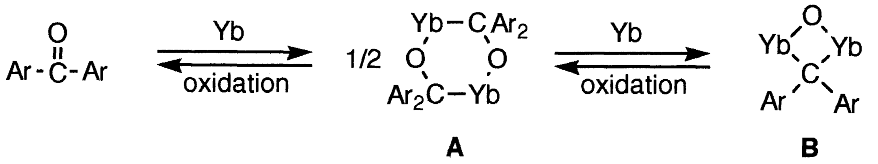
CHEMISTRY LETTERS, pp. 611-614, 1994.

Ytterbium Metal Mediated Desulfurization and Coupling Reaction of Diaryl Thioketones

Yoshikazu MAKIOKA, Shin-ya UEBORI, Masumi TSUNO, Yuki TANIGUCHI,
Ken TAKAKI, and Yuzo FUJIWARA
Department of Applied Chemistry, Faculty of Engineering, Hiroshima University,
Kagamiyama, Higashi-Hiroshima 724

Diaryl thioketones are selectively reduced with ytterbium metal to diarylmethanethiols, diarylmethanes or tetraarylethylenes, via thiometallacycle intermediates which undergo electrophilic coupling at thiocarbonyl carbon and sulfur.

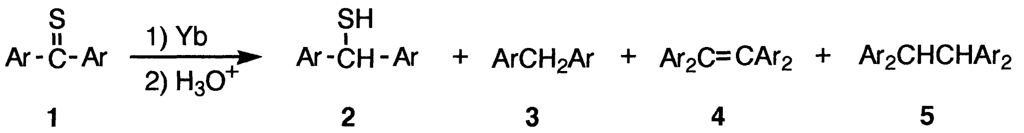
Although reactivities of thioketones in ionic and radical reactions have been well investigated, their reactions are often complicated because of ambident character of C=S and facility of C-S bond fission.[1] Previously, we have reported a convenient desulfurization of aromatic and aliphatic isothiocyanates with samarium diiodide, leading to the corresponding isocyanides in good yields.[2] We have also demonstrated that diaryl ketones are reduced with ytterbium metal to well characterized 6-membered oxometallacycle **A** which reacts with various electrophiles at carbonyl carbon[3] and that excess Yb metal reduces **A** to μ-oxo, μ-alkylidene complex **B** reversibly (Eq. 1).[4] If diaryl thioketones react with Yb metal in the similar fashion, their selective reduction, homocoupling and an unprecedented reaction with electrophiles would be anticipated. We report herein a preliminary result on these reactions.



(1)

When thiobenzophenone (**1a**) was treated with an equimolar amount of Yb metal at room temperature in benzene-hexamethylphosphoric triamide (4 : 1) for 2 h, diphenylmethanethiol (**2a**), diphenylmethane (**3a**), tetraphenylethylene (**4a**), and 1,1,2,2-tetraphenylethane (**5a**) were obtained in 72%, 8%, 13% and 7% yields, respectively (Eq. 2). Representative results under various conditions are summarized in Table 1. Ratio of the products **2a**-**5a** was significantly dependent on the reaction temperature and the amount of Yb used. Thus, the thiol **2a** was formed exclusively at low temperature (entry 1) , while the reaction at refluxing temperature afforded the ethylene **4a** as a main product (entry 3). Two equivalents of Yb metal caused the predominant formation of **3a** (entry 4).

Then, various diaryl thioketones **1** were treated with Yb metal under the two different conditions to cause selective homocoupling and desulfurization in the above reaction (Table 2). Diaryl thioketones **1** having



$$\underset{\mathbf{1}}{\text{Ar-}\overset{\text{S}}{\overset{\|}{\text{C}}}\text{-Ar}} \xrightarrow[\text{2) }H_3O^+]{\text{1) Yb}} \underset{\mathbf{2}}{\text{Ar-}\overset{\text{SH}}{\overset{|}{\text{C}}}\text{H-Ar}} + \underset{\mathbf{3}}{ArCH_2Ar} + \underset{\mathbf{4}}{Ar_2C{=}CAr_2} + \underset{\mathbf{5}}{Ar_2CHCHAr_2} \qquad (2)$$

a : Ar=C_6H_5
b : Ar=*p*-MeC_6H_4
c : Ar=*p*-$MeOC_6H_4$
d : Ar=*p*-$Me_2NC_6H_4$
e : Ar=*p*-FC_6H_4

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

Entry	Yb /equiv.	Temp	Time /h	Product and Yield/%[a]			
				2a	**3a**	**4a**	**5a**
1	1[b]	-35 °C	4	94	2	3	–
2	1	rt	2	72	8	13	7
3	1	reflux	2	7	12	64	5
4	2	rt	20	–	80	–	9

a) GC yield based on **1a**. b) THF-HMPA (2 : 1).

