Pergamon

Tetrahedron Letters, Vol. 35, No. 42, pp. 7789-7792, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $7.00+0.00

0040-4039(94)01679-8

Facile Formation of Lanthanoid(III) Thiolates from Benzophenone-Catalyzed Reaction of Lanthanoid Metals and Disulfides, and Their Use as Sulfenylating Reagents

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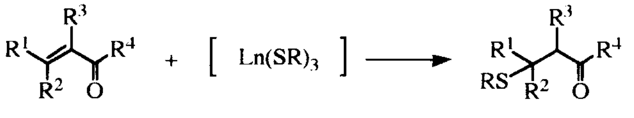
Abstract: Lanthanoid metal reacts with diaryl and -alkyl disulfides in the presence of a catalytic amount of benzophenone to generate lanthanoid (III) thiolates. Lanthanoid thiolates thus formed in situ, react with enones to give Michael adducts in good yields.

Recently, we reported that reaction of lanthanoid metals (Yb, Sm) with diaryl ketones such as benzophenone produced the corresponding dianionic complexes that react easily with a variety of electrophiles like ketones, esters, epoxides, nitriles, carbon dioxide, and acetylenes producing adducts.[1] We have succeeded in isolating and structurally characterizing the ytterbium(II)-benzophenone dianionic complex and showed that this anionic complex formation reaction is reversible to generate an active lanthanoid metals.[2] Lanthanoid reagents have unique properties such as strong reducing ability, oxophilicity and thiophilicity etc. Therefore, it is of interest to investigate the reaction of lanthanoid metals with sulfur compounds.[3] In a hope that the lanthanoid metal activated in this manner should react with disulfides, we investigated the reaction of lanthanoid metals with diaryl and -alkyl disulfides in the presence of a catalytic amount of benzophenone. We have now found that the reaction of diaryl and -alkyl sulfides with lanthanoid metals activated by benzophenone affords lanthanoid(III) thiolates (Eq. 1), and that the thiolates thus formed *in situ*, react with enones to give Michael adducts (Eq 2). In this communication we wish to report these results.

$$\underset{(\mathrm{Ln} = \mathrm{Yb, Sm})}{\mathrm{Ln}} + 3/2\ \mathrm{RS\text{-}SR} \xrightarrow[\mathrm{THF\text{-}HMPA}]{\mathrm{Ph_2CO\ cat.}} \left[\ \mathrm{Ln(SR)_3}\ \right] \qquad (1)$$

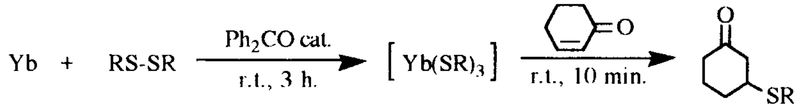


(2)

Little is known about lanthanoid chalcogenolate complexes.[4] Nakamura et al. reported the isolations of $[\mathrm{Ln(SPh)_2(thf)}]_n$ and $[\mathrm{Ln}(\mu\text{-SPh})(\mathrm{C_8H_8})(\mathrm{thf})_n]_2$ (Ln=Yb, Sm) by the reaction of lanthanoid metals with diphenyl disulfide.[5]

The representative results for benzophenone-catalyzed reaction of disulfides with 2-cyclohexenone mediated by ytterbium metal are shown in Table 1. The typical preparation of 3-phenylthiocyclohexanone is as follows (entry 1): A mixture of Yb metal (40 mesh, 173 mg, 1 mmol), diphenyl disulfide (327 mg, 1.5 mmol) and a catalytic amount of benzophenone (9 mg, 0.05 mmol) in THF (4 mL) - HMPA (1 mL) was stirred at room temperature for 3 h under argon. Ytterbium metal was dissolved to form a clean green solution and the color of the mixture turned to yellow and the homogeneous solution changed to a suspension as the reaction proceeded, indicating the formation of Yb(III) species *via* Yb(II) from Yb(O). Then, 2-cyclohexenone (96 mg, 1.0 mmol) was added to the mixture by a syringe. The mixture was stirred at room temperature for 10 min. Usual work-up followed by SiO_2 column chromatography (hexane-ethyl acetate) gave 3-phenylthiocyclohexanone (167 mg, 81%) as an yellow oil, which gave satisfactory IR, NMR, Mass spectral data and elemental analysis.

