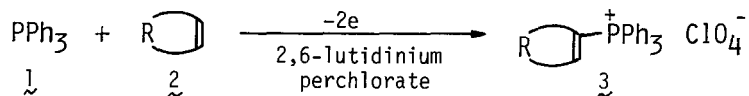


REACTION OF TRIPHENYLPHOSPHINE RADICAL CATION WITH
 CYCLOALKENES: ELECTROCHEMICAL ONE-STEP PREPARATION
 OF 1-CYCLOALKENYLTRIPHENYLPHOSPHONIUM SALTS

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Summary: Constant current electrolysis of triphenylphosphine in dichloromethane at a graphite anode in the presence of cycloalkenes gave the corresponding 1-cycloalkenylphosphonium salts in reasonable yields.

Although 1-alkenylphosphonium salts, as well as vinyltriphenylphosphonium bromide (Schweizer's reagent),¹⁾ have been shown to be useful for the synthesis of carbocyclic²⁾ and heterocyclic rings³⁾ and allyl amines,⁴⁾ the methods of their preparation^{1,5,6)} usually involve rather tedious multi-step procedures. Meanwhile, results on the reactivity of triphenylphosphine radical cation towards various nucleophiles⁷⁾ have suggested that electrochemical oxidation of triphenylphosphine (1) in the presence of alkenes may become an efficient method to obtain the phosphonium salts. We report here a facile one-step preparation of 1-cycloalkenyltriphenylphosphonium perchlorate (3) under mild conditions. Some of the phosphonium salts



3 have been prepared from cycloalkyltriphenylphosphonium ylides and phenylselenyl bromide via three reaction steps.⁶⁾

General procedure for the electrochemical preparation of 3 is as follows. A solution of 1 (3 mmol) and a cycloalkene 2 (15 mmol) in dry CH₂Cl₂ (40 ml) containing 0.2 M 2,6-lutidinium perchlorate, and anhydrous K₂CO₃ (3 g) were placed in an undivided electrolysis cell equipped with a graphite anode and a stainless steel cathode through a silicon stopper. The system was subjected to constant current electrolysis (20 mA; current density, 1.07 mA/cm²) at ambient temperature under an N₂ atmosphere until 2 F per mol of 1 had been passed (ca. 8 hr). The electrolyzed solution, after the K₂CO₃ being removed by filtration, was evaporated to almost dryness under reduced pressure. Water (100 ml) was added to the residue, and the mixture was extracted with CHCl₃ (50 ml x 4). The extracts were dried with MgSO₄ and condensed to ca. 5 ml under reduced pressure. The phosphonium salt 3 separated out when the residue was added dropwise to ether (100 ml) with stirring. The results are summarized in Table I.

The phosphonium salts $\underline{3}$ were easily converted to the corresponding phosphine oxide $\underline{4}$, $\text{R-P}^{(O)}\text{Ph}_2$, by the action of sodium hydroxide in ethanol—water according to the method of Saleh et al.⁶⁾ (Table II).

Table I. Electrochemical Preparation of $\underline{3}$

Cycloalkene (2)	Yield(%) ^a of $\underline{3}$	Mp.(°C)
\underline{a} Cyclopentene	53	277 - 279 (278 - 280) ⁶⁾
\underline{b} Cyclohexene	53	290 - 291 (289 - 290) ⁶⁾
\underline{c} Cycloheptene	56	214 - 216 (216 - 218) ⁶⁾
\underline{d} Cyclooctene	53 ^b	197 - 199
\underline{e} Norbornene	66 ^c	192 - 194

^aIsolated yield based on the amount of $\underline{1}$ used.

^bNMR(DMSO- d_6) δ : 7.20-8.20(m, 15H), 5.90(d, 1H, J=12 Hz), 1.05-2.40(m, 12H).

IR(KBr) cm^{-1} : 1620(C=C), 1100(ClO_4^-).

^cNMR(DMSO- d_6) δ : 7.1-8.1(m, 16H), 3.85(d, 1H, J=6 Hz), 2.20(s, 1H), 0.8-1.9(m, 6H).

Table II. Reaction of $\underline{3}$ with NaOH ^a

Compound	Yield(%) ^b of $\underline{4}$	Mp.(°C)
$\underline{3a}$	78	95 - 96 (93 - 94) ⁶⁾
$\underline{3b}$	85	117 - 118 (118 - 120) ⁶⁾
$\underline{3c}$	94	Oil (Oil) ⁶⁾
$\underline{3d}$	78 ^c	Oil
$\underline{3e}$	91 ^d	145 - 147

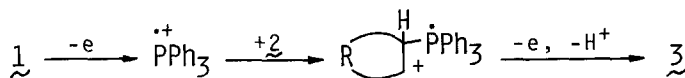
^aGeneral procedure, see ref. 6.

^bIsolated yield based on $\underline{3}$.

^cNMR(CDCl_3) δ : 7.1-8.0(m, 10H), 5.25(d, 1H, J=8 Hz), 0.75-2.2(m, 12H). IR(CHCl_3): 1630 cm^{-1} . MS(m/z): 310(M^+).

^dNMR(CDCl_3) δ : 6.9-8.0(m, 11H), 2.0-2.35(m, 2H), 0.8-1.5(m, 6H). IR(CHCl_3): 1630 cm^{-1} . MS(m/z): 294(M^+).

The electrochemical transformation of $\underline{1}$ to $\underline{3}$ can be also effected, though in lower yields, by controlled potential electrolysis in acetonitrile at the voltammetric peak potential of $\underline{1}$ (1.4 V vs. Ag wire). About 2 F per mol of $\underline{1}$ was found to be consumed in the electrolysis. Since the oxidation potentials of $\underline{2}$ are higher than that of $\underline{1}$,⁸⁾ these results suggest that the process for the formation of $\underline{3}$ is represented as shown below in analogy with the reactions of triphenylphosphine radical cation with other nucleophiles.⁷⁾



References and Notes

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- 8) The voltammetric peak potentials of $\underline{2}$ (0.5 mM) in acetonitrile (0.1 M NaClO_4) were as follows: $\underline{2a}$, 1.9; $\underline{2b}$, 1.8; $\underline{2c}$, 2.1; $\underline{2d}$, 2.1; $\underline{2e}$, 1.9 V vs. Ag wire (at a glassy carbon electrode, at 25°C; voltage sweep rate, 50 mV s^{-1}).

(Received in Japan 22 January 1985)