn-1-ylphosphonate (3). Distillate **9** (66.1 g) dissolved in 60 mL of Et_2O was applied to a column of 100 g of Al_2O_3 (basic, Brockman activity No. 1). The product was eluted from the column with Et_2O and the Et_2O eluates were concentrated to give 60 g of liquid residue. GLC retention times on an analytical 15% Se-30 column, 170 °C, were: 0.7, 7.7, 9.6, 11.5 (A, **11** intensity unchanged from starting material), 15.4, 19.0, 23.3 (D, **3**). Fractional distillation of this material gave three fractions: (a) a high-boiling fraction, bp 89–92 °C (0.012 Torr), 31.6 g (36% from **2**), identified as dimethyl 4,4-diethoxy-1-butyn-1-ylphosphonate (**3**); (b) an intermediate fraction, bp 74–88 °C (0.01 Torr), consisting of a mixture of **11** and **3**; (c) a lower boiling point fraction, rich in allene **11** (9.4 g), bp 57–74 °C (0.01 Torr). Careful repeated fractional distillation of this allene (fraction c) using a 150-mm Vigreux column gave 4.8 g of pure dimethyl 1,1-diethoxy-2,3-butadien-2-ylphosphonate (**11**), bp 94–95 °C (0.26 Torr). GLC retention times for **3** and **11** on 5% QF-1 column were 9.1 and 3.6 min, respectively, using isothermal conditions (160 °C).

For Dimethyl 1,1-Diethoxy-2,3-butadien-2-ylphosphonate (11): IR (neat) 3.27; 3.35, 3.45, 5.09, 5.14, 6.9, 7.20, 7.3, 7.94, 8.1, 8.45, 8.95, 9.45, 9.66, 10.9, 11.2, 13.2 μ; NMR (C_6D_6) δ 1.13 (t, J = 7 Hz, CH_3CH_2), ~3.55 (ABq, J = 7 Hz, CH_2O), 3.58 (d, J = 11.5 Hz, CH_3OP), 4.78 (2d, J = 12 Hz, $CH_2{=}C{=}C$), 5.30 (2t, J = 5, 2 Hz, $CH(OEt)_2$); mass spectrum m/e 250 (0.1), 221 (1.4), 205 (15.8), 193 (1), 177 (21.4), 176 (6.8), 175 (3.6), 149 (13.3), 148 (12.2), 117 (10.4), 109 (15.6), 103 (100), 96 (9.9), 95 (7.7), 79 (15.2), 75 (68.5), 68 (10.7), 51 (5.3), 47 (29).

Anal. Calcd for $C_{10}H_{19}O_5P$: C, 48.04; H, 7.65; P, 12.38. Found: C, 48.11; H, 7.42; P, 12.19.

For Dimethyl 4,4-Diethoxy-1-butyn-1-ylphosphonate (3): IR (neat) 3.37, 3.47, 4.53, absence of allene absorptions, 6.9, 7.06, 7.27, 7.43, 7.8, 8.0, 8.47, 8.94, 9.7, 10.84, 11.24, 11.95, 12.74 μ; NMR ($CDCl_3$) δ 1.23 (t, J = 7 Hz, CH_3), 2.67 (2d, J = 4.0, 5.5 Hz, CH_2), 3.61 (2q, J = 7 Hz, CH_2O), 3.60 (d, J = 12.5 Hz, CH_3OP), 4.69 (t, J = 5.5 Hz, CH(OR)); mass spectrum m/e 249 (0.1), 221 (0.8), 219 (0.1), 206 (1.1), 205 (12.1), 204 (1.4), 193 (0.7), 178 (2), 177 (25.9), 176 (5.3), 175 (3.2), 163 (3.3), 149 (7.7), 148 (13.2), 147 (2.7), 121 (1.8), 117 (5.6), 116 (3.3), 110 (1.1), 109 (13.6), 103 (96.6), 96 (7.0), 79 (12.3), 75 (52.1), 47 (100).

Anal. Calcd for $C_{10}H_{19}O_5P$: C, 48.04; H, 7.65; P, 12.38. Found: C, 47.97; H, 7.49; P, 12.12.