Table 1. Yb Metal Mediated Reaction of Dialkyl Disulfides with 2-Cyclohexenone[a)]



Entry	R	Yield (%)[b)]
1	Ph	81
2	p-Tolyl	82
3	p-ClC$_6$H$_4$	77
4	Me	0[c)]
5	Me	10
6	Me	31[d)]
7	Me	58[e)], (79)[e,f)]
8	Me	- (6)[c,e,f)]
9	^{t}Bu	8
10	^{t}Bu	10[d)]

a) Yb (1 mmol), disulfide (1.5 mmol), Ph_2CO (5 mol%), 2-cyclohexenone (1mmol), THF (4 mL), HMPA (1 mL). b) Isolated yield based on 2-cyclohexenone. c) No Ph_2CO used. d) 6 h at the first stage. e) 40 °C, 24 h at the first stage. f) Numbers in parentheses are GLC yields.

Diaryl disulfides (entries 1-3, Table 1) smoothly react with ytterbium metal to afford the corresponding 3-sulfenylcyclohexanones in high yield. Addition of HMPA (1 mL) to THF (4 mL) gives the best result. 1,3-Dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU), *N*-methyl-2-pyrrolidone, tetramethylurea and 1,3-dimethyl-2-imidazolizinone (DMI) also work as a co-solvent instead of HMPA. The combination of acetonitrile-HMPA instead of THF-HMPA is also good enough to cause the reaction of diphenyl disulfide with 2-cyclohexenone at room temperature although longer reaction time (1 day) is needed, to give 3-phenylthiocyclohexanone in 51% isolated yield. The reaction of the aryl thiolate complexes with 2-cyclohexenone gave the best results at room temperature and the yield of 3-phenylthiocyclohexanone decreased at both higher or lower temperatures. Prolonged reaction time resulted in a complex reaction. The use of equimolar amounts of an aryl thiolate and an enone gives the best result and the use of excess enone gives inferior yields.

As is apparent from entries 4-6 and 8-10 in Table 1, dialkyl disulfides give lower yields. The addition of a catalytic amount of benzophenone enhances the reaction of disulfides with ytterbium dramatically. Especially, in the case of dialkyl disulfides, no reaction takes place without benzophenone (entry 4).

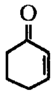
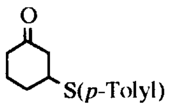
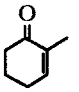
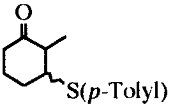
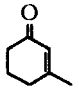
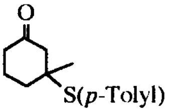
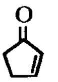
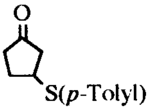
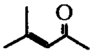
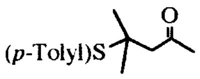
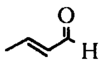
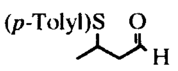
However, even with dialkyl disulfides such as dimethyl disulfide, the reaction gave the corresponding adduct in good yield at elevated temperature (40 °C) when benzophenone was added (entry 7). It was also found that the reaction proceeded with samarium metal to give the similar results.

Stoichiometric reaction of the ytterbium-benzophenone dianionic complex with diphenyl disulfide afforded benzophenone in 68% isolated yield along with diphenylmethanol (32%). However, in the present reaction, benzophenone was detected during the reaction, but diphenylmethanol, the reduction product was not detected after the reaction. These results show that benzophenone acts as a catalyst in this reaction.

