Synthetic Utility of Umpoled Diaryl Thioketone−Lanthanoid Intermediates: Desulfurization, Cross Coupling with Electrophiles, and Desulfurizative Homocoupling

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Introduction

Lanthanoid reagents have been extensively utilized in organic synthesis because of their unique properties.[1] For example, the strong reducing ability of low-valent lanthanoids has provided a facile reduction of many functional groups and a convenient method for reductive carbon−carbon bond formation.[2] Oxophilicity and high coordination numbers of trivalent lanthanoids have enabled them to act as new Lewis acids.[3] However, these properties have been less explored in organic sulfur chemistry, since little is known about the reactivity of the lanthanoid reagents toward sulfur functionality.[4,5]

Previously, we reported that the carbonyl carbons of diaryl ketones were umpoled[6] by the reaction with ytterbium metal, and the thus formed ytterbium−benzophenone dianionic complexes were successfully characterized by X-ray analyses.[7] The anionic carbonyl carbons were nucleophilic and were coupled with various electrophiles such as ketones, esters, and epoxides.[8] Diaryl imines were also reduced by lanthanoid metals in a similar manner, and α-amino acids were obtained by treatment of the lanthanoid−diaryl imine intermediates with carbon dioxide.[9] We have applied this methodology to diaryl thioketones to study their reductive reactions with lanthanoids, and we have found that, by choosing the reaction conditions, various transformations such as desulfurization, cross coupling with electrophiles, and desulfurizative homocoupling *via* the expected dianion complexes are possible. We now report the formation and reactivity of lanthanoid−diaryl thioketone dianionic intermediates.[10]

Results and Discussion

Treatment of thiobenzophenone (**1a**) with an equimolar amount of ytterbium or samarium metal in benzene−hexamethylphosphoramide (HMPA) (4:1) or tetrahydrofuran (THF)−HMPA (2:1) afforded a red homogeneous solution. Quenching the reaction with H_2O gave diphenylmethanethiol (**2a**), diphenylmethane (**3a**), tetraphenylethene (**4a**), and 1,1,2,2-tetraphenylethane (**5a**). Table 1 summarizes the results of the reaction of **1a** with ytterbium metal under various conditions. The reaction pathways are shown in Scheme 1. At room temperature, little difference was observed between THF and benzene solvent (entries 1 and 2). In THF, the yield of **2a** was improved by carrying out the reactions at lower temperature, and **2a** was selectively obtained in 94% yield at −35 °C (entry 4). Reaction did not take place at −78 °C. Higher temperatures caused a more complicated reaction, and **2a**−**5a** were all formed with low selectivity (entry 7). Under the refluxing conditions in benzene instead of THF, olefin **4a** was obtained in 64% yield (entry 8). The desulfurized product **3a** can be selectively obtained by treatment of **1a** with 2 equiv of ytterbium metal at room temperature for 20 h (entries 5 and 6). Without HMPA, **1a** and ytterbium were recovered quantitatively. Similar results were obtained when samarium was used instead of ytterbium, but none of the products were obtained from **1a** and samarium(II) diiodide or magnesium. It has been reported that reaction of **1a** with metallic sodium gives a mixture of thioketyl and dianionic intermediates,[11] but further reductive desulfurization does not occur. On the other hand, dimeric olefin **4a** is formed by desulfurizative homocoupling of **1a** with a d-block transition metal like copper.[12] Our results show that lanthanoid metals possess both features of these two types of metals, which can be controlled by changing the reaction temperature or the metal proportion.

