Novel Reaction of Selenobenzophenones with Alkyllithiums Leading to Symmetrical Olefins

Kentaro Okuma,* Gen Koda, Seiji Okumura, and Atsuyoshi Ohno[†]
Department of Chemistry, Faculty of Science, Fukuoka University, Jonan-ku, Fukuoka 814-80
[†]*Institute for Chemical Research, Kyoto University, Uji, Kyoto 611*

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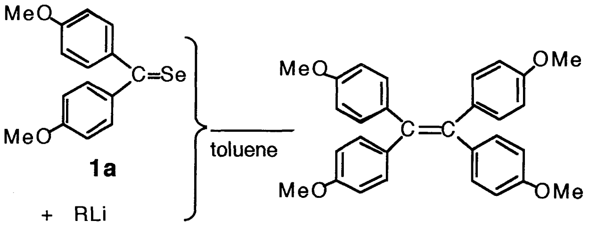
The reaction of selenobenzophenones with alkyllithiums or Grignard Reagents exclusively affords symmetrical tetraarylethylenes as selenophilic products. The reaction might proceed through episelenide (selenirane) intermediates.

Recently, there has been a great deal of interest in the selenocarbonyl compounds.[1-4] The reaction of selenoketones with alkyllithium was originally reported by Back *et al.*; di-tert-butyl selenoketone reacted with alkyllithium to give selenophilic and carbophilic adducts along with the reduction products.[5] Similarly, Ishii *et al.* found that the reaction of sterically hindered tetramethylindaneselone with alkyllithium afforded the corresponding carbophilic and selenophilic adducts along with the reduction product.[6] Okazaki *et al.* found that 2,4,6-tri-*tert*-butylselenobenzaldehyde reacted with alkyllithium to give selenophilic and carbophilic products along with the corresponding stilbene derivative.[7] However, there is no report on the reaction of less hindered selenocarbonyl compounds with alkyllithiums because of their instability. We previously reported the isolation of selenobenzophenones (**1**), which showed different reactivity from thiocarbonyl compounds.[8, 9] We report herein an unprecedented reaction of selenobenzophenones with alkyllithium and Grignard reagents to give exclusively symmetrical tetraarylethylenes (**2**).

Treatment of 4,4'-dimethoxyselenobenzophenone (**1a**) with butyllithium resulted in the formation of tetra-4-methoxyphenylethylene (**2a**) in 53% yield (Scheme 1). Surprisingly, no selenophilic products such as benzhydryl butyl selenide could be detected from the reaction.



2a

Scheme 1.

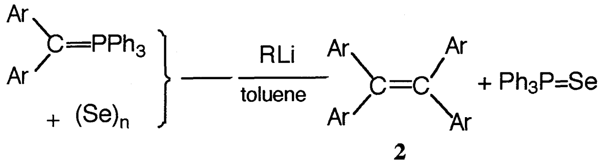
Table 1. Reaction of 4,4'-dimethoxyselenobenzophenone with alkyllithiums

Alkyllithium	Temperature	**2a** (Yield/%)
Butyllithium	0 (°C)	43
Butyllithium	-78	53
tert-Butyllithium	-78	68
Methyllithium	-78	66
Phenyllithium	0	56
Phenyllithium	-78	70

The yields depended insignificantly on the reaction temperature or solvent used: for example, Table 1 shows the results in toluene whereas **2a** was obtained in 40% yield by the reaction with butyllithium in THF at 0°C.

We have obtained symmetrical olefins in 40-65% yields from the reaction of selenobenzophenones generated in situ starting from diarylmethylenetriphenylphosphoranes in the presence of elemental selenium followed by the addition of alkyllithium. A typical procedure was run as follows: To a solution of diphenylmethylenetriphenylphosphorane (5 mmol) in toluene was added elemental selenium (15 mmol). After refluxing for 30 min, the green suspension was filtered. To this filtrate was added phenyllithium in cyclohexane-ether solution (1.8 M, 3 mL) at 0 °C. Immediately, the green solution was turned into pale orange. The solution was poured into water, extracted with dichloromethane. After chromatographic separation, tetraphenylethylene was obtained in 40% yield along with diphenyl diselenide (38%) and triphenylphosphine selenide (75%). The results were shown in Table 2.