Dimethyl 1,1-Diethoxy-2-*cis*-buten-2-ylphosphonate (12). A solution of 2.0 g (0.008 M) of **11** in 100 mL of EtOH containing 0.1 g of 5% Pd/C was hydrogenated at atmospheric pressure until a theoretical amount of H_2 was absorbed. The mixture was filtered, and the solvent was evaporated under reduced pressure to yield a residue which, when distilled, gave 1.55 g (77%) of product, bp 69–72 °C (0.1 Torr). The olefin was purified by preperative TLC using silica gel G as adsorbent and acetone–hexane (1/1) as the developing solvent to give pure **12**: IR (neat) 3.30, 6.08, 7.98, 9.43, 9.68, 11.4, 11.9, 12.4, 13.3 μ; NMR ($CDCl_3$) δ 1.21 (t, J = 7 Hz, CH_3CH_2), 2.06 (m, J = 1, 5, 7 Hz, $CH_3CH{=}$), 3.61 (ABq, J = 7 Hz, CH_2OP), 3.76 (d, J = 11 Hz, CH_3OP), 5.06 (m, J = 1, 1, 5 Hz, $CHCH{=}C$), 6.90 (m, J = 1, 7, 48 Hz, $CH{=}C$); mass spectrum m/e 252 (0.1), 251 (0.2), 237 (2.6), 223 (7.8), 221 (0.6), 209 (5.3), 208 (11.7), 207 (80.6), 206 (23), 191 (3.1), 179 (81.7), 178 (13.9), 177 (100), 163 (14.9), 150 (10.5), 149 (18.4), 147 (28.2), 145 (10.1), 135 (74.9), 127 (3.8), 117 (10.1), 110 (16.1), 109 (45.1), 103 (85.9), 96 (42.3), 95 (24.8), 92 (10.1), 79 (42.3), 75 (41.7), 69 (18.8), 68 (9.1), 55 (19.4), 53 (41.1), 52 (20.6), 51 (6.8), 45 (19.4), 43 (41.1), 42 (20.8), 41 (6.8), 37 (54.6), 35 (28.2), 33 (14.2), 32 (7.3), 31 (25.4), 29 (40), 21 (53), 19 (43.9), 18 (45.6), 17 (41.1).

Anal. Calcd for $C_{10}H_{21}O_5P$: C, 47.62; H, 8.39; P, 12.28. Found: C, 47.68; H, 8.50; P, 12.07.

Preparation of 3 by Reaction of 2 with $NaP(O)(OMe)_2$. A solution of $NaP(O)(OMe)_2$ in THF was prepared by reacting 3.8 g (0.0345 M) of $(MeO)_2P(O)H$ and 0.792 g (0.033 M) of NaH in 20 mL of THF. The solution was cooled to −70 °C and 6.63 g (0.03 M) of **2** added rapidly. The mixture was stirred 8 h while the dry ice–acetone bath was warming up to room temperature. The precipitated NaBr was removed by centrifugation and the centrifugate concentrated to yield a residue. Distillation of this residue yielded 1.3 g (17%) of **3**, bp 105–135 °C (0.1 Torr), with IR and NMR spectra the same as those obtained for **3** from Al_2O_3 isomerization of **9** (see above). Some allenyl- and alkenylphosphonate impurities were detected by IR in the product **3**, as evidenced by IR absorptions at 6.03, 6.1, 6.2, and 5.05 μ. The yield of **3** obtained by adding a 1.3 M solution of $NaP(O)(OMe)_2$ to a room temperature solution of **2** in THF (reaction mixture stirred 20 h, room temperature) was 10.6%.

Thermolysis and Alumina Isomerization Experiments with Distillate 9 and Phosponate 3. (A) Distillate **9**, rich in **11** and **1** (samples of 0.15 g), was heated 100–120 °C for periods of up to 36 h. The thermolysis was followed by IR. No significant change in the IR spectrum of **9** was observed. The IR spectrum after 9 h was the same as that of **9** at the start: IR (neat) 3.34, 3.37, 3.45, 3.5, 4.5, 5.07 (s), 5.13 (sh), 6.11, 6.19, (w), 6.73, 6.88, 7.15 (w), 7.25, 7.48, 7.93, 8.95, 9.43, 9.63, 10.8, 11.9, and 12.2 μ. Similar results were obtained for **3**.

(B) A solution of 0.172 g of **9** in 0.236 g of $(MeO)_3P$ was heated 100–120 °C. After 4 h, IR absorptions at 6.12, 6.19, and 12.5 μ appeared and were unchanged by continued heating. IR spectrum of the solution (9 h heating time) (neat): 3.35, 3.38, 3.5, 4.6 (w), 5.1 (w), 6.11, 6.19 (s), 6.7, 6.92, 7.08, 7.18, 7.5, 7.9, 8.34, 9.35, 9.6, 10.3, 10.85, 11.05, 12.14, 12.65, and 13.95 μ.

(C) The distillate **9**, indicated above in A, was applied to an Al_2O_3 column, basic Brockman activity No. 1, 1 × 7 cm, and eluted with Et_2O to give 1.22 g of isomerized product having an IR spectrum: IR (neat) 3.35, 3.45, 4.5, 5.08, 5.13, 6.2, 6.9, 7.28, 7.4, 7.5, 7.9, 8.95, 9.45, 9.7, 10.92, 11.95, and 12.75 μ. The allene IR absorptions (5.08, 5.13) were those typical of **11** rather than the type observed for **9**, indicating a change affecting the allene IR absorption.