Formation of **2a** and **3a** suggests that the thiocarbonyl carbon of **1a** is umpoled by a two- or four-electron transfer from ytterbium in the same manner whereby carbonyl carbons of diaryl ketones become nucleophilic by the reduction with lanthanoid metals.[7] In fact, treatment of the intermediates with deuterium oxide under various conditions affords the deuteriated **2a** and **3a** (Scheme 2). It should be noted that deuterium incorporation in **3a** is over 100%. This is evidence supporting that the unstable B shown in Scheme 1 is formed *in situ* by the reaction of **1a** with excess amounts of ytterbium. When the reaction mixture was oxidized with 5 equiv of benzil after the treatment of **1a** with ytterbium metal under the conditions to produce **3a** selectively as indicated in entry 6 of Table 1, **1a**, benzophenone, and **4a** were formed in 23%, 19%, and 16%

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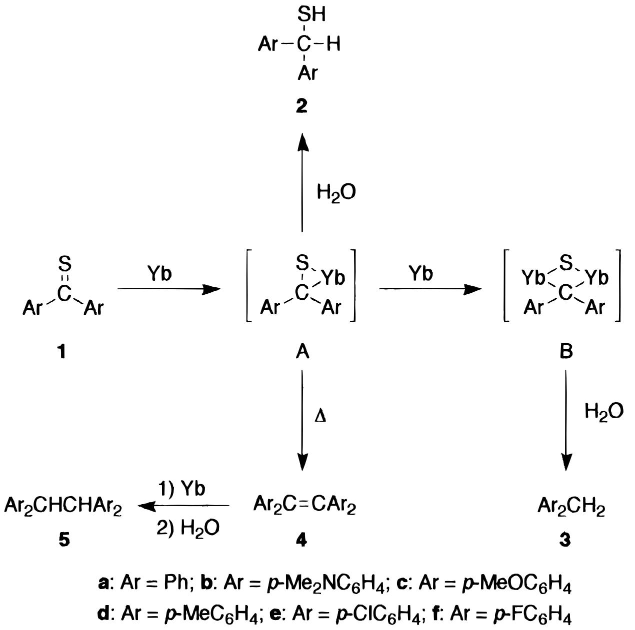
Table 1. Reaction of Thiobenzophenone (1a) with Ytterbium Metal

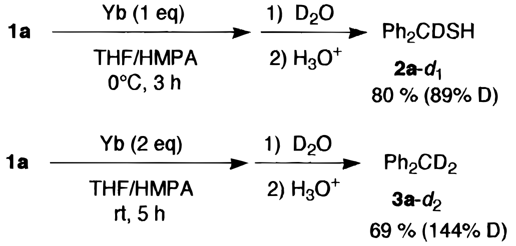
entry	solvent[a]	Yb (equiv)	T (°C)	time (h)	product and yield (%)[b] 2a	3a	4a	5a
1	benzene	1	rt	2	72	8	13	7
2	THF	1	rt	2	65	17	0	16
3	THF	1	0	3	81	10	0	7
4	THF	1	−35	4	94	3	0	3
5	THF	2	rt	20	20	72	0	8
6	benzene	2	rt	20	0	80	0	9
7	THF	1	reflux	2	32	40	17	7
8	benzene	1	reflux	2	12	7	64	5

[a] HMPA was contained as a cosolvent. [b] GC yield based on **1a**.

Scheme 1



Scheme 2



yields, respectively, along with decreased amounts of **3a** (24%). A similar result was obtained by exposing the same mixture to air. Thus, the desulfurization process, leading to B *via* A, is electronically reversible, although **1a** was not regenerated quantitatively.[7a]

With respect to the products and their selectivity, these results are quite different from those of the reaction of benzophenone with ytterbium metal as previously reported.[7a] Only diphenylmethanol was obtained from benzophenone quantitatively by the stoichiometric reaction in THF−HMPA, while deoxygenative reductions of the ketone to **3a** using excess amounts of ytterbium resulted in lower yield (13%). Furthermore, neither **4a** nor **5a** is formed in the reaction of benzophenone with ytterbium metal under similar conditions. This feature was also observed in the reduction of heterocumulenes with a lanthanoid reagent.[13] Samarium(II) iodide desulfurizes isothiocyanates to give isocyanides, whereas oxalic amides are formed by the reduction of isocyanates. This peculiar reactivity of lanthanoids to carbon−sulfur double bonds is due to their strong reducing ability and thiophilicity.