Table 2. Reaction of diarylmethylenetriphenylphosphoranes with selenium and alkyllithiums



2

Ar	Alkyllithium	Olefin (Yield/%)
Ph	Butyllithium	55
Ph	Methyllithium	45
Ph	Phenyllithium	40
p-Tol	Butyllithium	65
p-Tol	Methyllithium	46
p-Tol	Phenyllithium	42

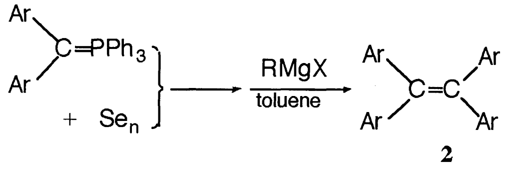
Other selenophilic or carbophilic products were not obtained in the present reaction.

These results were quite different from those of previously reported reactions of hindered selenoketones. Di-*tert*-butylselenoketone reacted with alkyllithium to afford the corresponding selenophilic adducts owing to its steric hindrance.[5] Tetramethylindaneseleone reacted with alkyllithiums to give the seleno- and carbophilic adducts along with the reduction products.[6]

The first reaction of thiobenzophenone with Grignard reagents was realized over seven decades. Schönberg reported that the reaction of thiobenzophenone with phenylmagnesium bromide afforded the corresponding tetraphenylethylene sulfides.[10] Thiobenzophenone reacted with alkyllithiums to afford the corresponding carbophilic adducts along with small amounts of thiophilic adducts.[11,12] Dagonneau and Vialle reported the reaction of thiobenzophenone with Grignard reagents, which gave mainly the compounds resulting from addition of the organic radical to sulfur atom.[13]

We then tried the reaction of selenobenzophenones with Grignard reagents. Interestingly, the same products, tetraarylethylenes, were obtained in this case as shown in Table 3.

Table 3. Reaction of diarylmethylenetriphenylphosphoranes with elemental selenium and RMgX[a]

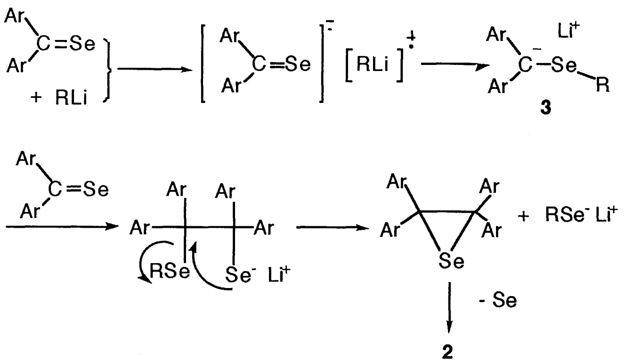


Ylide Ar	RMgX	Products **2**	 Ph_3P=Se
Ph	PhMgBr	55	85[b]
Ph	MeMgI	30	85
p-Tol	PhMgBr	60	80[b]
p-Tol	MeMgBr	45	83
p-$MeOC_6H_4$	PhMgBr	63	85[b]
p-$MeOC_6H_4$	MeMgBr	46	82

[a] The reaction was carried out at 0 °C. Olefins **2** were obtained even at low temperature (-78 °C).

[b] Diphenyl diselenide was obtained in 42-58% yields.

The difference in the reactivity might be owing to the difference of hardness between sulfur and selenium. In the case of thiones, hard base such as alkyllithium acts as only nucleophiles, whereas Grignard reagents afford electron transfer products. Selenobenzophenone, which is softer base than thiobenzophenone and sterically congested selones, affords only the electron transferred reaction products.



Scheme 2.

Tetraarylethylene might be formed as follows: an alkyllithium attacks selenocarbonyl selenium via electron transfer manner to afford alkylselenated radical anion, which change into carbanion (**3**).[14] This anion reacts with another selenobenzophenone to give tetraarylethylene episelenide. This compound easily extrudes selenium to give the corresponding tetraarylethylenes (Scheme 2). Episelenides are usually very unstable and are converted into olefins. Quite few examples for the isolation of sterically hindered episelenides were reported.[2,15]

The lower polarity and greater bond length of the selenocarbonyl bonds might stabilize α-radical anion of selenium.

In summary, we have found that the reaction of selenobenzophenones with alkyllithium or Grignard reagents afforded exclusively tetraarylethylenes in moderate yields.

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References and Notes

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14 Another selenophilic pathway is also possible: Arylselenodiarylcarbanion (**3**) reacted with lithium ion to afford diarylcarbene intermediate, which further reacted with selenobenzophenone to give **2**.

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