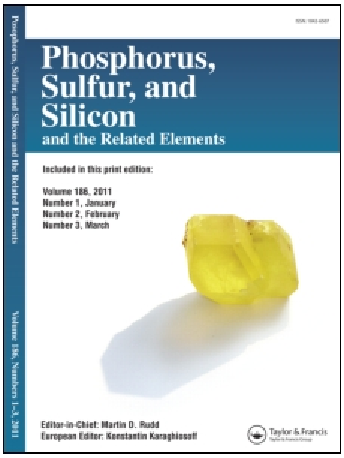


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

HIGH YIELD SYNTHESIS OF α-PHOSPHONYL ORGANOSULFUR COMPOUNDS

Massoud Garossian[a][b]
[a] Department of Chemistry, University of Kurdistan, Sanandaj, Iran [b] Department of Chemistry, University of Utah, Salt Lake City, Utah, USA

To cite this Article Garossian, Massoud(1994) 'HIGH YIELD SYNTHESIS OF α-PHOSPHONYL ORGANOSULFUR COMPOUNDS', Phosphorus, Sulfur, and Silicon and the Related Elements, 88: 1, 279 — 282
To link to this Article: DOI: 10.1080/10426509408036933
URL: http://dx.doi.org/10.1080/10426509408036933

Phosphorus, Sulfur, and Silicon, 1994, Vol. 88, pp. 279–282
Reprints available directly from the publisher
Photocopying permitted by license only

Communication

HIGH YIELD SYNTHESIS OF α-PHOSPHONYL ORGANOSULFUR COMPOUNDS

MASSOUD GAROSSIAN
Department of Chemistry, University of Kurdistan, P.O. Box 416, Sanandaj, Iran
Department of Chemistry, University of Utah, Salt Lake City, Utah 84112 USA

(Received April 5, 1993)

A new method for the preparation of a α-phosphonyl organosulfur compounds has been developed. The use of such compounds for preparation of vinylthioethers through Wadsworth-Emmons reaction are demonstrated.

Key words: Synthesis; α-phosphonyl organosulfur compounds.

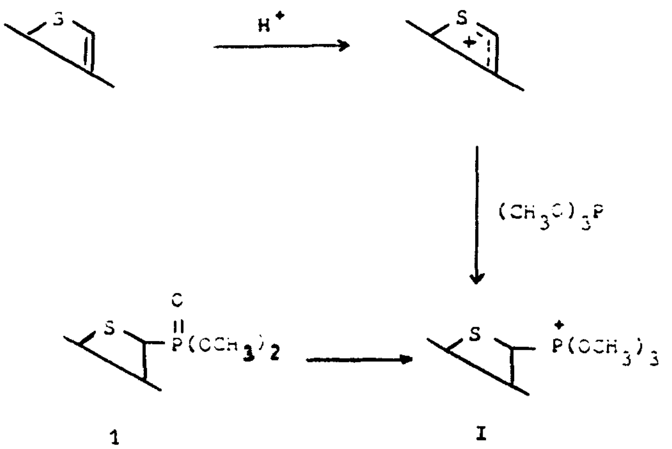
The use of Wittig-Horner reagents[1] has important organic applications. However, only those phosphonates having a resonance stabilizing group will give good yields of olefins with carbonyl compounds.[2] The ability of bivalent sulfur to stabilize an adjacent carbanion lends further versatility to the phosphonate modification of the Wittig synthesis.[3]

The potential importance of the extension of the carbon skeletons of carbonyl compounds by two or more carbons using reagents of general structure 1 suggests the need for a new way to prepare a variety of these types of compounds.