Table 2. Synthesis of Diarylmethanes 3 from 1 and Ytterbium Metal[a]

entry	thioketone 1	products (% yield[b])			
1	**1b**	**2b** (0)	**3b** (22)	**4b** (73)	**5b** (0)
2	**1c**	**2c** (0)	**3c** (53)	**4c** (44)	**5c** (0)
3	**1d**	**2d** (15)	**3d** (67)	**4d** (9)	**5d** (0)
4	**1a**	**2a** (0)	**3a** (80)	**4a** (0)	**5a** (9)
5	**1e**		—[c]		
6	**1f**		—[c]		

[a] Conditions: Yb (2 equiv), benzene−HMPA (4:1), rt, 20 h. [b] Isolated yields for entries 1 and 2 and GC yields for entries 3 and 4. [c] No reaction.

Table 3. Synthesis of Tetraarylethenes 4 from 1 and Ytterbium Metal[a]

entry	thioketone **1**	products (% yield[b])			
1	**1b**	**2b** (0)	**3b** (8)	**4b** (71)	**5b** (0)
2	**1c**	**2c** (0)	**3c** (4)	**4c** (53)	**5c** (0)
3	**1d**	**2d** (0)	**3d** (12)	**4d** (62)	**5d** (0)
4	**1a**	**2a** (7)	**3a** (12)	**4a** (64)	**5a** (5)
5	**1e**		—[c]		
6	**1f**		—[c]		

[a] Conditions: Yb (1 equiv), benzene−HMPA (4:1), reflux, 2 h. [b] Isolated yields for entries 1 and 2 and GC yields for entries 3 and 4. [c] Complex reactions occurred.

Other diaryl thioketones could also be desulfurized by lanthanoid metals to give diarylmethanes **3** and tetraarylethenes **4**, depending on their substituents and reaction conditions. Results of the reaction of diaryl thioketones **1a**−**f** with excess amounts of ytterbium metal are listed in Table 2. Yields of diarylmethane **3** decrease as the substituents become more electron donating (entries 1−4). In particular, **4b** was predominantly obtained in 73% yield in spite of the treatment of **1b** with 2 equiv of ytterbium (entry 1). Diaryl thioketones **1e** and **1f**, having chloro and fluoro groups, did not react with ytterbium and were recovered quantitatively. Table 3 summarizes the results on the desulfurizative homocoupling reaction of **1a**−**f** under the refluxing conditions. In all cases except **1e** and **1f**, **4a**−**d** were formed predominantly in good yields. The substituent effects shown in Tables 2 and 3 are completely opposite to those of copper-mediated desulfurizative homocoupling of diaryl thioketones affording symmetrical olefins **4**, in which thiopinacol coupling and subsequent desulfurization were proposed as a reaction mechanism. Interestingly, **4a** and **3a** were obtained in 66 and 30% yields, respectively, by heating the ytterbium−thiobenzophenone dianionic intermediate A formed at −35 °C, while it was converted to **2a**, not to the thiopinacol, on quenching with H_2O at this temperature as described above. Thus, the present desulfurizative homocoupling could be promoted by C−S bond cleavage of intermediate A followed by dimerization of the unstable diarylcarbene intermediate.[14,15]

Formation of deuteriated **2a** suggests the possibility of nucleophilic coupling of diaryl thioketones with many kinds of substrates. In fact, adducts are obtained from

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[14] Attempts to capture the carbene intermediate with various olefinic compounds failed.

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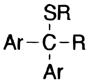
Table 4. Coupling Reaction of Thioketone 1 with Various Electrophiles

entry	thioketone **1**	electrophile	time (h)	products (% yield)[a]
1	**1a**	MeI	0.5	**6a** (82)
2	**1b**	MeI	0.5	**6b** (39), **7** (40)
3	**1a**	EtBr	5	**6c** (84)
4	**1a**	$Br(CH_2)_2Br$	5	**8a** (74)
5	**1b**	$Br(CH_2)_2Br$	5	**8b** (50)
6	**1a**	$Br(CH_2)_3Br$	4	**8c** (66)
7	**1b**	$Br(CH_2)_3Br$	4	**8d** (51)
8	**1a**	$(CH_3)_2CO$	0.5	**9** (72)

[a] GC yield based on the diaryl thioketone **1**.

