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# Anodic Oxidation of Triphenylphosphine in the Presence of Allylic Silanes. A Facile Electrochemical Preparation of Allyltriphenylphosphonium Tetrafloroborates

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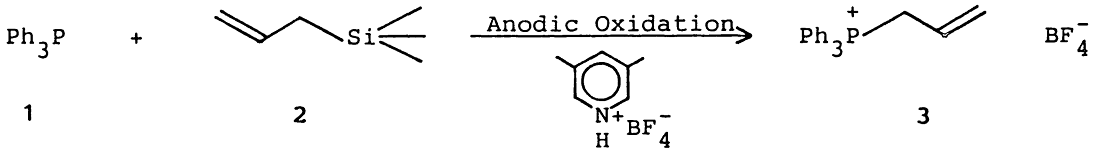
Electrochemically generated triphenylphosphine radical cation reacts with allylic silanes to give the corresponding allyltriphenylphosphonium tetrafloroborates.

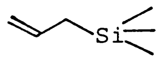
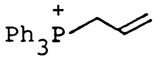
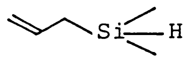
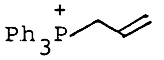
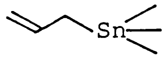
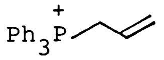
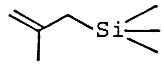
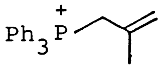
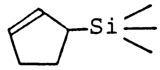
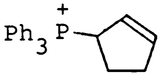
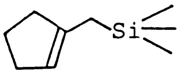
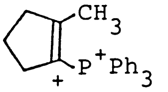
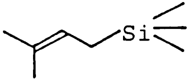
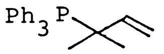
In the course of studies on the reactions of electrochemically generated triphenylphosphine radical cation ($Ph_3P^{+\bullet}$),[1] we have shown that 1-cycloalkenyltriphenylphosphonium salts can easily be prepared by electrochemical oxidation of **1** in the presence of cycloalkenes.[2] Since the addition of electrophiles to allylic silanes (**2**) are well known,[3] the reaction of the radical cation of **1** with **2** seems feasible. The present communication describes that allyltriphenylphosphonium tetrafloroborates (**3**) are easily obtained by electrochemical oxidation of **1** in the presence of **2**.



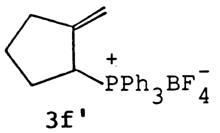
**1** **2** **3**

General procedure for the electrochemical preparation of **3** is as follows. A solution of **1** (3 mmol) and an allylic silane (**2**) (1.5 mmol) in dry $CH_2Cl_2$ (40 ml) containing 0.2 M 3,5-lutidinium tetrafloroborate was placed in an undivided electrolysis cell equipped with a glassy carbon anode and a Pb cathode through a silicon stopper. The system was subjected to constant current electrolysis (current density, 1.10 $mA/cm^2$) at ambient temperature under an $N_2$ atmosphere until 1.8 F per mol of 1 had been passed. The results are summarized in Table 1.[4]

Table 1.

| | Allylic silanes (2) | Products (3)[a)] | Yields/%[b)] |
|---|---|---|---|
| a |  |  | 71 |
| b |  |  | 72 |
| c |  |  | 61 |
| d |  |  | 68 |
| e |  |  | 21 |
| f |  |  | 24 |
| g |  |  | 0 |

a) Counter anion: $BF_4^-$. b) Isolated yields.


3f'

The electrolyses of **1** in the presence of allylic silanes, **2a**, **2d**, and **2e** gave allylphosphonium salts **3a**, **3d**, and **3e**, respectively. Allylphosphonium salt **3a** was also prepared from dimethylallylsilane (**2b**) or allylstannane **2c**. On electrolysis with **2f**, 1-alkenylphosphonium salt **3f** was obtained. The isolation of **3f** is rationalized by the prototropic rearrangement of the initially formed allylphosphonium salt **3f'**. Electrolysis with **2g** having two substituents at the terminal position of the allylic group did not give the expected phosphonium salt **3g**.

The yield of **3** changed with the cathode materials used. For example, electrolysis of **1** with **2a** by the use of a Pb plate cathode gave **3a** in 65% yield after 2 F per mol of **1** had been passed, while with a stainless steel plate or a Pt plate as cathode the yields of **3a** decreased to 51 and 23% , respectively. The detailed investigation of this electrochemical process is now in progress.

References

1) H. Ohmori, K. Sakai, N. Nagai, Y. Mizuki, and M. Masui, Chem. Pharm. Bull., 33, 373 (1985) and references cited therein.
2) H. Ohmori, T. Takanami, and M. Masui, Tetrahedron Lett., 26, 2199 (1985).
3) W. P. Weber, "Silicon Reagents for Organic Synthesis," Springer-Verlag, Berlin (1983), p. 173.

4) All the compounds were characterized by $^1H$-NMR and IR spectroscopy. For example, the spectral data of **3a** are as follows: Mp 161—162 °C; NMR ($CDCl_3$): δ 4.2 (dd, J = 6 and 15 Hz, 2H), 5.3—5.7 (m, 3H), 7.5—7.9 (m, 15H); IR ($CHCl_3$): 1590 $cm^{-1}$.

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