H, C_4 H's and $NCCH_2CH_2CH_2CCO_2$); λ_{max} (EtOH) 287 nm; *m/e* 269.

Methyl *N*-(β-3,4-Dimethoxyphenethyl)-α-pyrrolidinylideneacetate (1a). Using the procedure described above, methyl 6-chloro-2-hexynoate (3.00 g), sodium iodide (3.00 g), sodium carbonate (anhydrous, 2.12 g), and 3,4-dimethoxyphenethylamine (3.60 g) afforded 1a (4.04 g, 71%) which was recrystallized from methanol-water (mp 90–100°): λ_{max} (CH_2Cl_2) 1670, 1590 cm^{-1}; δ_{TMS} ($CDCl_3$) 6.72 (m, 3 H, phenyl), 4.54 (s, 1 H, vinyl), 3.85 (s, 6 H, methoxyl), 3.62 (s, 3 H, methyl ester), 3.40 (m, 6 H, C_5 H's and phenethyl H's), 2.88 (m, 2 H, C_3 H's), and 1.85 (m, 2 H, C_4 H's); λ_{max} (EtOH) 290 nm; *m/e* 305.

Anal. Calcd for $C_{17}H_{23}NO_4$: C, 66.86; H, 7.59. Found: C, 66.88; H, 7.61.

General Procedure. To a solution of lithium diisopropylamide (1.1 equiv prepared from diisopropylamine and 1.8 *M* butyllithium in hexane) in 100 ml of anhydrous THF prepared under a nitrogen atmosphere at −78° was added the unsaturated ester in 3 ml of THF (dropwise). The solution was allowed to warm to 0° before cooling to −78° and rapidly adding benzeneselenenyl bromide (1.1 equiv, prepared by adding 0.55 equiv of bromine to 0.55 equiv of diphenyl diselenide in 3 ml of THF).[8] The solution was warmed to 0° and water, acetic acid, and 30% hydrogen peroxide were added rapidly. In all cases the reaction temperature was maintained below 25° until gas evolution ceased (30–60 min). The solution was poured into saturated sodium bicarbonate and extracted with methylene chloride. The combined extracts were washed with saturated aqueous NaCl, dried (Na_2SO_4), concentrated in vacuo, and purified as indicated below.

***N*-(β-3,4-Dimethoxyphenethyl)-2-carbomethoxymethylpyrrole (2a).** Chromatography of crude product [prepared as described above from 1a (0.50 g)] on silica gel with 5% THF–$CHCl_3$ gave 0.43 g (86%) of **2a:** λ_{max} (CH_2Cl_2) 3050 (w), 3000 (w), 2955, 1740, 1725, 1710, 1640, 1515, 1235, 1150, and 1030 cm^{-1}; δ_{TMS} ($CDCl_3$) 8.13 (d, *J* = 6 Hz, 1 H, C_5 H), 6.67–6.83 (m, 3 H, phenyl), 6.28 (dd, *J* = 6, 1.5 Hz, 1 H, C_4 H), 5.48 (m, 1 H, C_3 H), 3.83 (s, 9 H, carbomethoxyl and methoxyl), 3.75 (s, 2 H, $-CH_2CO_2-$), 3.73 (t, *J* = 8 Hz, 2 H, NCH_2C), 2.77 (t, *J* = 8 Hz, 2 H, benzylic); *m/e* 303.

***N*-(5-Carbomethoxypentyl)-2-carbomethoxymethylpyrrole (2b).** Alkylation and aromatization of 1b (0.38 g) gave 0.27 g (71%) of 2b (oil), purified by chromatography on silica gel: λ_{max} (CH_2Cl_2) 3030, 2950, 1735, 1730, 1610, 1420, 1125, and 1040 cm^{-1}; δ_{TMS} ($CDCl_3$) 8.11 (d, *J* = 6 Hz, 1 H, C_5 H), 6.30 (dd, *J* = 6 Hz, 1 H, C_4 H), 5.57 (m, 1 H, C_3 H), 3.60–3.95 (m, 10 H, $-CO_2CH_3$, $-CO_2CH_3$, NCH_2C, and $-CH_2CO_2$), 2.30 (m, 2 H, $-CH_2\mathbf{CH_2}CO_2$), and 1.1–1.7 [m, 6 H, $-(CH_2)_3-$]; λ_{max} (EtOH) 270 nm.