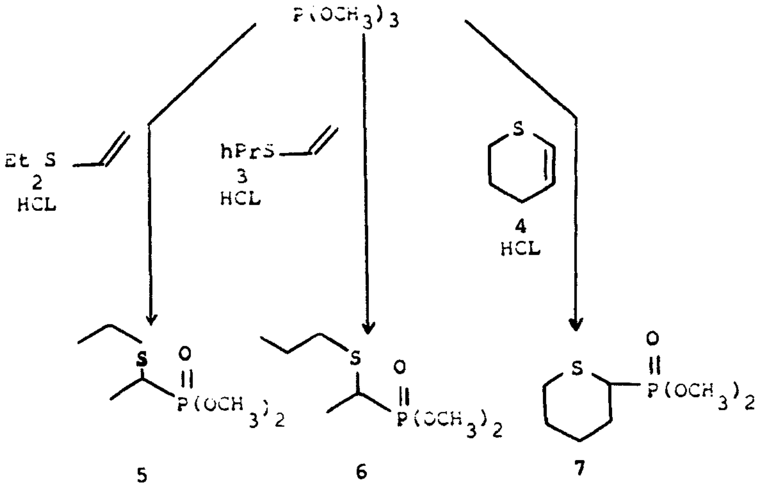
Although the common method for preparation of α-phosphonyl organosulfur compounds is via the corresponding α-halothioethers, the yields in many cases are low due to elimination as the side reaction.[4] Based upon the fact that alcohols can be protected as acetals by their reaction with enol ethers under acidic conditions,[5] I reasoned that trivalent phosphorous compounds should act as nucleophiles under similar conditions to form carbon-phosphorous bonds. The reaction presumably would proceed to an Arbuzov-like intermediate I which would then react further to form the α-phosphonyl organosulfur 1 as shown in Scheme 1.

The reaction of vinyl ethers with triphenyl phosphine and trimethyl phosphite in the presence of Hydrogen Chloride produces the corresponding α-alkoxy phosphonium salts and α-alkoxy phosphonates respectively.[5,7] I wish to report preliminary results on the reaction of equimolar amounts of trimethyl phosphite with ethyl vinyl thio ether 2, propyl vinyl thio ether 3, and 2–3 dihydro thio pyran 4 in anhydrous ether in presence of dry Hydrogen-Chloride at 0 to give over 90% yield of dimethyl (α-ethyl thio ethyl) phosphonate 5; dimethyl (α-ethyl thio propyl) phosphonate 6 and dimethyl (2-tetrahydropyranyl) phosphonate 7, respectively as shown in Scheme 2.

With high yield of phosphonates 5–7 in hand, studies of Wadsworth-Emmons[8] reaction using these substrates were undertaken. Phosphonate 5 and 6 was used



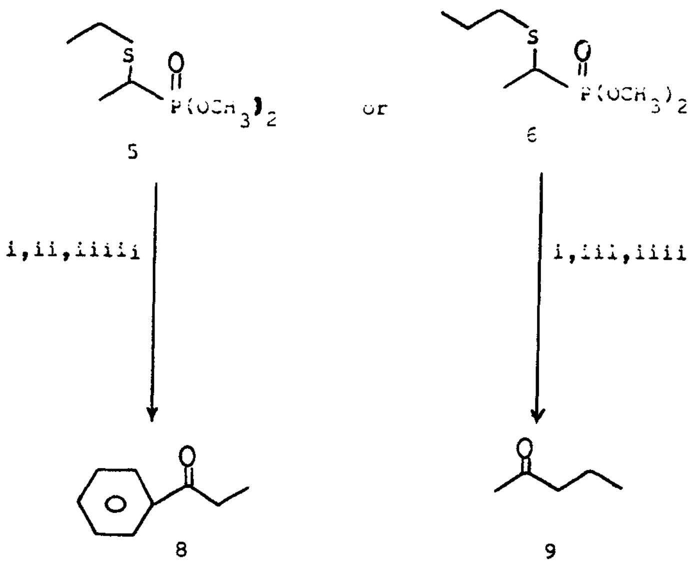
SCHEME 1



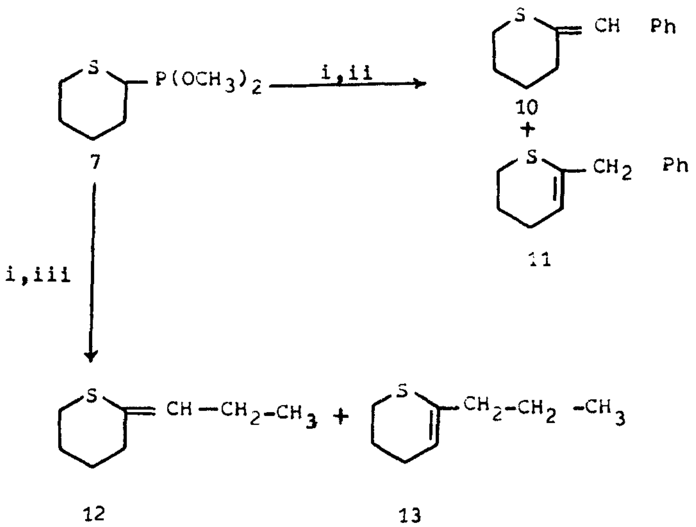
SCHEME 2

in a two-carbon addition to benzaldehyde and propionaldehyde to give 1-phenyl-2-propanone 8 (88 and 75%) and 2-propanone 9 (80 and 86%) following hydrolysis of their corresponding vinyl thio ethers (Scheme 3).