1a,b and various electrophiles (eq 1 and Table 4).

$$\mathbf{1} \xrightarrow[\substack{\text{THF, HMPA} \\ 0^\circ\text{C, 3 h}}]{\text{Yb (1 eq)}} \xrightarrow[0^\circ\text{C}]{\text{electrophile (2.7 eq)}} \text{adducts } \mathbf{6\text{-}9} \qquad (1)$$

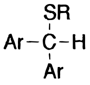


$$\mathrm{Ar-\overset{SR}{\underset{Ar}{C}}-R}$$

6a: Ar = Ph; R = Me

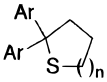
6b: Ar = *p*-MeC$_6$H$_4$; R = Me

6c: Ar = Ph; R = Et



$$\mathrm{Ar-\overset{SR}{\underset{Ar}{C}}-H}$$

7: Ar = *p*-MeC$_6$H$_4$; R = Me

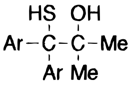


8a: Ar = Ph; n = 1

8b: Ar = *p*-MeC$_6$H$_4$; n = 1

8c: Ar = Ph; n = 2

8d: Ar = *p*-MeC$_6$H$_4$; n = 2



$$\mathrm{Ar-\overset{HS}{\underset{Ar}{C}}-\overset{OH}{\underset{Me}{C}}-Me}$$

9: Ar = Ph

Reaction of **1a** with alkyl monohalides produced C- and S-alkylated thiobenzophenone derivatives **6** in high yields (entries 1 and 3).[16] Thianes **8a,b** and thiolanes **8c,d**, five- and six-membered cyclic sulfides, were provided from α,ω-dihaloalkanes (entries 4–7). These results also support the existence of intermediate A. As shown in entry 8, acetone reacted with dianionic thiobenzophenone to afford the β-hydroxy thiol **9** in good yield.

In conclusion, reaction of diaryl thioketones with lanthanoid metals (Yb, Sm) affords mainly three types of compounds: (1) adducts **6**–**10** by the coupling reactions of lanthanoid–diaryl thioketones dianionic intermediates with electrophiles, (2) diarylmethanes by four-electron reduction of diaryl thioketones **1**, and (3) tetraarylethenes by desulfurizative homocoupling of **1**. It is worth noting that each of these compounds can be selectively obtained by choosing the reaction conditions. Further synthetic applications of these reactions are now underway.

Experimental Section

General. ^{1}H and ^{13}C NMR spectra were recorded at 270 MHz, and chemical shifts are reported in ppm on the δ scale relative to internal TMS. GC analyses were carried out on a 1 m × 3.2 mm i.d. column of 2% silicon OV-17 on 60–80 mesh Uniport HP. Mass spectra were obtained at 70 eV. Melting points are uncorrected.

Materials. Materials were commercially available unless otherwise noted. Ytterbium and samarium (40 mesh) were washed with anhydrous *n*-hexane and were dried *in vacuo* for 3 days. Benzene and tetrahydrofuran were dried with sodium benzophenone ketyl and distilled under argon. Hexamethylphosphoramide (*Caution*: HMPA is highly toxic and suspected of being a carcinogen) was dried over CaH$_2$ at 100 °C and distilled under reduced pressure. Diaryl thioketones **1a**–**f** were prepared according to the reported method[17] and purified by bulb-to-bulb distillation or recrystallization from ether/*n*-hexane.

General Procedure for the Reaction of Thiobenzophenone (1a) with Ytterbium Metal. All reactions were carried out under argon. Ytterbium (173 mg, 1.0 mmol) was placed in a 10-mL round-bottomed flask equipped with a rubber septum and a reflux condenser, if necessary. HMPA (1 mL) was added, and then methyl iodide (2 μL) was added to activate the ytterbium. After a few minutes of stirring, a solution of thiobenzophenone (198 mg, 1.0 mmol) in benzene (4 mL) was added *via* cannula under argon. The reaction mixture was stirred for an appropriate time after the reaction started. The reaction mixture was treated with 2 M HCl (5 mL) and extracted with diethyl ether (3 × 30 mL). The organic layer was washed with saturated aqueous NaCl solution and dried over anhydrous magnesium sulfate. Yields of the products were determined by GC using *n*-tetracosane as an internal standard. The products were isolated by liquid chromatography (silica gel, *n*-hexane/ethyl acetate, 100/1) after the solvent was evaporated *in vacuo*.

