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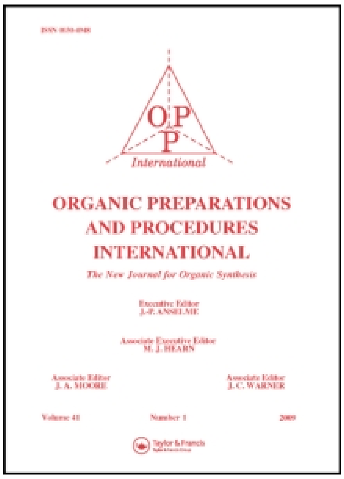

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A NOVEL SYNTHESIS OF α-ARYLSELENOPHOSPHORANES

Li Wang[a]; Zhi-Zhen Huang[a]; Hang Li[a]; Xian Huang[a]
[a] Department of Chemistry, Hangzhou University, Hangzhou, Zhejiang, P R CHINA

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OPPI BRIEFS

A NOVEL SYNTHESIS OF α-ARYLSELENOPHOSPHORANES

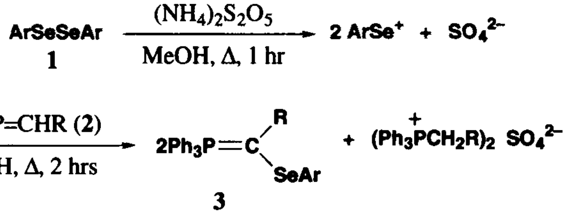
Submitted by Li Wang, Zhi-Zhen Huang, Hang Li and Xian Huang*
(04/11/94)

Department of Chemistry, Hangzhou University
Hangzhou, Zhejiang 310028, P. R. CHINA

With the development of the well-known Wittig reaction, α-heteroatom substituted phosphoranes have been given more attention and increasingly find important applications in organic synthesis.[1-5] Recently, it was reported that α-aryl selenophosphoranes may be obtained by reacting phosphoranes with arylseleno halide[2-4] or dialkylselenenyl dichloride.[5] The greatest drawback of these methods is the difficulty in the preparation of the starting materials and the need for these reactions to be carried out in the absence of oxygen.

Recently, it was reported that areneselenium cations can easily be obtained from diselenides by oxidative reaction with peroxydisulphate.[6] Since areneselenium cations are active electrophiles and phosphoranes are strong nucleophiles, we thought that phosphoranes could react readily with areneselenium cations to provide a convenient method for the synthesis of α-arylselenophosphoranes. The experimental results showed that heating diaryl diselenides with ammonium peroxydisulphate in methanol at reflux for 1 hr, the areneselenium cation could be generated *in situ*.

This was followed by reflux with 4 equivalents of phosphorane **2** for 2 hrs to give α-arylselenophosphorane **3** in good yields.



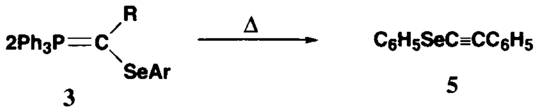
$$\underset{\mathbf{1}}{\mathrm{ArSeSeAr}} \xrightarrow[\mathrm{MeOH},\ \Delta,\ 1\ \mathrm{hr}]{(NH_4)_2S_2O_5} 2\ \mathrm{ArSe}^+ + SO_4^{2-}$$

$$\xrightarrow[\mathrm{MeOH},\ \Delta,\ 2\ \mathrm{hrs}]{4\ Ph_3P{=}CHR\ (\mathbf{2})} \underset{\mathbf{3}}{2Ph_3P{=}C(R)(SeAr)} + (Ph_3\overset{+}{P}CH_2R)_2\ SO_4^{2-}$$

a) Ar = C_6H_5, R = COOMe b) Ar = C_6H_5, R = COOEt
c) Ar = C_6H_5, R = COC_5H_5 d) Ar = 4-ClC_6H_4, R = COOMe
e) Ar = 4-ClC_6H_4, R = COOEt f) Ar = 4-ClC_6H_4, R = COC_6H_5

The advantages of this method are more easily obtained starting materials, milder reaction conditions (including no need to exclude air), simpler manipulation (one-pot reaction) and improved yields compared with previous methods.

