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HIGH YIELD SYNTHESIS OF α -ALKOXYPHOSPHONIUM SALTS AND α -ALKOXYPHOSPHONATES

William W. Epstein^a; Massoud Garrossian^a

^a Department of Chemistry, University of Utah, Salt Lake City, Utah

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SHORT COMMUNICATION

High Yield Synthesis of α -Alkoxyphosphonium Salts and α -Alkoxyphosphonates

WILLIAM W. EPSTEIN* and MASSOUD GARROSSIAN

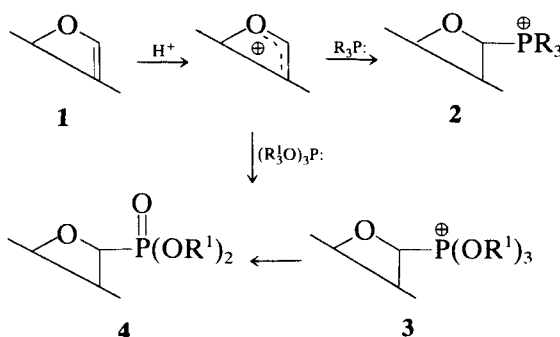
Department of Chemistry, University of Utah, Salt Lake City, Utah, 84112

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The recent work of Ley *et al.*¹ on α -alkoxyphosphorane compounds from cyclic enoethers has prompted us to report our findings in this area. In addition to cyclic enol ethers we have studied the acyclic case as well as the use of phosphite in place of triphenylphosphine. Using this approach we have prepared alkoxy- as well as 5- and 6-membered oxyheterocyclic phosphonium salts and phosphonates in high yield.

Key Words: Synthesis; cyclic and acyclic; alkoxyphosphonium salts; and alkoxyphosphonates.


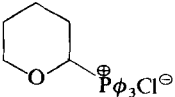

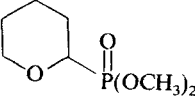

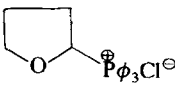

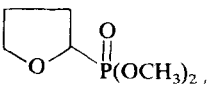
Although the common method for preparation of α -alkoxyphosphonium salts and α -alkoxyphosphonates is *via* the corresponding α -haloether,² the yields in many cases are low due to elimination as a side reaction.³ Based upon the fact that alcohols can be protected as acetals by their reaction with enol ethers under acidic conditions,⁴ we reasoned that trivalent phosphorus compounds should act as nucleophiles under similar conditions to form carbon-phosphorus bonds. This concept is outlined in Scheme 1.



SCHEME 1

The reactions involving triarylphosphines would give the desired phosphonium salts (2) directly while reactions with trialkylphosphites presumably would proceed to an Arbuzov-like intermediate (3) which would then react further to form the phosphonate (4). Using this enol ether approach we have been able to prepare a variety of the corresponding phosphonium chlorides and phosphonates from triphenyl phosphine or trimethyl phosphite and gaseous HCl in greater than 87% yield as shown in Table I.

TABLE I
 Yield data for α -alkoxy phosphorus Compounds

Enol Ether	Trivalent phosphorus compound		Product	Yield
$\text{CH}_3\text{CH}_2\text{—O—CH=CH}_2$	$\phi_3\text{P}$	2a	$\text{Et—O—CH—P}^+\phi_3\text{Cl}^-$ $\quad \quad $ $\quad \quad \text{CH}_3$	96%
$\text{CH}_3\text{CH}_2\text{—O—CH=CH}_2$	$(\text{CH}_3\text{O})_3\text{P}$	4a	$\text{Et—O—CH—P(=O)(OCH}_3)_2$ $\quad \quad $ $\quad \quad \text{CH}_3$	94%
	$\phi_3\text{P}$	2b		88%
	$(\text{CH}_3\text{O})_3\text{P}$	4b		87.5%
	$\phi_3\text{P}$	2c		99%
	$(\text{CH}_3\text{O})_3\text{P}$	4c		90%

As noted earlier¹ the phosphonium chlorides did not give acceptable combustion analyses but the spectral data and other reactions leave little doubt as to their structure.

