Anodic Oxidation of Triphenylphosphine in the Presence of Enol Silyl Ethers or Enol Esters. Electrochemical One-step Preparation of 2-Oxocycloalkyltriphenylphosphonium Tetrafluoroborates

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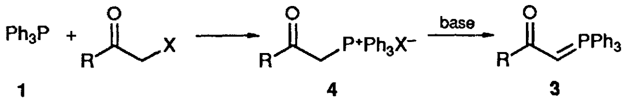
Electrochemical oxidation of triphenylphosphine in the presence of cyclic enol silyl ethers or enol esters gave 2-oxocycloalkyltriphenylphosphonium salts, which underwent the Wittig reaction with aldehydes to afford (*E*)-2-alkylidenecycloalkan-1-ones.

The triphenylphosphine radical cation [$Ph_3P^{+\cdot}$] **2**[1] generated by electrochemical oxidation of triphenylphosphine **1** reacts with electron-rich alkenes to form phosphonium salts with a P–C bond.[2] 2-Oxoalkylidenetriphenylphosphoranes **3** are valuable intermediates in Wittig alkenation reactions providing enones and heterocyclic compounds.[3] The preparation of acyclic 2-oxoalkyltriphenylphosphonium salts **4**, the precursor of **3**, is straightforward and may be accomplished by nucleophilic substitution of α-haloketones with **1** (Scheme 1).[4] However, 2-oxocycloalkyltriphenylphosphonium salts cannot be prepared in this way.[5] An alternative approach to the cyclic phosphonium salts involves multi-step sequences, resulting in low overall yields of the desired products.[6]



Scheme 1

In this communication we describe a new one-step synthesis of 2-oxocycloalkyltriphenylphosphonium tetrafluroborates **5** based on the anodic oxidation of triphenylphosphine **1** in the presence of an enol silyl ether or enol esters (Scheme 2).

Enol silyl ether **6** and two enol esters with five- to seven-membered rings, *viz*, enol phosphates **7** and enol acetates **8**, were chosen, and their optimal electrolysis conditions were determined with the five-membered rings substrates **6a**, **7a** and **8a**. The enol acetate **8a** was the most efficient substrate. Table 1 summarizes the results of constant-current electrolysis (CCE) performed in an undivided cell under a dry nitrogen atmosphere. All the substrates were converted to 2-oxocycloalkyltriphenylphosphonium tetrafluoroborate **5**.† The CCE required **1** in excess over the enol

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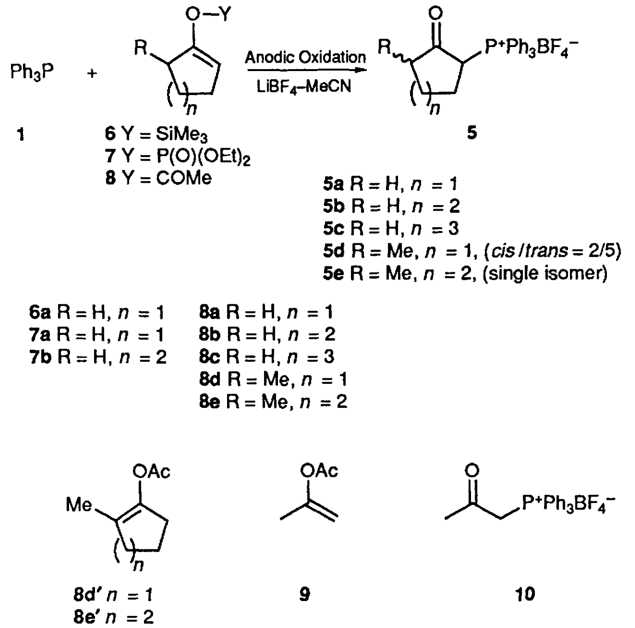
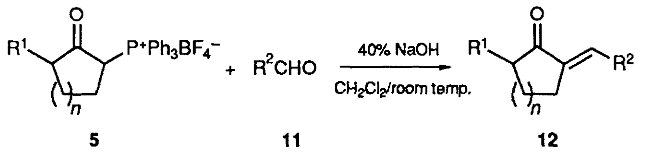
† **5a**: m.p. 228–230 °C (from CH_2Cl_2–diethyl ether); IR (KBr) 1723 cm^{-1} (C=O); ^1H NMR (CD_3CN) δ 4.72–4.63 (1H, m, HCP^+Ph_3); ^{13}C NMR (CD_3CN) δ 211.3 (C=O), 44.6 (J_{PC} 55.7 Hz, CP^+Ph_3), 39.9, 28.1, 22.4.



