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The Binary Reagent PhSeSePh–CuOTf: a Useful Phenylselenenylating Agent

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The binary reagent PhSeSePh–CuOTf has been found to be useful for the conversion of alkynyltrimethylsilanes into 1-phenylselenoalk-1-ynes as well as for phenylselenolactonization and phenylselenoetherification.

Recently we reported that the binary reagent PhSSPh–CuOTf¹ was a powerful source of PhS⁺, making possible the direct conversion of alkynyltrimethylsilanes into alkynyl phenyl sulphides.² Here we report that a further binary reagent, PhSeSePh–CuOTf, is useful both for the conversion of alkynyltrimethylsilanes into 1-phenylselenoalk-1-ynes as well as for phenylselenolactonization and phenylselenoetherification. The reactivity of these binary reagents is different from those of representative organoselenium reagents such as PhSeCl, PhSeBr and PhSeOTf.

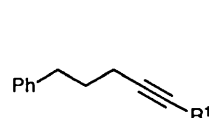
1-Phenylselenoalk-1-ynes, prepared by generating acetylide anions with butyllithium followed by treatment with benzene-selenenyl halide,^{3,4} are converted into (*Z*)-1-phenylselenoalk-1-enes in a highly stereoselective manner.⁵ We thought that the direct transformation of alkynyltrimethylsilanes, which are frequently utilized as general synthetic intermediates in organic synthesis, to 1-phenylselenoalk-1-ynes would be effected by the binary reagent PhSeSePh–CuOTf. 1-Phenylselenoalk-1-ynes are too reactive under oxidation conditions to be utilized as general synthetic intermediates. After several attempts, it was found that treatment of the alkynyltrimethylsilane **1** with PhSeSePh (1.2 equiv.), (CuOTf)₂–benzene (1.2 equiv.) and CaCO₃ (2 mol equiv.) in refluxing dioxane for 2.5 h afforded the desired 1-phenylselenoalk-1-yne **2** in 89% yield. Likewise, the alkynyltrimethylsilanes **3**⁶ and **5**⁷ were converted into the corresponding 1-phenylselenoalk-1-ynes **4** and **6** in 91 and 87% yields, respectively. Furthermore, the alkynyltrimethylsilane **7**⁸ was transformed into **8** in 92% yield.

The binary reagent PhSeSePh–CuOTf (0.33 mmol) was also effective in converting 1-trimethylsilylprop-1-yne **9** (0.99 mmol) into 1-phenylselenoprop-1-yne **10** in a sealed tube (68% yield based on PhSeSePh), which is a lithioprop-2-ynyl alcohol equivalent.⁹

The presence of the two reagents was found to be essential for the above transformations, the active species not being PhSeOTf as evidenced by recovery of PhSeSePh after treatment with (CuOTf)₂–benzene (1 equiv.) in refluxing dioxane for 4 h. Attempted detection of the complex by recording the ¹H NMR spectra of a mixture of PhSeSePh and (CuOTf)₂–benzene in [²H₆]dioxane at various temperatures however, gave negative results.

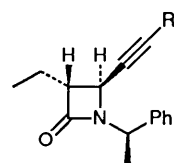
The advantage of the binary reagent PhSeSePh–CuOTf as a source of PhSe⁺ for the conversion of alkynyltrimethylsilanes into 1-phenylselenoalk-1-ynes was demonstrated by recovery of unchanged **1** after it had been treated with either PhSeCl–CaCO₃ or PhSeBr–CaCO₃ under the reaction conditions described above. However, use of PhSeOTf¹⁰ (1.2 equiv.) yielded **2** (12%) and recovery of **1** (47%), whilst use of an excess of reagent (1.8 equiv.), resulted in the formation of **11** (12%).

These binary reagents have also been found to be useful for phenylselenolactonization.^{10,11} Thus, treatment of the acid **12**