Table 2. Ytterbium Metal Promoted Homocoupling and Desulfurization of Diaryl Thioketones (**1**)

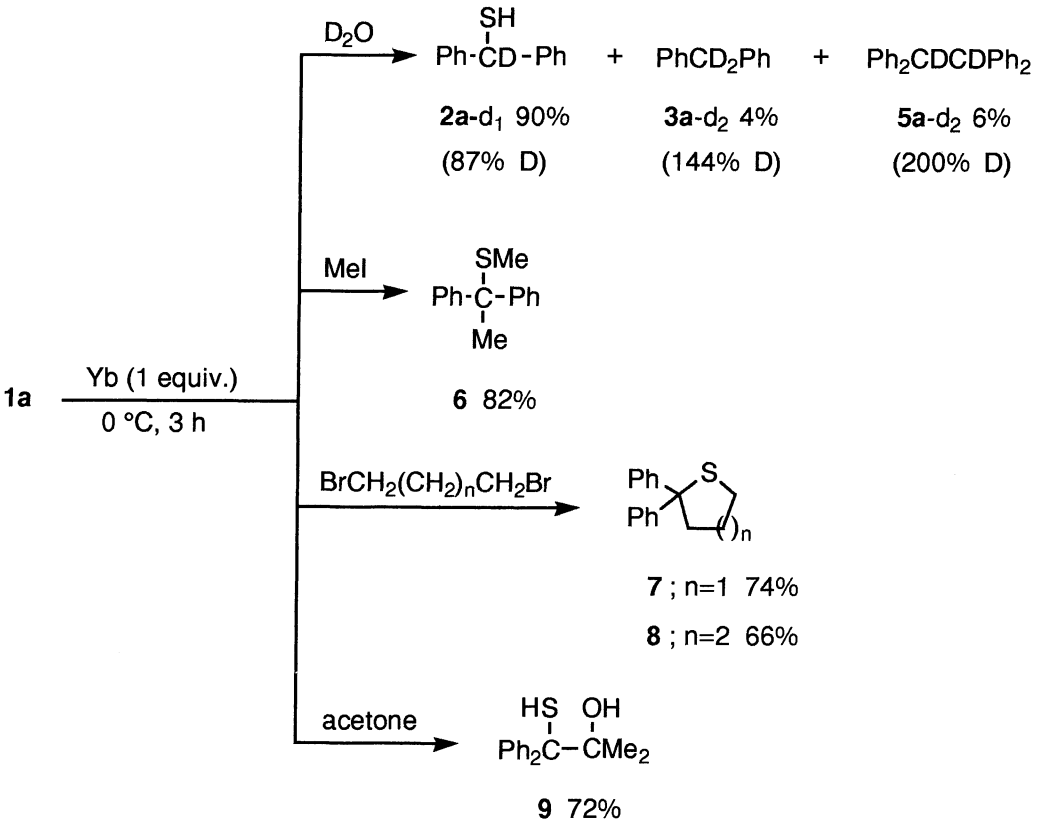
Entry	Thioketone **1**	Method[a]	Product and Yield/%[b,c]			
			3		**4**	
1	**1a**	A	**3a**	12	**4a**	64
2	**1b**	A	**3b**	12	**4b**	62
3	**1c**	A	**3c**	4	**4c**	53
4	**1d**	A	**3d**	8	**4d**	71
5	**1e**	A	**3e**	–[d]	**4e**	–[d]
6	**1a**	B	**3a**	80	**4a**	0
7	**1b**	B	**3b**	67	**4b**	9
8	**1c**	B	**3c**	53	**4c**	44
9	**1d**	B	**3d**	22	**4d**	73
10	**1e**	B	no reaction			

a) Method A: Yb (1 equiv.), reflux for 2 h. Method B: Yb (2 equiv.), rt for 20 h. b)Isolated yield (GC yield for entries 1, 2, 6, and 7) based on **1**. c) **2** was also obtained in 7% (entry 1) and 15% yields (entry 7). **5** was detected in 5-9 % yield (entries 1, 2, 6 and 7). d) An untractable mixture was obtained.