These products were fully characterized and compared with authentic materials. Likewise, phosphonate 7 was transformed into a mixture of (E)- and (Z)-2-(phenylmethylene)-tetrahydrothiopyran 10 and 2-(phynylmethyl)-2,3-dihydrothiopyrane 11 when it was treated with benzaldehyde and (E)-(Z)-2-(ethylmethylene)-tetrahydrothiopyrane 12 and 2-propyl-2,3-dihydropyrane 13 on reaction with propionaldehyde (Scheme 4). The vinyl sulfides 11 and 13 are the results of Basic Promoted of vinyl sulfides 10 and 12, respectively.



SCHEME 3 i, THF, n-BuLi, −78°; benzaldehyde, THF, −78°; iii, Propionaldehyde, THF, −78. iiii, H_2O, $TiCl_4$.



SCHEME 4 i, THF, n-BuLi, −78°; ii, benzaldehyde, THF, −78°; iii, Propionaldehyde, THF, −78°.

EXPERIMENTAL

Boiling points are uncorrected and are reported in degrees centigrade. The NMR spectra were measured with a varian EM-390. Signal positions are reported in PPm downfield from tetramethylsilane (δ scale) as an internal standard. GCMS data were obtained from a varian MAT 112-S instrument fitted with a 6′ × 1/8″ glass carbowax 20 m (1%) column. Preparative GC were carried out with a thermal A-90-P Chromatograph with a thermal conductivity detector using a SE-30 column. Microanalyses were done by the Chemalytics, Inc. All solvents and chemicals were purified in the usual manner prior to their use.

General Procedure for Preparation of α-phosphonyl Organosulfur Compounds

To a solution of an equimolar amount (200 mmol each) of trimethyl phosphite, vinyl thio ether and 150 ml of anhydrous ethyl ether in a 250 ml, three-necked, round bottom flask equipped with a condenser, magnetic stirrer, and gas inlet tube was added under an N_2 atmosphere approximately 160 mmol of dry HCL gas.

The solution was stirred at room temperature for 30 min and the solvent was removed by distillation. The residue was distilled *in vacuo* to give the corresponding α-phosphonyl organosulfur compounds. 5: Dimethyl (α-ethyl thio ethyl) phosphonate: colorless liquid, 90%, b.p. 77–78°C (0.5 mmHg), M.S. m/e 199 (M^+), anal. calcd. for $C_6H_{15}O_3PS$: c, 36.36; H, 7.58; P, 15.66. Found: C, 36.15; H, 7.70; P, 15.75. ^1H NMR ($CDCL_3$) δ 4.10 (6H, d, j = 15 Hz), 2.81–3.10 (3H, m), 1.60–1.85 (6H, m), ^{31}P NMR ($CDCL_3/H_3PO_4$) = 26.7.

6: Dimethyl (α-ethyl thio propyl) phosphonate: colorless liquid, 95%. b.p. 80–81°C (0.5 mmHg), M.S. m/e 213 (M^+), anal. calcd. for $C_7H_{17}O_3PS$: C, 40.00; H, 7.14; P, 14.76. Found: C, 39.95; H, 7.01; P, 14.59. ^1H NMR ($CDCL_3$) δ 4.15 (6H, d, j = 15 Hz), 2.85–3.17 (3H, m) 1.65–1.88 (8H, m), ^{31}P NMR ($CDCL_3/H_3PO_4$) = 26.2.

7: Dimethyl (2-tetrahydrothiopyranyl) phosphonate: colorless liquid, 92%, b.p. 98–100 (0.3 mmHg), M.S. m/e 209 (M^+), anal. calcd. for $C_7H_{15}O_3PS$: C, 40.00; H, 7.14; P, 14.76. Found: C, 40.25; H, 7.09; P, 14.50. ^1H NMR ($CDCL_3$) 4.15 (6H, d, j = 12 Hz), 2.80–3.20 (3H, m) ^{31}P NMR ($CDCL_3/H_3PO_4$) = 25.6.