2-(Carboethoxymethyl)-5-methylfuran (2c). Alkylation and aromatization of 1c (1.7 g) gave 1.58 g (94%) as a light yellow liquid (unstable in air): λ_{max} (film) 3010, 2950, 1745, 1700, 1640, 1380, 1120, and 1045 cm^{-1}; δ_{TMS} ($CDCl_3$) 6.07 (m, 1 , C_4 H), 5.92 (m, 1 H, C_3 H), 4.12 (q, *J* = 7.2 Hz, 2 H, $O\mathbf{CH_2}CH_3$), 3.60 (s, 2 H,$-CH_2CO_2$), 2.23 (s, 3 H, C_5 methyl), and 1.21 (t, *J* = 7.2 Hz, 3, H, $-CH_2\mathbf{CH_3}$); *m/e* 168; λ_{max} EtOH) 223 nm.

2-(Carboethoxymethyl)-5-methylthiophene (2d). Alkylation and aromatization of 1d (0.93 g) gave an oil (0.88 g) which was chromatographed on silica gel with 10% ethyl acetate–chloroform to give 0.76 g (81%) of **2d:** λ_{max} (film) 2950, 2920, 2870, 1740, 1695, 1580, 1185 (s), and 1040 cm^{-1}; δ_{TMS} ($CDCl_3$) 7.40 (m, 1 H, C_4 H), 6.60 (m, 1 H, C_3 H), 4.13 (q, *J* = 7 Hz, 2 H, $O\mathbf{CH_2}CH_3$), 3.70 (s, 2 H, $-CH_2CO_2$), 2.40 (s, 3 H, C_5 methyl), 1.28 (t, *J* = 7 Hz, 3 H, $-CH_2\mathbf{CH_3}$); *m/e* 184; λ_{max} (EtOH) 242 nm.

Acknowledgment. We gratefull acknowledge the Research Corporation for support of this work.

Registry No.—**1a**, 53906-86-8; **1b**, 53906-87-9; **1c**, 40954-15-2; **1d**, 40954-17-4; **2a**, 53906-88-0; **2b**, 53906-89-1; **2c**, 53906-90-4; **2d**, 53906-91-5; methyl 6-chloro-2-hexynoate, 51804-12-7; methyl 6-aminohexanoate, 2780-89-4; 3,4-dimethoxyphenethylamine, 120-20-7.

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(1) R. B. Gammill and T. A. Bryson, *Tetrahedron Lett.*, 3963 (1974).
(2) All compounds were analyzed by ir, ^1H NMR, ^{13}C NMR, uv, and high-resolution mass spectra.
(3) In no case did the ester side chain of **1b** interfere with the γ-alkylation of the extended enolate (e.g., proton transfer, acylation, Michael-like addition to enamino ester).
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(5) (a) G. Wittig, R. Roderer, and S. Fischer, *Tetrahedron Lett.*, 3517 (1973); (b) T. A. Narwid and A. I. Meyers, *J. Org. Chem.*, **39**, 2574 (1974).
(6) See ref 8a and references cited therein.
(7) For the spectral properties of compounds **1c** and **1d**, see ref 5, for the spectral properties of compound **1a**, see ref 1.
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Rearrangement of Allylic Phosphonates

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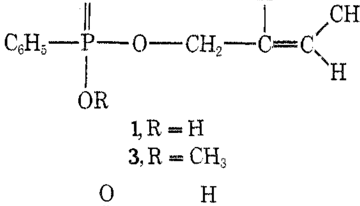
Received September 23, 1974

Allylic phosphates and pyrophosphates are key intermediates in the biosynthesis of terpenoids, steroids, and many other natural products. In view of the extensive studies on such systems and the intense current interest in head-to-head processes such as the farnesyl pyrophosphate → squalene conversion,[1] it is surprising that no example of an allylic isomerization of a phosphate, phosphonate, or phosphinate has been reported. Solvolysis of linaloyl phosphate in 70% aqueous acetone gave no detectable internal return to geranyl and neryl phosphates.[2] In the spontaneous decomposition of geranyl and neryl diphenyl phosphates in ether, linaloyl diphenyl phosphate was suggested as an intermediate, but could not be detected.[3] Finally, a labeled allyl diphenylphosphinate showed no scrambling of the allyl group at 220°.[4] We wish to report a simple system in which allylic isomerization is facile and some evidence which suggests the mechanism of the rearrangement.

