a reflux condenser fitted with a calcium chloride drying tube were placed 300 ml of methanol and 2.76 g (0.12 g-atom) of sodium metal. After all of the sodium had reacted, 0.12 mol of thiol was added and the resulting solution was stirred for 15 min. To the thiolate solution, 9.28 g (0.04 mol) of 3,4,5-trichloro-2,6-pyridinedicarbonitrile was added. The solution immediately became yellow in color, and a slight exotherm was observed. After stirring for several minutes, the contents of the flask solidified to a bright yellow, solid mass. The solid was filtered off and vacuum dried. The solid was recrystallized from methylene chloride–hexane or ethanol when necessary.

Reaction of 1 with 1 Equiv of Sodium Methanethiolate. In a 1-l., three-neck flask equipped with a magnetic stirrer, a rubber septum, and a reflux condenser fitted with a calcium chloride drying tube were placed 600 ml of methanol and 2.30 g (0.10 g-atom) of sodium metal. After all of the sodium had reacted, 6 ml of methanethiol (*stench*) was added to the methanol solution. The solution was allowed to stir for 0.5 hr, and then 23.25 g (0.10 mol) of 3,4,5-trichloro-2,6-pyridinedicarbonitrile was added. The reaction mixture immediately became yellow in color. The reaction mixture was heated to reflux (to make the system homogeneous) and then allowed to cool slowly to room temperature. Flat, white crystals separated which were filtered and dried to give 9.50 g of recovered 3,4,5-trichloro-2,6-pyridinedicarbonitrile, mp 198–200°. The methanol was removed from the filtrate in vacuo, leaving, after vacuum drying, 12.77 g of a pale yellow solid. The solid was treated with 100 ml of boiling 95% ethanol, and the resulting yellow solution was filtered. Upon cooling, long, bright yellow needles separated. The crystallization liquor was decanted, and the remaining needles were recrystallized from 50 ml of 95% ethanol to give, after vacuum drying, 0.78 g of 3,4,5-tris(methylthio)-2,6-pyridinedicarbonitrile (**2**, R = CH_3), mp 98–100°. Cooling the previously decanted crystallization liquor (see above) gave an additional 0.33 g, mp 98–100°.

Registry No.—**1**, 17824-85-0; sodium methanethiolate, 5188-07-8; sodium benzenethiolate, 930-69-8; sodium 4-methylbenzenethiolate, 10486-08-5; sodium 4-*tert*-butylbenzenethiolate, 5787-50-8; sodium 4-bromobenzenethiolate, 13457-82-4; sodium 2-naphthalenethiolate, 875-83-2.

References and Notes

(1) Analytical Laboratory, The Dow Chemical Co.

(2) R. E. Banks, R. N. Haszeldine, J. V. Latham, and I. M. Young, *J. Chem. Soc.*, 594 (1965); A. Roedig and K. Grohe, *Chem. Ber.*, **98**, 923 (1965); S. M. Roberts and H. Suschitzky, *Chem. Commun.*, 893 (1967); W. T. Flowers, R. N. Haszeldine, and S. A. Majid, *Tetrahedron Lett.*, 2503 (1967); Ya. N. Ivashchenko, L. S. Sologub, S. D. Moshchitskii, and A. V. Kirsanov, *Zh. Obshch. Khim.*, 1695 (1969).

(3) This compound is prepared by the vapor phase chlorination of 2,6-pyridinedicarbonitrile. See W. H. Taplin III (to the Dow Chemical Co.), U.S. Patent 3,420,833 (Jan 7, 1969); R. M. Bimber (to Diamond Shamrock Corp.), U.S. Patent 3,325,503 (June 13, 1967).

(4) All melting points are uncorrected. All new compounds gave satisfactory elemental analyses and ir and NMR spectra. The 100-MHz proton spectra were recorded on a Varian HA-100 spectrometer with an internal lock on tetramethylsilane. The carbon-13 spectrum was recorded at 25.2 MHz on a Varian XL-100-15 spectrometer equipped with a Digilab NMR-3 Fourier transform system.

A Convenient Preparation of Unsymmetrically Substituted Pyrroles, Furans, and Thiophenes

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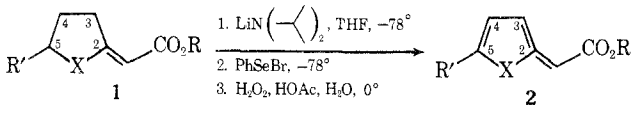
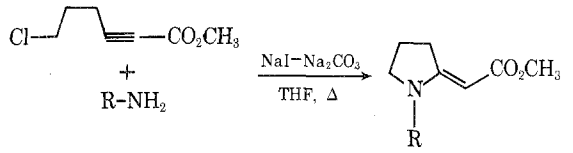
We wish to report a facile and versatile synthesis of substituted pyrroles, furans, and thiophenes. During one phase of a study of conjugated enamines,[1] we have found that enamino esters (**1a** and **1b**), enol ether esters (**1c**), or thioenol ether esters (**1d**) undergo γ-alkylation with benzeneselenenyl bromide. Oxidation (H_2O_2) and elimination of benzeneseleninic acid, followed by in situ double bond isomerization, afforded pyrrole (**2a** or **2b**), furan (**2c**), or thiophene (**2d**) in good yield.



