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Synthesis and Reaction of (3-Phenylseleno-1-alkenyl)triphenylphosphonium Salts

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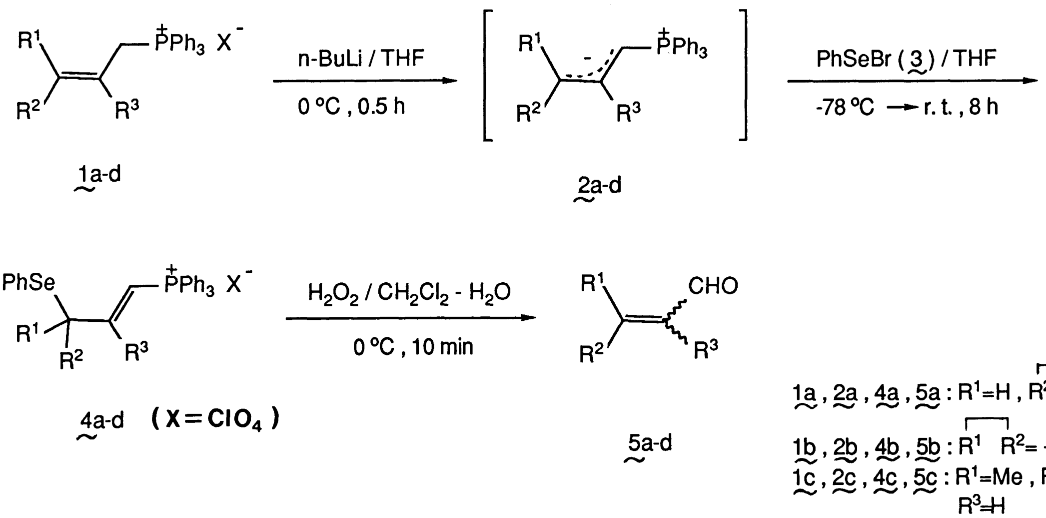
The reaction of allylic triphenylphosphonium ylides with benzeneselenenyl bromide gave (3-phenylseleno-1-alkenyl)triphenylphosphonium salts in good yields. Oxidation of the salts produced α,β-unsaturated aldehydes.

We have recently reported the synthesis and synthetic applications of (1-cycloalkenyl)-[1] and (cycloalkylidenemethyl)phosphonium salts.[2] In connection with our continuing interest in synthesis and utilization of unsaturated systems having the phosphonium group, we have explored the possibility of synthesis of α-seleno-substituted allylic phosphonium salts, which can be expected to be versatile intermediate reagents for the synthesis of allenyl- and/or 1,3-dienylphosphonium salts.

The reaction of a phosphonium ylide **2a**, generated from a [1-(cyclohexenyl)-methyl]triphenylphosphonium salt **1a**[2] (30 mmol) and butyllithium (33 mmol) in tetrahydrofuran (THF) (40 ml) at 0 °C for 0.5 h, with benzeneselenenyl bromide (**3**) (36 mmol) in THF (50 ml) was carried out at -78 °C to room temperature for 8 h. After the reaction mixture was quenched by the addition of 5% hydroperchloric acid and extracted with CH_2Cl_2, the organic layer was evaporated. The residue was recrystallized from CH_2Cl_2/ether to give a regiospecific γ-phenylseleno-substituted phosphonium salt, [(2-phenylselenocyclohexylidene)methyl]triphenylphosphonium



1a, **2a**, **4a**, **5a**: R^1=H, R^2 R^3= -$(CH_2)_4$-
1b, **2b**, **4b**, **5b**: R^1 R^2= -$(CH_2)_5$-, R^3=H
1c, **2c**, **4c**, **5c**: R^1=Me, R^2=CH_2CH_2CH=CMe_2, R^3=H
1d, **2d**, **4d**, **5d**: R^1=H, R^2=Me, R^3=H

Scheme 1.

perchlorate (4a)$^{3)}$ (90% yield), but no α-selenenylated phosphonium salt was produced. Similar reaction of various allylic phosphonium ylides 2b-d with 3 gave regiospecific γ-selenenylated phosphonium salts 4b-d$^{4)}$ in 90-97% yields (Table 1). These results indicate that, regardless of substituents of the starting phosphonium salts 1, selenenylation of allylic ylides 2 took place at γ-position.

Treatment of the salts 4a-d (1 mmol) in CH_2Cl_2-H_2O (8 ml, 1:1) with H_2O_2 (30%, 2 mmol) at 0 °C for 10 min did not lead to the expected 1,3-dienyl- and/or allenylphosphonium salts, but α,β-unsaturated aldehydes 5a-d$^{5)}$ were exclusively obtained in 57-80% yields (Table 1). These results demonstrate that intermediate allylic selenoxides formed by the oxidation of 4a-d with H_2O_2 underwent the [2,3]-sigmatropic rearrangement to give selenic esters, followed by hydrolysis and elimination of the phosphonium group to produce 5a-d. Formation of aldehydes and ketones via the [2,3]-sigmatropic rearrangement has been similarly known by the oxidation of γ-chloroallyl selenides.$^{6)}$

Table 1. Synthesis and Reaction of (3-Phenylseleno-1-alkenyl)triphenylphosphonium Salts 4a-d

Starting salts 1	γ-Selenenylated salts 4 (yield$^{a)}$/%)	Aldehydes 5 (yield$^{a)}$/%)
1a	4a (90)	5a (75)
1b	4b (90)	5b (80)
1c	4c (97)	5c (57)
1d	4d (90)	5d (61)

a) Isolated yield.

References

1) T. Minami, H. Sako, T. Ikehira, T. Hanamoto, and I. Hirao, J. Org. Chem., 48, 2569 (1983); G. Saleh, T. Minami, Y. Ohshiro, and T. Agawa, Chem. Ber., 112, 355 (1979).

2) T. Minami, S. Shikita, S. So, M. Nakayama, and I. Yamamoto, J. Org. Chem., 53, 2937 (1988).

3) 4a: mp 194 °C; ^{1}H NMR ($CDCl_3$) δ 1.20-3.00 (m, 8H, CH_2), 4.60-4.88 (br s, 1H, CHSePh), 5.84 (d, J=22 Hz, 1H, vinylic H), 7.00-7.36 (m, 5H, SePh), and 7.36-8.00 (m, 15H, phenyl H); ^{13}C NMR δ 21.1, 26.3, 30.0 (d, $^{3}J_{pc}$=6.9 Hz), 31.9, 50.4 (d, $^{3}J_{pc}$=18.9 Hz), 100.9 (d, $^{1}J_{pc}$=87.7 Hz), 119.0 (d, $^{1}J_{pc}$=90.3 Hz), 128.1, 129.2, 130.3 (d, $^{3}J_{pc}$=12.9 Hz), 132.9 (d, $^{2}J_{pc}$=11.2 Hz), 134.5, 134.8 (d, $^{4}J_{pc}$=3.4 Hz), and 172.7.

4) 4b ($X=BF_4$): mp 169-171 °C; 4c: viscous oil; 4d: mp 162-163 °C. Identification for the salts 4b-d was unambiguously made from ^{1}H and ^{13}C NMR spectral data.

5) Preparative thin layer chromatography (silica gel, ethyl acetate/hexane (1/7)) of crude products gave pure samples 5a-d.

6) See, for example: P. Lerouge and C. Paulmier, Tetrahedron Lett., 25, 1983 (1984); H. J. Reich, J. Org. Chem., 40, 2570 (1975); C. Paulmier, "Selenium Reagents and Intermediates in Organic Synthesis," Pergamon Press, Oxford (1986), p. 143 and references cited therein.

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