The same scale reaction was also carried out in THF (6 mL)–HMPA (3 mL). Reactions with samarium and other alkali or alkaline earth metals were performed in a similar manner. The amounts of ytterbium, reaction temperatures, and yields of the products **2**–**5a** are shown in Table 1.

Diphenylmethanethiol (2a):[18] colorless liquid; IR (neat) 2550, 1590 cm^{-1}; MS *m/z* 167 (Ph$_2$CH$^+$); ^{1}H NMR (CDCl$_3$) δ 2.26 (d, J = 5.0 Hz, 1 H), 5.44 (d, J = 5.0 Hz, 1 H), 7.19–7.42 (m, 10 H); ^{13}C NMR (CDCl$_3$) δ 47.8 (1 C), 127.2 (2 C), 127.8 (4 C), 128.5 (4 C), 143.4 (2 C).

Diphenylmethane (3a):[19] colorless liquid; MS *m/z* 168 (M$^+$); ^{1}H NMR (CDCl$_3$) δ 3.98 (s, 2 H), 7.17–7.31 (m, 10 H); ^{13}C NMR (CDCl$_3$) δ 41.9 (1 C), 126.0 (2 C), 128.4 (4 C), 128.9 (4 C), 141.1 (2 C).

Tetraphenylethene (4a):[20] colorless crystals; mp 224–225 °C (lit.[20] mp 223–224 °C); IR (Nujol) 3040, 1590 cm^{-1}; MS *m/z* 332 (M$^+$); ^{1}H NMR (CDCl$_3$) δ 7.06 (br-s, 20 H); ^{13}C NMR (CDCl$_3$) δ 126.4 (8 C), 127.6 (4 C), 131.3 (8 C), 141.0 (2 C), 143.7 (4 C).

1,1,2,2-Tetraphenylethane (5a):[21] colorless crystals; mp 208–209 °C (lit.[21] mp 210 °C); IR (Nujol) 3085, 1598 cm^{-1}; MS *m/z* 334 (M$^+$); ^{1}H NMR (CDCl$_3$) δ 4.69 (s, 2 H), 6.92–7.25 (m, 20 H); ^{13}C NMR (CDCl$_3$) δ 59.7 (2 C), 127.5 (4 C), 128.4 (8 C), 128.9 (8 C), 140.2 (4 C).

Treatment of the Intermediates with D$_2$O. The intermediates were prepared as mentioned above under the conditions shown in Scheme 2. To the solution of the intermediates, was added 1.0 mL of D$_2$O. Yields of the products were determined by GC after the usual workup. Deuterium contents were determined by ^{1}H NMR spectra of the isolated products in CCl$_4$.

Oxidation of the Intermediates. The intermediates formed by the reaction of **1** (1 mmol) with ytterbium (2 mmol) were oxidized by adding benzil (5 mmol) or exposing the reaction mixture to air. Yields of the products were determined by GC as above after the usual workup.

Reaction of Diaryl Thioketone 1 with Ytterbium: Synthesis of Diarylmethanes. Reactions were performed as mentioned above, except 2 equiv (2 mmol) of ytterbium was used and the reaction time was longer (20 h). Results are listed in Table 2.

Bis(4-(dimethylamino)phenyl)methane (3b):[22] yellow crystals; mp 88–89 °C (lit.[22] mp 90 °C); ^{1}H NMR (C$_6$D$_6$) δ 2.58 (s, 12 H), 3.97 (s, 2 H), 6.68 (d, J = 8.6 Hz, 4 H), 7.22 (d, J = 8.6 Hz, 4 H); ^{13}C NMR (C$_6$D$_6$) δ 40.0 (4 C), 40.6 (1 C), 113.3 (4 C), 128.5 (2 C), 130.8 (4 C), 149.5 (2 C).

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(16) Treatment of B with methyl iodide afforded the 2, 2-diphenylpropane in 14% yield together with **6a** in 11%.