General Procedure for Synthesis of Vinylthioethers

To a solution of phosphonate (50 mmol) and 100 ml of anhydrous THF at −78°C under N_2 atmosphere in a 250 ml, three-necked, round bottom flask equipped with a condenser, magnetic stirrer, and a dropping funnel; was added n-BuLi (50 mmol) in hexane over a period of 30 min to give a dark-red solution to which 50 mmol of aldehyde in 30 ml of THF was added dropwise at −78°C during 30 min. The mixture was stirred at room temperature for 1 h, then refluxed for another 1 h, followed by the usual work-up. Vinyl sulfides 10,11 and 12,13 were purified by kgelrohr distillation in 85% and 81% yield, respectively. Each pair was furthur separated by preparative GC, SE-30 Column, Vinyl sulfides 10 and 12 were obtained as mixtures of E and Z geometrical isomers without determining their compositions. ^1H NMR, analytical and mass spectral data of them are as follows.

10: (E)- and (Z)-(phenylmethylene)-tetrahydrothiopyrane: colorless oil; M.S. m/e 191 (M^+) anal. calcd. for $C_{12}H_{14}S$; C, 75.79, H, 7.37. Found: C, 75.83; H, 7.32. ^1H NMR ($CDCL_3$) δ 7.30–8.05 (10H, m, aromatic), 5.85 and 6.05 (2H, S, =CH), 2.05–2.28 (4H, m, —CH_2—C=C—), 1.80–1.98 (4H, m, —CH_2—S—), 1.00–1.60 (8H, m, —CH_2—CH_2—).

11: 2-(Phenyl methyl)-2,3-dihydrothiopyrane: colorless oil; M.S. m/e 191 (M^+) anal. Calcd. for $C_{12}H_{14}S$: C, 75.79; H, 7.37. Found: C, 75.73; H, 7.40. ^1H NMR ($CDCL_3$) δ 7.60 (5H, m), 5.05 (1H, t, =CH, J_{HH} = 7.1 Hz), 3.10 (2H, S, —CH_2—), 2.40 (2H, t, —CH_2—C=C—, J_{HH} = 6.5 Hz), 1.95 (2H, t, —CH_2—S, J_{HH} = 7.10 Hz), 1.05–1.70 (4H, m, —CH_2—CH_2—).

12: (E)-(Z)-2-(ethylmethylene)-tetrahydrothiopyrane: colorless liquid; M.S. m/e 143 (M^+). Anal. calcd. for $C_8H_{14}S$: C, 67.61; H, 9.86. Found: C, 67.66. H, 9.90. ^1H NMR ($CDCL_3$) 5.40 and 5.80 (2H, t, =CH, j_{HH} = 7.30 and 7.30 Hz), 1.80–2.55 (12H, —CH_2—CH=C and —CH_2—S—), 0.90–1.50 (14H, m, —CH_3, —CH_2—CH_2—).

13: 2-propyl-2,3-dihydropyrane: colorless liquid; M.S. m/e 143 (M^+). Anal. calcd. for $C_8H_{14}S$: C, 67.61; H, 9.86. Found: C, 67.80; H, 9.55. ^1H NMR ($CDCL_3$) δ 5.50 (1H, t, =CH, j_{HH} = 7.2 Hz), 1.75–2.40 (6H, m, —CH_2—C=C—, —CH_2—S), 0.85–1.60 (7H, m, —CH_2—C—, —CH_3).

BIBLIOGRAPHY

1. L. Horner, *Chem. Ber.*, **92,** 2499 (1959).
2. A. W. Johnson, 'Ylide Chemistry,' Academic Press, New York, NY, 1966; M. Schlosser, *Top Stereochem.*, **5,** 1 (1970); R. Thomas and T. Boutagy; *Chem. Rev.*, **74,** 87 (1974).
3. M. Mibołajczyk, *et al.*, *J. Org. Chem.*, **44,** 2967 (1979); E. J. Corey and J. L. Shulman, *J. Am. Chem. Soc.*, **92,** 5522 (1970).
4. V. D. Gen, *et al.*, *J. Org. Chem.*, **44,** 2911 (1974); J. Thiem and H. Paulsen, *Phosphorous*, **6,** 51 (1975); E. Schaumann and F. Grabley; *Justus Liebigs Ann Chem*, 88 (1977).
5. A. Jones and D. Wood, *J. Chem. Soc.*, 5400 (1964); D. A. Clark and P. L. Fuchs, *Synthesis*, 628 (1977).
6. S. V. Ley, *et al.*, *Tetrahedron*, **41,** 3825 (1985).
7. W. W. Epstein and M. Garrossian, *Phosphorous and Sulfur*, **35,** 349 (1988).
8. W. S. Wadsworth and W. D. Emmons, *J. Am. Chem. Soc.*, **83,** 1733 (1961).