Diisopropyl 4,4-Diethoxy-1-butyn-1-ylphosphonate (14). A solution of 44.2 g (0.2 M) of **2** and 62.4 g (0.3 M) of $(i\text{-}Pro)_3P$ was heated 105 °C for 2 h. Distillation of the solution yielded 25 g (40%)

of crude product, bp 132–150 °C (0.15 Torr). Careful fractional distillation using a 15-cm Vigreux column yielded 5 g of analytically pure **14**: bp 127–128 °C (0.025 Torr); IR (neat) 3.36, 3.42, 3.47, 4.52, 4.62 (w), 6.18, 6.8, 6.9, 7.2, 7.25, 7.4, 7.9, 8.21, 9.0, 9.35, 10.1, 11.1, 11.2, 12.9, 13.2 μ; NMR (C_6D_6) δ 1.08 (t, J = 7 Hz, CH_3C), 1.27 (d, J = 6 Hz, $(CH_3)_2CH$), 2.16 (2d, J = 6.4, 4.2 Hz, CH_2C), 3.43 (ABq J = 7 Hz, CH_2O), 4.50 (t, J = 6.4 Hz, CHO), 4.83 (m, J = 6.0, 8.8 Hz, CHO); mass spectrum m/e 307 (0.3), 306 (0.4), 291 (0.2), 263 (0.5), 262 (0.4), 261 (1.9), 260 (0.5), 259 (0.3), 249 (0.4), 245 (1.0), 235 (0.1), 233 (0.9), 232 (1.8), 221 (0.9), 220 (0.7), 219 (0.9), 218 (1.6), 217 (2.5), 214 (0.4), 207 (0.7), 205 (1.3), 204 (1.2), 203 (10.1), 201 (0.8), 195 (0.5), 193 (2.5), 192 (0.6), 190 (7.3), 189 (2.7), 179 (1.3), 178 (3.1), 177 (29.3), 176 (4.5), 175 (2.8), 174 (2.3), 173 (1.9), 165 (2), 162 (2.6), 161 (2.5), 159 (3), 150 (2.1), 149 (33.3), 148 (32), 147 (4.7), 142 (1.4), 135 (3.1), 133 (2), 132 (2.7), 131 (7.6), 130 (1), 123 (2.4), 121 (29.8), 120 (35.6), 114 (1), 109 (1), 108 (1.1), 105 (1), 104 (2.7), 103 (100), 102 (3.2), 99 (1.2), 97 (1.7), 96 (3.2), 81 (2), 75 (53.3), 65 (3.8), 59 (2.5) 47 (35.6), 43 (11.2), 42 (2.2), 41 (8.8), 40 (2.1), 39 (6.7), 31 (3.3), 29 (2.8), 28 (5.2), 27 (5.0).

Anal. Calcd for $C_{14}H_{27}O_5P$: C, 54.89; H, 8.88; P, 10.11. Found: C, 54.71; H, 8.80; P, 9.92.

The DCH Salt of 4,4-Diethoxy-2-butyn-1-ylphosphonate (4). A solution of 1 g (0.004 M) of **3** in 5 mL of Me_3SiCl was refluxed 54 h. The excess Me_3SiCl was evaporated in vacuo, and the residue was dissolved in 20 mL EtOH containing 0.725 g of DCH. The solution was left overnight at room temperature and then evaporated to yield a residue. Recrystallization of this residue yielded 0.67 g of crude **4**. Two additional recrystallizations resulted in 0.29 g (40%) of analytically pure **4**, mp 134–140 °C d; IR (KBr) 3.42, 3.5 3.34–4.5 (br NH_2HO_3P absorptions), 4.52, 6.18, 6.65, 6.87, 7.25, 7.42, 7.82, 7.95, 8.52, 9.25, 9.8, 10.75 μ; NMR ($CDCl_3$) δ 1.25 (t, J = 7 Hz, CH_3CH_2), 1.0–2.18 (cyclohexyl methylene proton hump), 2.57 (t, J = 5 Hz, CH_2), 3.0 (hump, CH–NH_2), 3.7 (ABq, J = 7 Hz, CH_2O), 4.67 (t, J = 5 Hz, CH_2C).

Anal. Calcd for $C_{20}H_{38}NO_5P$: C, 59.87; H, 9.73; N, 3.36; P, 7.68. Found: C, 59.53; H, 9.49; N, 3.46; P, 7.67.