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Bis(4-methoxyphenyl)methane (3c):[19] colorless needles; mp 45−46 °C (lit.[19] mp 49.0−50.0 °C); ^{1}H NMR ($CDCl_3$) δ 3.76 (s, 6 H), 3.85 (s, 2 H), 6.81 (d, $J = 8.6$ Hz, 4 H), 7.08 (d, $J = 8.6$ Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 40.1 (1 C), 55.2 (2 C), 113.8 (4 C), 129.7 (4 C), 133.7 (2 C), 157.8 (2 C).

Bis(4-methylphenyl)methane (3d):[23] colorless oil; MS *m/z* 196 (M^+); ^{1}H NMR ($CDCl_3$) δ 2.30 (s, 6 H), 3.89 (s, 2 H), 7.07 (s, 8 H); ^{13}C NMR ($CDCl_3$) δ 21.0 (2 C), 41.0 (1 C), 128.7 (4 C), 129.1 (4 C), 135.4 (2 C), 138.3 (2 C).

Bis(4-methylphenyl)methanethiol (2d): colorless oil; IR (neat) 2556, 1510 cm^{-1}; MS *m/z* 228 (M^+); ^{1}H NMR ($CDCl_3$) δ 2.22 (d, $J = 4.8$ Hz, 1 H), 2.31 (s, 6 H), 5.38 (d, $J = 4.8$ Hz, 1 H), 7.10 (d, $J = 7.9$ Hz, 4 H), 7.28 (d, $J = 7.9$ Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 21.0 (2 C), 47.3 (1 C), 127.6 (4 C), 129.2 (4 C), 136.8 (2 C), 140.7 (2 C). Anal. Calcd for $C_{15}H_{16}S$: C, 78.90; H, 7.06. Found: C, 78.82; H, 7.04.

Reaction of Diaryl Thioketone 1 with Ytterbium: Synthesis of Tetraarylethenes. The procedure was similar to the general procedure for the reaction of thiobenzophenone **1a** with ytterbium except for carrying out the reaction at reflux temperature for 2 h. Yields of **4a** and **4b** were determined by GC, as above, but yields of **4c** and **4d** were reported as isolated. Results are listed in Table 3.

Tetrakis(4-(dimethylamino)phenyl)ethene (4b): yellow crystals; mp 282−283 °C dec; IR (Nujol) 1347 cm^{-1}; ^{1}H NMR (C_6D_6) δ 2.48 (s, 24 H), 6.52 (d, $J = 8.9$ Hz, 8 H), 7.51 (d, $J = 8.9$ Hz, 8 H); ^{13}C NMR (C_6D_6) δ 40.0 (8 C), 112.2 (8 C), 133.2 (8 C), 134.6 (4 C), 138.1 (2 C), 148.8 (4 C). Anal. Calcd for $C_{34}H_{40}N_2$: C, 80.91; H, 7.99; N, 11.10. Found: C, 80.76; H, 7.94; N, 10.86.

Tetrakis(4-methoxyphenyl)ethene (4 C):[12b] colorless crystals; mp 182−183 °C (lit.[12b] mp 181−182 °C); ^{1}H NMR ($CDCl_3$) δ 3.73 (d, 12 H), 6.33 (d, $J = 8.9$ Hz, 8 H), 6.93 (d, $J = 8.9$ Hz, 8 H); ^{13}C NMR ($CDCl_3$) δ 55.0 (4 C), 113.0 (8 C), 132.5 (8 C), 136.9 (4 C), 138.3 (2 C), 157.7 (4 C).

Tetrakis(4-methylphenyl)ethene (4d):[24] colorless crystals; mp 151−153 °C (lit.[24] mp 151 °C); MS *m/z* 388 (M^+); ^{1}H NMR ($CDCl_3$) δ 2.25 (s, 12 H), 6.87 (s, 16 H); ^{13}C NMR ($CDCl_3$) δ 21.2 (4 C), 128.3 (8 C), 131.2 (8 C), 135.6 (4 C), 139.8 (2 C), 141.3 (4 C).