	% yield
a, X = N—$(CH_2)_7$—$C_6H_3(OCH_3)_2$; R = CH_3; R′ = H	**2a**, 86
b, X = N—$(CH_2)_5CO_2CH_3$; R = CH_3; R′ = H	**2b**, 71
c, X = O; R = CH_2CH_3; R′ = CH_3	**2c**, 94
d, X = S; R = CH_2CH_3; R′ = CH_3	**2d**, 95

Spectral analyses of the products were consistent with the proposed structures.[2] The most notable change in going from **1** to **2** was the disappearance of vinyl absorptions in the ^1H NMR spectra of **1** and appearance of low-field methylene singlets in **2**. Also, disappearance of aliphatic ring proton absorptions of **1** and appearances of low-field multiplets characteristic of pyrroles, furans, and thiophenes were consistent with the assigned product. The infrared and ultraviolet spectra also showed absorption changes characteristic of conjugated esters being converted to unconjugated esters.[3]

The utility of this facile conversion is further supported by the ease of preparation of the enamino esters. For example, **1b** was prepared by concomitant Michael addition–alkylation of methyl 6-aminohexanoate with methyl 6-chloro-2-hexynoate in the presence of sodium iodide and sodium carbonate. Overnight reflux under nitrogen in THF



typically gave an 85% yield of enamino ester on work-up. Benzylamine, butylamine, phenethylamines, and ammonia have also been used in this process (70–95%).

Similarly, the relative simplicity of the preparation of **1c** and **1d** by epoxide or sulfide ring opening with the dianion of ethyl acetoacetate allows for the synthesis of a variety of tetrahydrofurylidene acetates and tetrahydrothiophenylidene acetates, and consequently a variety of furans and thiophenes, respectively.[4] The γ-alkylation of enamino esters[1] coupled with this aromatization sequence should give 3-substituted pyrroles.[5]

It is interesting to note that in this work we have not found evidence for sulfur oxidation in the oxidation–elimination sequence. This seems to confirm other qualitative reports of the relative ease of selenium oxidation compared to that of sulfur.[6]

Experimental Section[7]

Methyl *N*-(5-Carbomethoxypentyl)-α-pyrrolidinylideneacetate (1b). Methyl 6-chloro-2-hexynoate (3.13 g), methyl 6-aminohexanoate (3.00 g), sodium iodide (3.75 g), and sodium carbonate (2.65 g) were added to tetrahydrofuran (anhydrous, 60 ml) and refluxed for 20 hr under an atmosphere of nitrogen. After cooling, the reaction mixture was poured into water (100 ml) and methylene chloride (100 ml). The organic layer was separated, and the aqueous layer was extracted with methylene chloride (3 × 50 ml). The combined organic extracts were washed with aqueous sodium chloride (saturated, 50 ml), dried (Na_2SO_4), and concentrated under reduced pressure to give 5.55 g of crude product. Chromatography on alumina (50 g, Woelm activity grade III) with chloroform gave 5.25 g (100%) of **1b**: λ_{max} (film) 2950, 2860, 1735 (s), 1680 (s), 1595 (vs), 1435, 1140 (vs), 1060, and 780 cm^{-1}; δ_{TMS} ($CDCl_3$) 4.50 (t, J = 1.5 Hz, vinyl), 3.66 (s, 3 H, methoxyl), 3.59 (s, 3 H, methoxyl), 3.37 (t, J = 7 Hz, 2 H, C_5 H's), 3.15 (t, J = 7 Hz, 4 H, C_3 H's and NCH_2C), 2.31 (t, J = 7 Hz, 2 H, $-CH_2CO_2-$), 1.2–2.2 (m, 8

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, $-CH_2CH_2CO_2$), 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, OCH_2CH_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, $-CH_2CH_3$); *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, OCH_2CH_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, $-CH_2CH_3$); *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.

References and Notes

(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).
(4) T. A. Bryson, *J. Org. Chem.*, **38,** 3428 (1973).
(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.
(8) (a) H. J. Reich, I. L. Reich, and J. M. Renga, *J. Am. Chem. Soc.*, **95,** 5813 (1973); (b) *J. Org. Chem.*, **39,** 2133 (1974).

Rearrangement of Allylic Phosphonates

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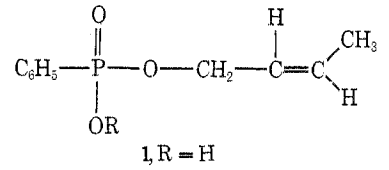
Allylic phosphates and pyrophosphates are key intermediates in the biosynthesis of terpenoids, steroids, and many other natural products. In view of the extensive studies on such systems and the intense current interest in head-to-head processes such as the farnesyl pyrophosphate → squalene conversion,[1] 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.

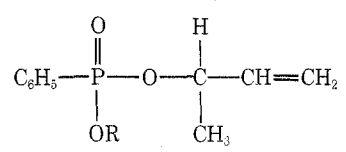
The compounds selected for study were crotyl phenylphosphonate (**1**) and α-methylallyl phenylphosphonate (**2**). The monoesters were obtained from the reaction of phenylphosphonodichloridate with 1 equiv of the corresponding alcohol, followed by aqueous work-up. The oily products could not be distilled, 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)



1, R = H
3, R = CH_3



2, R = H
4, R = CH_3