The compounds selected for study were crotyl phenylphosphonate (1) and α-methylallyl phenylphosphonate (2). The monoesters were obtained from the reaction of phenylphosphonodichloridate with 1 equiv of the corresponding alcohol, followed by aqueous work-up. The oily products could not be distilled, but were purified by an extraction sequence. Samples slowly deteriorated at room temperature, but could be stored for months at −10° without decomposition.

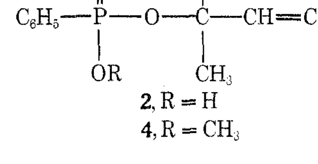
The interconversion of 1 and 2 was effected by heating a 10% solution of either compound in chlorobenzene or nitrobenzene. The isomerization was conveniently monitored by NMR; the methyl doublet of 2 occurs about 0.27 ppm upfield from the complex methyl region of the cis–trans mixture of 1. The equilibration was accompanied by some decomposition, but equilibrium could be approached from either side. The equilibrium mixture in nitrobenzene at 80° is ca. 30:70, favoring the more substituted double bond in 1.

The following experiments[5] are pertinent to the mechanism of the rearrangement. (1) The rate of isomerization is concentration dependent, becoming faster at higher concentrations. (2) The rearrangement is completely inhibited by pyridine, but is accelerated by trifluoroacetic acid. (3)



$C_6H_5-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OR}{|}}{P}}-O-CH_2-\overset{\overset{\displaystyle H}{|}}{C}=C\begin{smallmatrix}CH_3\\ H\end{smallmatrix}$

1, R = H
3, R = CH_3



$C_6H_5-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OR}{|}}{P}}-O-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH=CH_2$

2, R = H
4, R = CH_3

The reaction is ca. 2.5 times faster in nitrobenzene than in chlorobenzene under similar conditions. (4) Rearrangement cannot be observed in hydroxylic solvents; rather, the allylic group is cleaved. (5) The α-methylallyl methyl ester **4** undergoes isomerization to the crotyl methyl ester **3** at 130°, but at a rate ca. 20 times slower than the isomerization of **2** to **1** at the same temperature and concentration; this reaction is accelerated by the free acid **2**.

One intriguing mechanistic possibility for the isomerization is a 3,3-sigmatropic shift. This pathway has been demonstrated in the isomerization of allylic thiophosphates in which the oxygen to sulfur migration is accompanied by inversion of the allylic group.[6] An allyl phosphinate was found not to undergo such Claisen-type rearrangements,[4] but a monoallyl phosphonate such as **2** bears a labile acidic proton. The more nucleophilic oxygens in the anion of **2** might be more prone to initiate the sigmatropic shift.

The data clearly eliminate this possibility, however; the inhibition by pyridine indicates that the anion is inert, while the concentration dependence and effect of trifluoroacetic acid require that the reactive species is either the neutral or protonated **2**.

An ionic mechanism involving C–O cleavage to produce allylic cations is completely consistent with the observations. In hydroxylic solvents, the cations are intercepted without internal return and no isomerization is observed. The rate increase in nitrobenzene over chlorobenzene also supports this conclusion. The function of acid may be merely to prevent ionization of the strong phosphonic acid; in this case the neutral acid **2** would dissociate to an ion pair.[7] The isomerization of the neutral methyl ester **4** under nonacidic conditions shows that such a pathway is likely. On the other hand, the much slower isomerization of **4** suggests that **2** may react in a protonated form to produce a neutral phosphonic acid and an allylic cation which then recombine; such a mechanism seems required for the acid catalysis of isomerization of **4**. Cleavage in both neutral and protonated forms has been suggested for dibenzyl phosphate[8] and it appears that both mechanisms occur with rather similar energies for the allylic esters under the conditions described herein.

It thus appears that ionic mechanisms direct the isomerization of allyl phosphonates even in chlorobenzene. The detection of this rearrangement is a special case in a nonnucleophilic solvent; the possible significance of such rearrangements in biological systems remains unknown.