Coupling Reactions of Diaryl Thioketones 1 with Alkyl Halides. After the treatment of ytterbium (1.0 mL) with **1** (1.0 mmol) in THF (6 mL) and HMPA (3 mL) at 0 °C for 3 h, an alkyl halide (2.7 mmol) was added to the mixture. Stirring was continued at 0 °C for an appropriate time as indicated in Table 4. The usual workup followed by liquid chromatography (silica gel, *n*-hexane/ethyl acetate, 100/1) gave the alkylated products. Yields of the products were determined by GC using *n*-undecane as an internal standard.

1,1-Diphenylethyl methyl sulfide (6a): colorless oil; IR (neat) 3056 cm^{-1}; MS *m/z* 228 (M^+); ^{1}H NMR ($CDCl_3$) δ 1.83 (s, 3 H), 2.04 (s, 3 H), 7.20−7.50 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 13.2 (1 C), 29.6 (1 C), 55.4 (1 C), 126.5 (2 C), 127.9 (4 C), 128.0 (4 C), 145.9 (2 C). Anal. Calcd for $C_{15}H_{16}S$: C, 78.90; H, 7.06. Found: C, 78.90; H, 7.03.

1,1-Bis(4-methylphenyl)ethyl methyl sulfide (6b): colorless oil; IR (neat) 3000, 2950, 1437, 1305 cm^{-1}; MS *m/z* 209 ($M^+ - Me$), 91 (*p*-tol$^+$); ^{1}H NMR ($CDCl_3$) δ 1.82 (s, 3 H), 2.01 (s, 3 H), 2.33 (s, 6 H), 7.10 (d, $J = 5.8$ Hz, 4 H), 7.28 (d, $J = 5.8$ Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 13.2 (1 C), 20.9 (2 C), 29.7 (1 C), 54.9 (1 C), 127.8 (4 C), 128.7 (4 C), 136.1 (2 C), 143.1 (2 C). Anal. Calcd for $C_{17}H_{20}S$: C, 79.63; H, 7.86. Found: C, 79.52; H, 7.82.

1,1-Diphenylpropyl ethyl sulfide (6c): colorless oil; IR (neat) 3050 cm^{-1}; MS *m/z* 226 ($M^+ - Et$), 195 ($M^+ - SEt$); ^{1}H NMR ($CDCl_3$) δ 0.80 (t, $J = 7.4$ Hz, 3 H), 1.03 (t, $J = 7.4$ Hz, 3 H), 2.08 (q, $J = 7.4$ Hz, 2 H), 2.36 (q, $J = 7.4$ Hz, 2 H), 7.00−7.50 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 9.4 (1 C), 13.5 (1 C), 23.0 (1 C), 33.0 (1 C), 60.8 (1 C), 126.2 (4 C), 127.9 (4 C), 128.6 (2 C), 145.3 (2 C). Anal. Calcd for $C_{17}H_{20}S$: C, 79.63; H, 7.86. Found: C, 79.53; H, 7.73.

Bis(4-methylphenyl)methyl methyl sulfide (7): colorless oil; IR (neat) 3020, 2920, 1432, 1310 cm^{-1}; MS *m/z* 195 ($M^+ - SMe$), 91 (*p*-tol$^+$); ^{1}H NMR ($CDCl_3$) δ 1.97 (s, 3 H), 2.31 (s, 6 H), 4.99 (s, 1 H), 7.11 (d, $J = 8.1$ Hz, 4 H), 7.29 (d, $J = 8.1$ Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 15.9 (1 C), 21.0 (2 C), 55.5 (1 C), 128.1 (4 C), 129.2 (4 C), 136.7 (2 C), 138.4 (2 C). Anal. Calcd for $C_{16}H_{18}S$: C, 79.29; H, 7.49. Found: C, 79.17; H, 7.49.

2,2-Diphenylthiolane (8a): white needles; mp 71−72 °C; IR (Nujol) 3054 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.02 (quin, $J = 6.6$ Hz, 2 H), 2.66 (t, $J = 6.6$ Hz, 2 H), 3.09 (t, $J = 6.6$ Hz, 2 H), 7.14−7.45 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 28.5 (1 C), 32.9 (1 C), 44.1 (1 C), 67.8 (1 C), 126.3 (2 C), 127.5 (4 C), 128.0 (4 C), 146.9 (2 C). Anal. Calcd for $C_{16}H_{16}S$: C, 79.95; H, 6.71. Found: C, 79.86; H, 6.53.