electron releasing groups were converted to the coupling products **4** in good yields by the treatment with equimolar amount of Yb (entries 1-4). However, the reaction of 4,4'-difluorothiobenzophenone (**1e**) gave an untractable mixture (entry 5). In the reaction with two equivalents of Yb, the yields of diarylmethanes **3** decreased and those of tetraarylethylenes **4** increased with decreasing σ value of the substituents (entries 6-9). The reaction of **1e** did not take place under these conditions (entry 10). These substituent effects are inconsistent with the coupling reaction mediated by copper, in which acceleration by the electron withdrawing groups and retardation by electron releasing substituents were observed.5)

Interestingly, when the reaction of **1a** with Yb metal in THF-HMPA was quenched with deuterium oxide after treatment at 0 °C for 3 h, monodeuteriated thiol **2a**-d_1 (90% yield, 87% D), dideuteriated products **3a**-d_2 (4% yield, 144% D), and **5a**-d_2 (6% yield, 200% D) were isolated (Scheme 1). Formation of **5a**-d_2 clearly indicates that the tetraarylethanes **5** are formed by the further reduction of **4**,6) not by the coupling reaction of diarylmethyl radical.7) In addition, desulfurization seems to proceed via a dianion-like intermediate, leading to **3a**-d_2 finally.

The results on the deuteriation suggest a nucleophilic property of the thiocarbonyl carbon, and therefore coupling reaction with electrophiles would be expected. Indeed, **1a** reacted with methyl iodide under the similar conditions to give 1,1-diphenylethyl methyl sulfide (**6**) in 82% yield. 2,2-Diphenyl-thiolane (**7**) and -thiane (**8**) were also obtained in good yields by the reactions with 1,3-dibromopropane and 1,4-dibromobutane,



Scheme 1.

respectively. The reaction with acetone afforded 1,1-diphenyl-2-hydroxy-2-methyl-1-propanethiol (**9**) in 72% yield.

The reactions of diaryl thioketones **1** described above would be accounted for most likely by the intermediates similar to **A** and **B** in the reaction of diaryl ketones.4) Thus, thio-analogue of **A** affords **2** and reacts with various electrophiles to give the products **6**-**9**. However, this intermediate is less stable than A because of weak C-S bond and hence it decomposes to **4** at elevated temperature.8) In contrast, the reaction with two equivalents of Yb metal generates the intermediate corresponding to **B**, which yields the dideuteriated product **3**-d_2 on quenching with D_2O. When thio-analogue of **B** (Ar = Ph) is oxidized with benzil (5 equiv.) before quenching, thiobenzophenone (**1a**) and benzophenone are obtained in 23% and 19% yields, respectively along with **4a** (16%) and **3a** (24%),9) suggesting that the desulfurization is reversible in analogy with deoxygenation of diaryl ketones by Yb metal.4)

The results outlined here reveal a new aspect of the reduction of diaryl thioketones and a further work to study the reaction mechanism is now under way.

Support from the Ministry of Education, Science and Culture (Grant No. 05236106) is gratefully acknowledged.

References

1) A. Ohno, "Organic Chemistry of Sulfur," ed by S. Oae, Plenum, New York (1977), p. 189.
2) Y.-S. Liu, M.-Z. Bei, Z.-H. Zhou, K. Takaki, and Y. Fujiwara, *Chem. Lett.*, **1992**, 1143.
3) Z. Hou, K. Takamine, O. Aoki, H. Shiraishi, Y. Fujiwara, and H. Taniguchi, *J. Org. Chem.*, **53**, 6077 (1988), and references cited therein.
4) Z. Hou, H. Yamazaki, K. Kobayashi, Y. Fujiwara, and H. Taniguchi, *J. Chem. Soc., Chem. Commun.*, **1992**, 722; Z. Hou, H. Yamazaki, Y. Fujiwara, and H. Taniguchi, *Organometallics*, **11**, 2711 (1992).
5) J. Baran and P. Laszlo, *Tetrahedron Lett.*, **26**, 5135 (1985).
6) Z. Hou, H. Taniguchi, and Y. Fujiwara, *Chem. Lett.*, **1987**, 305.
7) Y. Ogata, M. Yamashita, and M. Mizutani, *Bull. Chem. Soc. Jpn.*, **49**, 1721 (1976).
8) An alternative process via thiirane for the formation of **4** seems less likely: Ref. 5; H. Alper and H. -N. Paik, *J. Org. Chem.*, **42**, 3522 (1977).
9) Thiobenzophenone (**1a**) and benzophenone were not detected in the absence of the oxidant as shown in Table 1 (entry 4).

(Received November 29, 1993)