The representative results for the 1,4-addition of ytterbium *p*-tolylthiolate to various enones are summarized in Table 2. Both cyclic and acyclic enones give rise to the corresponding adducts. Doubly substituted enones (entries 3 and 5, Table 2) on β-carbon are less reactive and give the Michael adducts in lower yields due to the steric hindrance. Competitive reaction of cyclohexenone (1 mmol) and 3-methyl-2-cyclohexenone (1 mmol) with ytterbium (*p*-tolyl)thiolate (1 mmol) gave 3-(p-tolylsulfenyl)-cyclohexanone in 91% yield along

Table 2. Yb Metal Mediated Reaction of Di-*p*-tolyl Disulfide with α,β-Unsaturated Ketones and Aldehydes[a)]

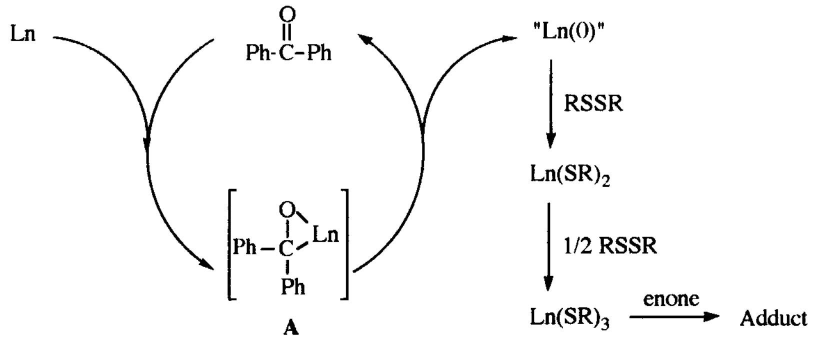
$$\mathrm{Yb} + (p\text{-Tolyl})_2\mathrm{S}_2 \xrightarrow[\text{r.t., 3 h}]{\mathrm{Ph_2CO}\text{ cat.}} \left[(p\text{-TolylS})_3\mathrm{Yb}\right] \xrightarrow[\text{r.t., 10 min}]{\text{Substrate}} \text{Michael Adducts}$$

Entry	Substrate	Product	Yield[b)]
1			82
2			60[c)]
3			11
4			65
5			35
6			76

a) Yb (1mmol), $(p\text{-Tol})_2\mathrm{S}_2$ (1.5 mmol), $\mathrm{Ph_2CO}$ (5 mol%), substrate (1 mmol), THF (4 mL), HMPA (1 mL). b) Isolated yield based on substrate. c) Ratio of *anti*/*syn* = 82/18.

with 3-methylcyclohexenone (98% recovery) . In the case of 2-methyl-2-cyclohexenone, two diastereomers were obtained in the ratio of 82:18 (entry 2, Table 2).

The possible mechanism for the benzophenone-catalyzed reaction of diaryl and -alkyl disulfides with Ln is shown in Scheme 1. Lanthanoid metal reacts with benzophenone to give the lanthanoid-benzophenone dianionic complex (**A**). The formation of the complex is a reversible reaction, and the complex affords activated Ln(0) and benzophenone.[2] The activated lanthanoid metal [Ln(0)] thus formed, would react smoothly with disulfides to give a divalent lanthanoid thiolate complex intermediate which would be further oxidized to a trivalent thiolate complex in the presence of excess disulfides. Thus formed Ln(III) thiolate complexes serve as a sulfenylating reagents. The oxidation state III of Ln in the thiolate complex was also supported by the fact that no pinacols, the reduction products, were formed when benzaldehyde, acetophenone and cyclohexanone were treated with the thiolate complex thus formed.[1]



Scheme 1. Possible Mechanism for Benzophenone-Catalyzed Reaction

The present work was supported by a Grant-in-Aid for Scientific Research on Priority Areas "New Development of Rare Earth Complexes" No 06241108 from the Ministry of Education, Science and Culture.

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(*Received in Japan* 23 *March* 1994; *accepted* 26 *May* 1994)