2,2-Bis(4-methylphenyl)thiolane (8b): colorless crystals; mp 48−49 °C; IR (Nujol) 3018, 1504 cm^{-1}; MS *m/z* 268 (M^+); ^{1}H NMR ($CDCl_3$) δ 2.01 (quin, $J = 6.9$ Hz, 2 H), 2.29 (s, 6 H), 2.62 (t, $J = 6.9$ Hz, 2 H), 3.07 (t, $J = 6.9$ Hz, 2 H), 7.06 (d, $J = 8.1$ Hz, 4 H), 7.31 (d, $J = 8.1$ Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 20.9 (2 C), 28.5 (1 C), 32.9 (1 C), 44.2 (1 C), 67.4 (1 C), 127.3 (4 C), 128.7 (4 C), 135.8 (2 C), 144.1 (2 C). Anal. Calcd for $C_{18}H_{20}S$: C, 80.54; H, 7.51. Found: C, 80.51; H, 7.51.

2,2-Diphenylthiane (8 C): white needles; mp 72−73 °C; IR (Nujol) 1590 cm^{-1}; MS *m/z* 254 (M^+); ^{1}H NMR ($CDCl_3$) δ 1.58−1.65 (m, 2 H), 1.78−1.87 (m, 2 H), 2.64 (t, $J = 5.6$ Hz, 2 H), 2.76 (t, $J = 5.8$ Hz, 2 H), 7.16−7.50 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 22.5 (1 C), 26.7 (1 C), 28.9 (1 C), 38.7 (1 C), 54.9 (1 C), 126.5 (2 C), 128.0 (4 C), 128.3 (4 C), 145.2 (2 C). Anal. Calcd for $C_{17}H_{18}S$: C, 80.26; H, 7.13. Found: C, 79.80; H, 6.78.

2,2-Bis(4-methylphenyl)thiane (8d): colorless crystals; mp 66−68 °C; IR (Nujol) 3021, 1508 cm^{-1}; MS *m/z* 282 (M^+); ^{1}H NMR ($CDCl_3$) δ 1.59 (m, 2 H), 1.80 (m, 2 H), 2.30 (s, 6 H), 2.61 (m, 2 H), 2.71 (m, 2 H), 7.10 (d, $J = 8.3$ Hz, 4 H), 7.26 (d, $J = 8.3$ Hz, 4 H); ^{13}C NMR ($CDCl_3$) δ 20.9 (2 C), 22.6 (1 C), 26.7 (1 C), 28.9 (1 C), 38.7 (1 C), 54.5 (1 C), 127.8 (4 C), 129.0 (4 C), 136.0 (2 C), 142.4 (2 C). Anal. Calcd for $C_{19}H_{22}S$: C, 80.80; H, 7.85. Found: C, 80.94; H, 7.75.

Coupling Reaction of Thiobenzophenone (1a) with Acetone. After the reaction of ytterbium (1.0 mmol) with **1a** (1.0 mmol) in THF (6 mL) and HMPA (3 mL) at 0 °C for 3 h, acetone (0.2 mL, 2.7 mmol) was added. Stirring was continued at 0 °C for 0.5 h. After the usual workup, 1,1-diphenyl-2-hydroxy-2-methylpropanethiol (**9**) was isolated by liquid chromatography (silica gel, *n*-hexane/ethyl acetate, 100/1) as a colorless oil: IR (neat) 3470, 2500 cm^{-1}; MS *m/z* 208 ($Ph_2CCMe_2^+$), 59 (Me_2COH^+); ^{1}H NMR ($CDCl_3$) δ 1.38 (s, 6 H), 2.34 (s, 1 H), 2.93 (br s, 1 H), 7.00−8.00 (m, 10 H). Anal. Calcd for $C_{16}H_{18}OS$: C, 74.37; H, 7.02. Found: C, 74.34; H, 6.94.

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