A possible mechanism involves initial electrophilic attack on **2** by areneselenium cation to form **4**, which could then undergo transylidation reaction with another equivalent of phosphorane to give α-aryl selenophosphorane **3**. α-Arylselenophosphoranes **3** are important intermediates. For example, α-arylseleno-acylphosphoranes can undergo intermolecular Wittig reaction to afford a convenient method for the synthesis of arylselenoacetylenes **5**.



EXPERIMENTAL SECTION

Melting points are uncorrected. IR spectra were recorded as KBr discs on Perkin Elmer 683 spectrophotometer. ^{1}H NMR spectra were obtained with a Varian Em-360A, Fx-90Q spectrometer in $CDCl_3$ using TMS as internal standard. Chemical shifts are expressed in δ (ppm). The microelemental analyses were carried out on Carlo Erba 1106 instrument. Diaryl diselenides were prepared as described.[7] Phosphoranes (**2**) were prepared as described.[2]

α-Arylselenophosphoranes 3.- General Procedure.- Diaryl diselenides (0.5mmol) and ammonium peroxydisulfate (0.55mmol) in methanol (10mL) were heated at reflux for 1 hr. After cooling, the phosphorane **2** (2mmol) was added and the mixture was refluxed for 2 hrs. The progress of the reaction was monitored by TLC (silica gel GF 3:5 pet ether:ethyl acetate as eluent). Then dichloromethane (30mL) was added to the reaction mixture and the solution was washed with water. The organic layer was dried ($MgSO_4$) and evaporated the solvent under vacuum. The crude product purified by recrystallization from ethyl acetate.

Compound 3a: Yield 90%; mp. 187-189°. IR: 1320, 1440, 1480, 1610 cm^{-1}. ^{1}H NMR: δ 3.52 (s, 3H) ,7.32-7.80 (m, 20H).

Anal. Calcd for $C_{27}H_{23}O_2PSe$: C, 66.25; H, 4.70. Found: C, 66.17; H, 4.97

Compound 3b: Yield 85%; 182-184°, lit.[2] 184-186°. IR: 1268, 1450, 1483, 1620 cm^{-1}. ^{1}H NMR: δ 0.72-1.03 (t, 3H), 3.71-4.08 (d, 2H) ,7.18-7.73 (m, 20H).

Compound 3c: Yield 89%; mp. 203-205°, lit.[4] 206-208°. IR: 1100, 1342, 1500, 1593 cm^{-1}. ^{1}H NMR: δ 7.38-7.81 (m, 25H).

Compound 3d: Yield 88%; mp. 158-160°. IR: 1271, 1443, 1480, 1623 cm^{-1}. ^{1}H NMR: δ 3.48 (s, 3H) 7.34-7.83 (m, 19H).

Anal. Calcd for $C_{27}H_{22}ClO_2PSe$: C, 61.85; H, 4.20. Found: C, 61.76; H, 4.23

Compound 3e: Yield 86%; mp. 152-154°. IR: 1271, 1440, 1482, 1612 cm^{-1}. ^{1}H NMR: δ 0.79-1.07 (t, 3H),3.82-4.23 (d, 2H), 7.33-7.80 (m, 19H).

Anal. Calcd for $C_{28}H_{24}ClO_2PSe$: C, 62.59; H, 4.44. Found: C, 62.81; H, 4.28

Compound 3f: Yield 92%; mp. 149-151°. IR: 1103, 1340, 1452, 1550, 1628 cm^{-1}. ^{1}H NMR: δ 7.18-7.73 (m, 24H).

Anal. Calcd for $C_{32}H_{24}ClOPSe$: C, 67.42; H, 4.20. Found: C, 67.42; H, 4.32

Phenylseleno Phenylacetylene (5).- The α-benzoyl-α-phenylselenophosphorane **3c** (2 mmol) was heated at 250°/1 torr for 1 hr in a Claisen flask. The distillate was collected in a receiver cooled in liquid nitrogen. Then the distillate was separated by chromatography on silica gel (10:1 petroleum ether-ether as eluent) to give 0.38g (75%) of phenylseleno phenylacetylene **5** as a colorless oil, lit.[4] 80°/0.3 torr. IR (film): 1445, 1484, 1578, 2165 cm^{-1}. ^1H NMR: δ 7.03-7.78 (m, 10H).

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