The Reaction of 3 and Distillate 9 with Me_3SiBr. Five grams (0.02 M) of **3** was added to 10 g (0.065 M) of Me_3SiBr (Pfaltz & Bauer or synthesis[23]). A violent exothermic reaction occurred with the evolution of a gas. The reaction mixture was heated at reflux 2.5 h. The NMR spectrum of the reaction mixture in CCl_4 revealed ^1H NMR absorptions at 0.27 ($(Me)_3SiO$), 1.13 (t, J = 7 Hz, $EtOMe_3Si$), 1.37 (t, J = 7 Hz, CH_3CH_2O), 3.63 (q, J = 7 Hz, $EtOMe_3Si$), 3.97 (t, J = 7 Hz, CH_2O), 5.7 (d, J = 8 Hz, CH=CHO), 7.1 (m, AB pattern, P(O)CH=CBrCH=CHO). The volatiles were evaporated under reduced pressure and a solution of DCH was added (3.62 g (0.02 M) in 70 mL of EtOH). The solution was concentrated to a small volume and Et_2O was added. A solid precipitated out, 3.9 g, which by IR and NMR appeared to be DCH·HBr, mp >300 °C. Attempts to obtain crystalline products from the filtrate were unsuccessful.

The DCH Salt of 2-Chloro-4-ethoxy-1,3-butadien-1-ylphosphonic Acid (17). A solution of 2.5 g (0.01 M) of **3** in 7.5 g of Me_3SiCl was refluxed for 2 days and allowed to stand at room temperature for 1 week. The volatiles were removed under vacuum and the residue was dissolved in 20 mL of EtOH containing 2.72 g (0.015 M) of DCH. After standing for 1.3 h, the solution was concentrated to half its volume. A precipitate resulted which was difficultly soluble in most common solvents such as $CHCl_3$, Me_2SO, and H_2O. This precipitate was recrystalized from hot EtOH to give analytically pure **17** in 0.4 g yield: IR (KBr) 3.4, 3.48, 3.4–4.3 (bands, broad absorptions for NH_2HO_3P), 6.1, 6.38, 6.45, 6.6, 6.85, 7.45, 7.6, 8.0, 8.3, 8.6, 9.33, 10.55, 11.0, 12.35, 13.75 μ; NMR (CD_3OD) δ 1.3 (t, J = 7 Hz, CH_3C), 1.0–2.12 (DCH methylene hump), 3.9 (q, J = 7 Hz, CH_2O), 5.73 (d, J = 8 Hz, HC=CHOEt), 7.33 (d, J = 8 Hz, CH=CHO), 7.33 (d, J = 16 Hz, C=CHP(O)).

Anal. Calcd for $C_{18}H_{33}ClNO_4P$: C, 54.87; H, 8.44; Cl, 9.01; N, 3.56; P, 7.86. Found: C, 55.16; H, 8.60; Cl, 8.89; N, 3.56; P, 7.86.

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Registry No.—**1**, 62521-29-3; **2**, 40274-30-4; **3**, 62521-30-6; **4**, 62521-32-8; **7**, 16548-21-3; **10**, 756-79-6; **11**, 62521-33-9; **12**, 62521-34-0; **14**, 62521-35-1; **17**, 62521-37-3; **26**, 62521-38-4; $(MeO)_3P$, 121-45-9; $(i\text{-Pro})_3P$, 116-17-6; TMS-Br, 2857-97-8.

References and Notes

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(6) Crystalline DCH salts were found to be convenient precursors for the synthesis of free aldehydophosphonic acids.[5] These latter compounds were potent inhibitors of PPal recombination with PPal dependent enzyme, AAT.
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(8) The reported yield[7] of **2** was obtained only when the triethyl orthoformate was redistilled freshly before use. The undistilled commercially available reagent contained products that resulted in the precipitation of ZnI_2 from the reaction mixture. Yields under these circumstances were considerably lower, ca. 20%.
(9) The impurity was also observed by Epsztein and Marszak.[7] These authors characterized it to be **7**. The NMR spectrum of **2**, in addition to the expected absorptions for **2**, exhibited additional absorptions at 4.23 ppm (d) with a J = ~1.8 Hz. This was assigned to the ether CH_2 of **7** and used to estimate the purity of **2**.
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(11) Peaks were labeled A, B, C, and D according to their retention times, component D having the longest time.
(12) Distillate **9** was used as the index of yield of **1**, since GLC and NMR estimates showed **9** always to be 40–60% rich in **1**.
(13) The principal fragmentation route for acetals such as $RCH_2CH_2C{\equiv}CCH(OEt)_2$, R = Br, I, was found to be significantly different (M → M–OEt → M–OEt–C_2H_4) and lends support for the structural assignment of **3**; unpublished results.
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