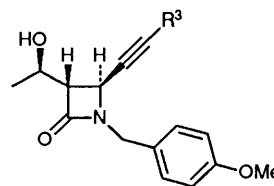
1; R¹ = SiMe₃

2; R¹ = SePh



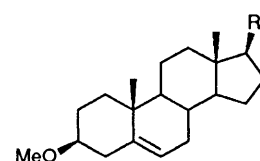
3; R² = SiMe₃

4; R² = SePh



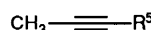
5; R³ = SiMe₃

6; R³ = SePh



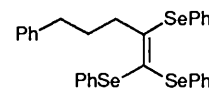
7; R⁴ = C≡C–SiMe₃

8; R⁴ = C≡C–SePh



9; R⁵ = SiMe₃

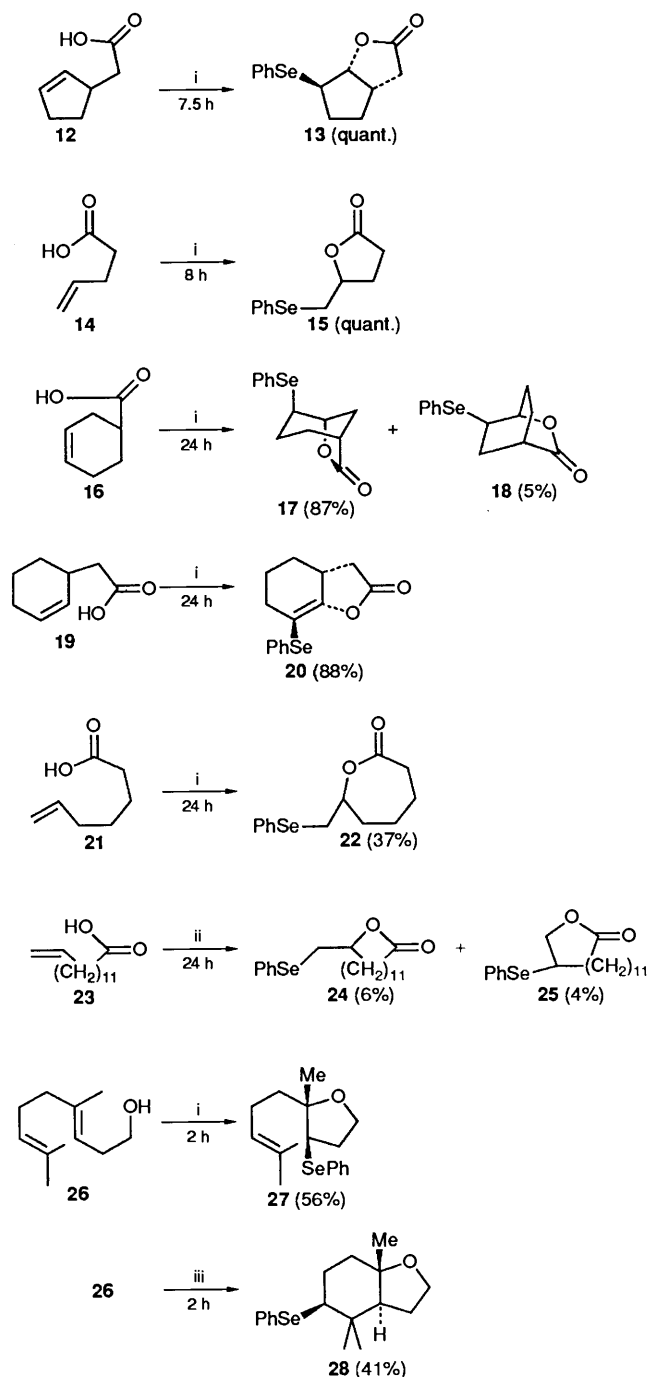
10; R⁵ = SePh



11

with PhSeSePh (1.2 equiv.), (CuOTf)₂–benzene (1.2 equiv.) and CaCO₃ (2 mol equiv.) in CH₂Cl₂ at 30 °C for 7.5 h afforded the lactone **13** (100%). Likewise, the acids **14**, **16**, **19** and **21** were converted into the corresponding lactones **15**, **17**, **20** and **22** in 100, 87, 88 and 37% yields, respectively. In the lactonization of **16**, the six-membered lactone **18** was also formed (5%). Interestingly, the use of dioxane as a solvent for the lactonization of **16** afforded **17** (40%) together with **18** (17%). In order to understand the above results, the following experiment was carried out. Treatment of a mixture of **17** and **18** (9.7:1; 90 mg, 0.32 mmol) with PhSeSePh (0.39 mmol), (CuOTf)₂–benzene (0.19 mmol) and CaCO₃ (0.64 mmol) in dioxane at 30 °C for 24 h gave a mixture of **17** and **18** (2.3:1, 45 mg), indicating that, to a certain extent, the rearrangement of **17** to **18** occurred in dioxane solvent. Unfortunately, these binary reagents failed to give a satisfactory result in the synthesis of macrolides. Thus, exposure of the acid **23** to PhSeSePh, (CuOTf)₂–benzene and BaCO₃ in refluxing DME provided **24** in only 6% yield together with **25** (4%).