Scheme 2



Scheme 3

Table 1 Anodic oxidation of **1** in the presence of enol silyl ether **6** or enol esters **7** and **8**[a]

Run	Compound (amount/mmol)	Product	Yield (%)[b]
1	**6a** (3.0)	**5a**	11
2	**7a** (3.0)	**5a**	29
3	**7a** (1.0)	**5a**	51 (25)[c]
4	**7b** (3.0)	**5b**	23
5	**8a** (3.0)	**5a**	47
6	**8a** (1.5)	**5a**	83 (45)[c]
7	**8a** (1.0)	**5a**	96
8	**8b** (3.0)	**5b**	53
9	**8b** (1.0)	**5b**	93
10	**8c** (1.0)	**5c**	93
11	**8d** (1.0)	**5d**	92
12	**8e** (1.0)	**5e**	94

[a] Electrolysis conditions: CCE of PPh_3 (3 mmol) in MeCN (40 ml) containing an enol silyl ether or an enol ester and $LiBF_4$ (0.2 M); anode: glassy carbon plate, cathode: lead plate; electrolysis current: 20 mA (current density, 1 mA cm^{-2}). After 2 F per mol of **1** had been passed the reaction mixture was worked-up in a conventional manner.§ [b] Isolated yield based on **6**, **7** and **8**. [c] Electrolysis was performed in air.

Table 2 Wittig reaction of **5** with aldehydes **11**

Product	R1	R2	*n*	Yield (%)[a]
(**12a**)	H	Pr^n	1	43
(**12b**)	H	$PhCH_2CH_2$	1	62
(**12c**)	H	$PhCH_2CH_2$	2	58
(**12d**)	Me	$PhCH_2CH_2$	1	56
(**12e**)	Me	$PhCH_2CH_2$	2	51

[a] Isolated yields, reaction conditions: **5**, **11**, CH_2Cl_2, NaOH.

esters **7** and **8** (runs 3, 6 and 7). Water contamination during the electrolysis decreased the yield of **5** (runs 3 and 6). Under the conditions adopted in run 7, other enol acetates **8b–e** were converted to the corresponding 2-oxoalkylphosphonium salts **5b–e** in excellent yields (runs 9–12).‡ The phosphonium salt **5d** derived from **8d** was a 2 : 5 mixture of *cis*- and *trans*-isomers. whereas **5e** was a single isomer for which the stereochemistry has yet to be assigned. However, no phosphonium salts were obtained from 1-acetoxy-2-methylcycloalkenes such as **8d′** and **e′**. The present method can also be applied to the synthesis of acyclic 2-oxoalkylphosphonium tetrafluoroborates. Isopropenyl acetate **9** was converted to the 2-oxoalkylphosphonium salt **10** in 94% yield.

To estimate the validity of the 2-oxocycloalkylphosphonium salts **5** as a building block in synthetic organic chemistry, we examined their Wittig reactions with aldehydes **11** (Scheme 3). As shown in Table 2 the reactions proceeded as expected to afford the corresponding (*E*)-2-alkylidenecycloalkan-1-ones **12**.¶

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‡ All the new compounds gave satisfactory analytical and spectral data.

§ The reaction mixture was concentrated *in vacuo*, treated with water and $CHCl_3$. The organic layer was dried, concentrated and poured dropwise into dry diethyl ether. The resulting precipitate was recrystallized from CH_2Cl_2–diethyl ether.

¶ The positions and the configurations of the double bonds in compounds **12a–e** were established by comparison of their ^1H NMR data with those of the authentic and related compounds reported in ref. 7.