EXPERIMENTAL

Melting points were determined on a Fisher-Johns Mel-Temp melting point apparatus and are reported uncorrected. 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; microanalysis were done by the Chemalytics, Inc.; GCMS data were obtained from a Varian MAT 112-S instrument fitted with a $6' \times 1/8''$ glass carbowax 20 m (1%) column. All solvents and chemicals were purified in the usual manner prior to their use.

General Procedure for Preparation of Phosphonium Chlorides 2

To a solution of 210 mmol of vinyl ether, 200 mmol of triphenyl phosphine and 300 ml of anhydrous ethyl ether under N_2 atmosphere in a 500 ml, three necked flask equipped with a gas inlet tube, mechanical stirrer, and reflux condenser at $0^\circ C$ was added approximately 210 mmol of dry hydrogen chloride gas. The reaction mixture was stirred at room temperature for 1 h, the precipitated salt was filtered, washed twice with 100 ml portions of anhydrous ether under N_2 atmosphere, and vacuum dried (~ 0.05 mm, room temperature).

2a: α -ethoxyethyl triphenylphosphonium chloride: 96%, m.p. $88-91^\circ$; 1H NMR ($CDCl_3$) δ 7.8 (15 H, m), 6.25 (1 H, m), 3.50–4.10 (2 H, m), 1.65–1.90 (3 H, d of d), 1.15 (3H, t).

2b: (2-tetrahydropyranyl)triphenyl phosphonium chloride: 88%, m.p. $124-126^\circ$; 1H NMR ($CDCl_3$) δ 7.7 (15 H, m), 6.05 (1 H, m), 4.10 (2 H, t), 1.5–2.0 (6 H, m).

2c: (2-tetrahydrofuranyl)triphenyl phosphonium chloride: 99% yield, m.p. $119-120^\circ$; 1H NMR ($CDCl_3$) δ 7.7 (15 H, m), 6.20 (1H, m), 3.5–4.0 (2 H, pair of q), 1.05–3.15 (4 H, m).

General Procedure for Preparation of Phosphonates 4

To a solution of 150 ml of anhydrous ethyl ether, 160 mmol of corresponding vinyl ethers and 160 mmol of trimethyl phosphite 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 phosphonates.

4a) dimethyl (α -ethoxyethyl)phosphonate: 94%, b.p. $56-57^\circ$ (0.5 mm); 1H NMR ($CDCl_3$) δ 1.2–1.6 (6 H, m), 1.7–1.9 (9 H, m). Anal. Calcd for $C_6H_{15}O_4P$. Calcd. C, 39.56; H, 8.30; P, 17.00. Found C, 39.39; H, 7.98; P, 16.80. M.S. (CI) $M + 1 = 182.9$.

4b) dimethyl(2-tetrahydropyranyl)phosphonate: 87.5%, b.p. $90-91^\circ$ (2 mm); 1H NMR ($CDCl_3$) δ 3.4–4.2 (9 H, m), 1.5–2.0 (6 H, m). Anal. Calcd. for $C_7H_{15}O_4P$. Calcd. C, 43.30; H, 7.79; P, 15.95. Found C, 43.40; H, 7.70; P, 15.85. M.S. (CI) $M + 1 = 195$.

4c) dimethyl(2-tetrahydrofuranyl)phosphonate: 90%, b.p. $80-82^\circ$ (0.7 mm). 1H NMR ($CDCl_3$) δ 3.6–4.3 (9 H, m), 1.55–1.95 (4 H, m). Anal. Calcd. for $C_6H_{13}O_4P$. Calcd. C, 40.01; H, 7.27; P, 17.19. Found C, 39.85; H, 7.02; P, 16.91. M.S. (CI), $M + 1 = 181$.

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