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Isolation and Reaction of Selenobenzophenones

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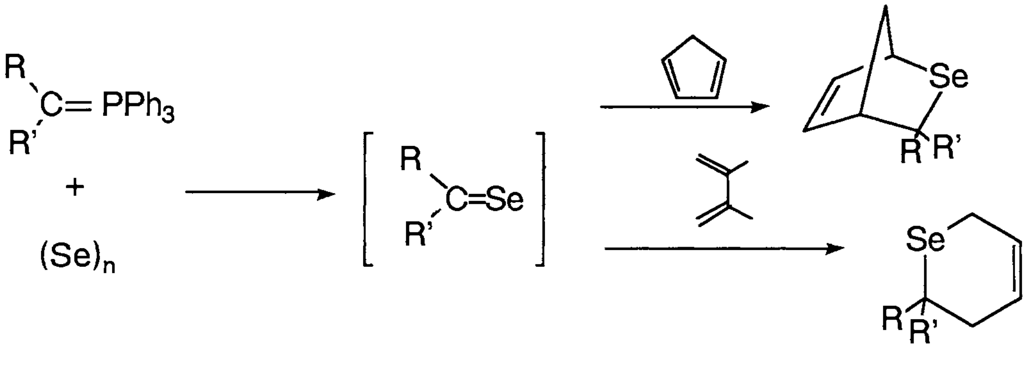
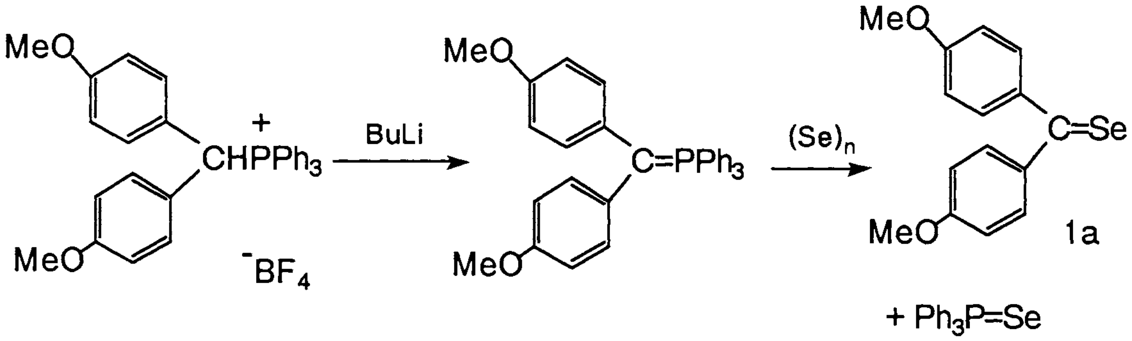
4,4'-Dimethoxy- and 4,4'-dimethylselenobenzophenones could be isolated in moderate yields by the reaction of the corresponding ylides with selenium. Their spectral data are described. The oxidaion of these compounds with mCPBA afforded the corresponding benzophenones in good yields. Attempted isolation of unsubstituted selenobenzophenone afforded only its dimer.

The formation and reaction of thio- and selenocarbonyl compounds are of current interest. In recent years, a number of research groups have demonstrated the generation and the trapping of selenocarbonyl compounds.[1] Thiobenzophenones were generally prepared in pure form by the reaction of phosphorus ylides with elemental sulfur.[2] We also found that selenocarbonyl compounds (selenoaldehydes and selenoketones) were also formed by the reaction of Wittig reagents with elemental selenium.[3]



However, there are a few reports on the synthesis of stable selenocarbonyl compounds, which contain *tert*-alkyl groups or electron donating groups on the selenocarbonyl α-carbons.[4] Recently, Erker *et al.* reported the reaction of diphenylmethylenetriphenylphosphorane with selenium.[5] They isolated selenobenzophenone dimer as yellowish green crystals, which structure was confirmed by X-ray crystallographic analysis. These results prompted us to investigate the possibility of isolation and characterization of selenobenzophenones (**1**). In this communication, we would like to report the isolation and reaction of 4,4'-dimethoxyselenobenzophenone (**1a**) and 4,4'-dimethylbenzophenone (**1b**).

Compound **1a** was isolated as follows: To a suspension of 4,4'-dimethoxybenzhydryltriphenylphosphonium tetrafluoroborate in benzene was added butyllithium. After stirring for 30 min, selenium powder was added portionwise to this solution and the mixture was refluxed for 1 h. The resulting suspension was filtered to give a green solution from which a green solid was obtained on evaporation of the solvent. It was chromatographed on a column of silica gel with pentane as eluent to give crude **1a** as green needles, which was crystallized from pentane to afford pure crystals of **1a**.[6] (mp 98-99 °C) Selenoketone **1a** is a green stable compound under nitrogen atmosphere, and can be stored in a refrigerator (-15 °C) for a long time. However, on exposure to the air, this compound decomposed to give the corresponding benzophenone and selenium after 15 h. The whole work-up must, therefore, be done under nitrogen atmosphere.