Experimental Section

Preparation of 3-Buten-2-yl Phenylphosphonate (2). A solution of phenylphosphonodichloridate (19.5 g) and pyridine (19 g) in anhydrous ether (300 ml) was stirred in an ice bath under argon while 3-buten-2-ol (6.0 g) was added over 15 min. After warming to room temperature, the mixture was poured into ice water containing 4 g of NaOH. The organic layer was separated, extracted with bicarbonate, and discarded. The aqueous layer and bicarbonate extract were acidified to pH <1 with concentrated HCl and extracted thrice with 75 ml of chloroform. Evaporation of the chloroform extracts gave a colorless oil which was treated[9] with a solution of 12 g of barium hydroxide in 120 ml of water. Ethanol (100 ml) was added and the precipitate was removed. The filtrate was concentrated on a vacuum pump to about one-half the volume, then adjusted to pH <1 with concentrated HCl and extracted with ether (3 × 50 ml). The organic layers were combined, dried, and evaporated to give 7.4 g of a viscous oil.

Anal. Calcd for $C_{10}H_{13}O_3P$: C, 56.58; H, 6.18. Found: C, 56.31; H, 5.93.

The NMR ($CDCl_3$, Varian A-60A) showed complex multiplets centered at δ 7.7 (2 H) and 7.3 (3 H) (aromatic protons) and at 5.7 (1 H) and 5.0 ppm (3 H) (vinyl and methine protons) plus a doublet for the methyl group at 1.31 ppm.

The 2-buten-1-yl phenylphosphinate **1**, a known compound,[10] was prepared from crotyl alcohol by a similar procedure. Its NMR spectrum ($CDCl_3$) showed multiplets at 7.7 (2 H) and 7.3 (3 H) (aromatic protons), 5.57 (2 H) (vinyl) and 4.5 (2 H) (methylene), and a broad doublet at 1.58 ppm (3 H) for the methyl group.

Equilibrations. Weighed samples of **2** or **1** in a NMR tube were diluted with 0.60 ml of chlorobenzene or nitrobenzene and immersed in a constant-temperature bath at 79.9°. The samples were withdrawn and NMR spectra recorded at regular intervals. Effects of pyridine, D_2O, and trifluoroacetic acid were determined by adding a known amount of each to the initial sample.

On one occasion, to confirm that **1** was the product from **2**, the equilibrated sample after 15 hr in chlorobenzene at 80° was pumped to dryness on a vacuum pump and put through the extraction sequence described above in the preparation of **2**. The NMR remained that of a mixture of **1** plus **2**.

Methyl 3-Buten-2-yl Phenylphosphonate (**4**). A solution of phenylphosphonodichloridate (25.4 g), pyridine (21 g), and 300 ml of ether was stirred in an ice bath under argon while first methanol (4.5 g) and then 3-buten-2-ol (8 g) were added dropwise. The mixture was filtered and the filtrate was washed with bicarbonate, dried over $MgSO_4$, and evaporated to give 15 g of colorless oil. The oil was fractionated by Kugelrohr distillation to give 9 g of **3** at 130° (0.01 mm).

Anal. Calcd for $C_{11}H_{15}O_3P$: C, 58.38; H, 6.69. Found: C, 58.14; H, 6.60.

Registry No.—**1**, 53940-78-6; **2**, 53940-79-7; **3**, 53940-80-0; **4**, 53940-81-1; phenylphosphonodichloridate, 824-72-6.

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(5) Most of these experiments were performed on both isomers, but the conversion of **2** into **1** proceeds to a greater extent and was examined more thoroughly. In view of the autocatalysis and the minor impurities in **2**, accurate kinetics were impractical and only qualitative rate trends are described.

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New Syntheses of Functional Arenesulfonyl Azides

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Received October 10, 1974

The synthesis of light-sensitive polymers containing sulfonyl azide groups requires functional monomers, which can be readily prepared from inexpensive starting materials. For the construction of these polymers two principles can be used: (a) reaction of an arenesulfonyl azide containing two functional groups with another difunctional monomer to produce addition or condensation polymers, and (b) reaction of a monofunctional arenesulfonyl azide with a multifunctional linear polymer. Mono-, as well as difunctional, arenesulfonyl azides were prior to our investigation virtually unknown.[1]

A readily available starting material for the synthesis of functional arenesulfonyl azides is 4-isocyanatobenzenesulfonyl chloride (1), which is obtained in high yield by phosgenation of sulfanilic acid.[4] In order to achieve a completely selective functionalization of 1, it was treated with excess ethylene glycol or triols at room temperature in acetonitrile