Finally, we have observed that the binary reagent is also useful for phenylselenoetherification.¹² Thus, homogeneraniol **26** was transformed into the cyclic ether **27** in (56%) by treatment



Scheme 1 Reagents and conditions: i, PhSeSePh (1.2 equiv.), CuOTf (1.2 equiv.), CaCO₃ (2.0 mol equiv.), CH₂Cl₂, 30 °C; ii, PhSeSePh (1.2 equiv.), CuOTf (1.2 equiv.), BaCO₃ (2.0 mol equiv.), DME, reflux; iii, PhSeSePh (1.2 equiv.), CuOTf (1.2 equiv.), CH₂Cl₂, 30 °C.

with PhSeSePh (1.2 equiv.), (CuOTf)₂-benzene (1.2 equiv.) and CaCO₃ (2 mol equiv.) in CH₂Cl₂ at 30 °C for 2 h. Interestingly, exposure of **26** to PhSeSePh (1.2 equiv.) and (CuOTf)₂-benzene (1.2 equiv.) in the absence of a base such as CaCO₃ (CH₂Cl₂ solvent, 30 °C, 2 h) afforded the bicyclic ether **28** (41%). These results are in accord with those effected by PhSeOTf.^{1,2}

Experimental

Typical Procedure: 5-Phenyl-1-phenylselenopent-1-yne 2.—To a stirred solution of **1** (255 mg, 1.18 mmol) in dioxane (3.4 ml) was added calcium carbonate (236 mg, 2.36 mmol), diphenyl

diselenide (442 mg, 1.41 mmol) and (CuOTf)₂-benzene (356 mg, 0.71 mmol) at room temperature. The mixture was refluxed and stirred for 2.5 h after which it was quenched with phosphate buffer (pH 7; 30 ml), and extracted with AcOEt. The combined organic extracts were washed with brine, dried (Na₂SO₄), and concentrated. The residue was purified by silica gel column chromatography (hexane) to give **2** (315 mg, 89%) as a colourless oil; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3080, 3040, 2950, 2870, 1580, 1500, 1480 and 1440; $\delta_{\text{H}}(100 \text{ MHz}; \text{CDCl}_3)$ 1.70–2.00 (2 H, m), 2.47 (2 H, t, *J* 7.0),* 2.77 (2 H, t, *J* 7.5) and 6.90–7.60 (10 H, m); *m/z* 300 (M⁺) (Found: M⁺, 300.0430. C₁₇H₁₆Se requires *M*, 300.0428).

8-Phenylseleno-2-oxabicyclo[3.3.0]octan-3-one 13.—To a stirred solution of (CuOTf)₂-benzene (101 mg, 0.20 mmol) in dioxane (1.0 ml) was added diphenyl diselenide (126 mg, 0.40 mmol), calcium carbonate (67 mg, 0.67 mmol) and the carboxylic acid **12** (42 mg, 0.34 mmol) at room temperature. The mixture was stirred at the same temperature for 7.5 h, quenched with phosphate buffer (pH 7; 9 ml), and extracted with AcOEt. The combined organic extracts were washed with brine, dried (Na₂SO₄), and concentrated. The residue was purified by silica gel column chromatography (benzene) to give **13** (94 mg, 100%) as a colourless oil; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3060, 2970, 2880, 1775, 1580, 1480, 1440, 1415, 1350, 1320, 1300, 1160 and 1000; $\delta_{\text{H}}(100 \text{ MHz}; \text{CDCl}_3)$ 1.50–1.60 (1 H, m), 1.80–1.90 (1 H, m), 2.10–2.30 (2 H, m), 2.34 (1 H, dd, *J* 18.3, 2.4), 2.82 (1 H, dd, *J* 18.3, 9.9), 3.00–3.20 (1 H, m), 3.80–3.90 (1 H, m), 4.91 (1 H, d, *J* 6.2), 7.20–7.40 (3 H, m) and 7.50–7.60 (2 H, m); *m/z* 282 (M⁺) (Found: M⁺, 282.0157. C₁₃H₁₄O₂Se requires *M*, 282.0158).

Acknowledgements

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* *J* Values in Hz.