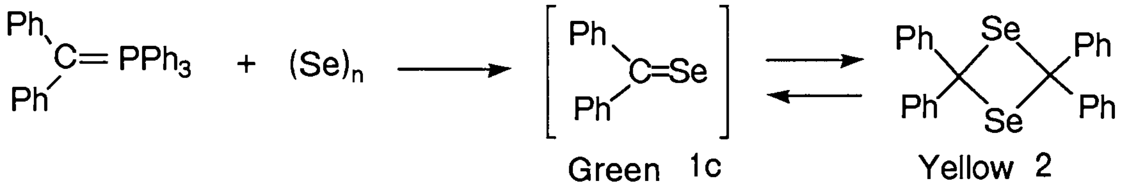


Isolation of 4,4'-dimethylselenobenzophenone **1b** was also tried. This compound was also characterized in solution by ^{13}C NMR spectrum, exact mass spectroscopy, and by trapping with cyclopentadiene. By careful work-up this compound was isolated in 38% yield.[7] It is less stable than **1a** and changed to the corresponding 4,4'-dimethylbenzophenone and selenium upon standing at room temperature for 1 h.

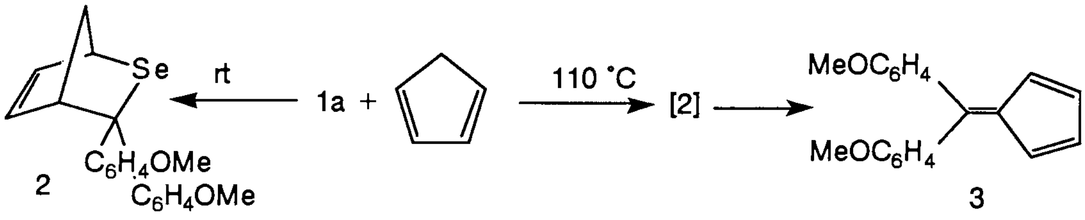
Table 1. Spectral Data of **1a** and **1b**

Compound	^{1}H NMR (δ $CDCl_3$)	^{13}C NMR (δ $CDCl_3$)	UV-vis(λ_{max}/nm(ε))
1a	3.87 (s, 6H), 6.82 (d, 4H), 7.79 (d, 4H)	55.6, 113.7, 131.2, 148.0, 162.9, 240.1 (C=Se)	360 (21500) 386 (sh, 11300) 744 (335)
1b	2.23 (s, 6H), 7.10 (d, 4H), 7.69 (d, 4H)	21.9, 128.7, 129.2, 142.4, 152.7, 244.4 (C=Se)	340 (15300) 368 (11900) 750 (240)

We then tried the isolation of unsubstituted selenobenzophenone (**1c**). In solution, this compound was generated by the reaction of diphenylmethylenetriphenylphosphorane with elemental selenium and its formation was confirmed by its ^{13}C NMR spectrum and the trapping with cyclopentadiene. However, we failed in its isolation because of its instability. A green solution of selenobenzophenone turned to pale greenish yellow crystals of dimer on evaporation of the solvent as stated by Erker et al.$^{5,8)}$



The reaction of **1a** with mCPBA gave the corresponding benzophenone in 86% yield, as expected. Treatment of **1a** with cyclopentadiene afforded cycloadduct (**2**) in 65% at room temperature. However, when the reaction was carried out at 110 °C for 18 h, 4,4′-dimethoxydiphenylfulvene (**3**) was isolated in 35% yield along with the cycloadduct **2** (28%). Compound **3** might be produced from the radical cleavage of the cycloadduct **2**. Actually, the oxidation of the cycloadduct afforded the fulvene in 45% yield.



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6) **1a**: exact mass; M^+ Calcd, 306.0159; Found, 306.0101. Anal. Found, C, 59.08; H, 4.61%: Calcd for $C_{15}H_{14}O_2Se$: C, 59.03; H, 4.62%.

7) **1b**: mp 74-75.5 °C. Exact mass; M^+ Calcd, 274.0261; Found, 274.0302. Anal. Found: C, 66.22; H, 5.03: Calcd for $C_{15}H_{14}Se$: C, 65.94; H, 5.16.

8) Dimer: mp 105-107 °C, (lit.$^{5)}$ 109 °C); MS (EI, 20 eV): m/e 493 (0.1%, M^++1), 246 (monomer's M^+, 100%); exact mass: monomer's M^+ (^{80}Se) Calcd. 245.9947, Found. 245.9950. We are grateful to Dr. Haruo Matsuyama of Tokyo Metropolitan University for the high-resolution mass spectroscopic analysis.

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