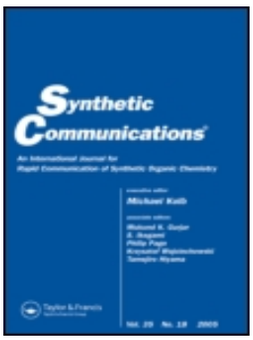

Synthetic Communications

An International Journal for Rapid Communication of Synthetic Organic Chemistry

ISSN: 0039-7911 (Print) 1532-2432 (Online) Journal homepage: http://www.tandfonline.com/loi/lsyc20

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To cite this article: Yu Jia , Mingfu Zhang , Fenggang Tao & Jingyao Zhou (2002) ALLYLATION OF ESTERS PROMOTED BY METALLIC DYSPROSIUM IN THE PRESENCE OF MERCURIC CHLORIDE, Synthetic Communications, 32:18, 2829-2835, DOI: 10.1081/SCC-120006467

To link to this article: http://dx.doi.org/10.1081/SCC-120006467

Published online: 18 Oct 2011.

MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016

SYNTHETIC COMMUNICATIONS
Vol. 32, No. 18, pp. 2829–2835, 2002

ALLYLATION OF ESTERS PROMOTED BY METALLIC DYSPROSIUM IN THE PRESENCE OF MERCURIC CHLORIDE

Yu Jia,* Mingfu Zhang, Fenggang Tao, and Jingyao Zhou

Department of Chemistry, Fudan University, Shanghai 200433, P.R. China

ABSTRACT

In the presence of mercuric chloride, the reactions of esters with allyl bromide and metallic dysprosium in anhydrous THF give diallyl alkyl carbinols in good yields. When γ-butyrolactone is used as the substrate, the corresponding product is 4-allyl-6-heptene-1, 4-diol.

Key Words: Metallic dysprosium; Allylation

With high coordinative activity and contribution of *f* orbitals to σ and π bonds, lanthanide metals exhibit unique reactivity in organic reactions and possess intriguing potential as reagents and catalysts.[1] Therefore their use for synthetic purposes is promising. In recent years, more and more attention has been paid to the utilization of lanthanides in organic synthesis. Some of the lanthanides, such as Ce,[2] Sm,[3] Yb,[4] etc.,

*Corresponding author. E-mail: yujia@fudan.edu.com

DOI: 10.1081/SCC-120006467 0039-7911 (Print); 1532-2432 (Online)

have been successfully investigated, and many interesting synthetic procedures have been developed. However, to our best knowledge no report other than our own,[5] has been found about the use of metallic dysprosium in organic reactions involving carbon–carbon bond formation.

Recently, we reported that metallic dysprosium is effective in promoting the allylation of ketones in the presence of mercuric chloride.[5] As the continuing study, we report herein the allylation of esters promoted by dysprosium metal, which affords the corresponding diallyl alkyl carbinols in good yields.

Diallyl alkyl carbinols are intermediates of great synthetic potential, since they can be used to synthesize a variety of compounds such as hydroxyl lactone,[6] polyacrylamide gel,[7] and some natural products.[8] They are normally prepared by the reactions of esters with allyl organometallic (such as Mg, Zn, etc.) reagents or allyl boranes.[9] We report here a new method to synthesize them by allylation of esters promoted by metallic dysprosium in the presence of mercuric chloride.

First, we carried out the reaction of ethyl benzoate with allyl bromide and dysprosium powder in anhydrous THF, and no products were found by TLC after 12 h (Table 1, Entry 1). When a catalytic amount of Lewis acid $BF_3{\cdot}Et_2O$ was added, which enhanced the electrophilic activity of ester through coordination, the reaction gave the corresponding 4-phenyl-1,6-heptadiene-4-ol in low yield (Entry 2). When a catalytic amount of $HgCl_2$ was added, the yield of 4-phenyl-1,6-heptadiene-4-ol increased considerably (Entry 3). Evidently the catalytic effect of $HgCl_2$ is better than that of $BF_3{\cdot}Et_2O$. As mentioned in our previous paper,[5] the mercuric chloride, which reacted with the metallic dysprosium to form the highly reactive dysprosium amalgam, functioned in this reaction as an initiator.

In the presence of catalytic amount of $HgCl_2$, allyl bromide and metallic dysprosium could react with aromatic and aliphatic esters to give the corresponding diallyl alkyl carbinols in good yields, as shown in Scheme 1.

When γ-butyrolactone was used as the substrate, the corresponding product is 4-allyl-6-heptene-1,4-diol (Scheme 2).

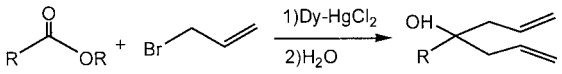
A number of aromatic and aliphatic esters were used in this reaction, and the results are summarized in Table 1.

In our previous work,[5] we found that the addition of sodium iodide could increase the yield of allylation product considerably in the reaction of ketone with allyl bromide and dysprosium powder. But when one equivalent of sodium iodide was added in this reaction (Entries 6–8), unexpectedly the yield of diallyl alkyl carbinol was not increased.

Table 1. The Allylation of Esters Promoted by Metallic Dysprosium

Entry	Esters	Substrate Molar Ratio[a] (RCOOR[1] / Allyl halide/ Dy)	Conditions	Product	Yield[e] (%)
1	$C_6H_5CO_2Et$	1.0/2.5/2.5[b]	r.t.(12 h)	–	–
2	$C_6H_5CO_2Et$	1.0/2.0/2.5[c]	r.t.(24 h)	**1a**	16[f]
3	$C_6H_5CO_2Et$	1.0/2.5/2.5	0°C(2 h), r.t.(4 h)	**1a**	73
4	$C_6H_5CH_2CO_2Me$	1.0/2.5/2.5	0°C(2 h), r.t.(4 h)	**1b**	87
5	*m*-$ClC_6H_4CO_2Et$	1.0/2.5/2.5	0°C(2 h), r.t.(4 h)	**1c**	81
6	$C_6H_5CO_2Et$	1.0/2.5/2.5[d]	0°C(2 h), r.t.(4 h)	**1a**	70
7	$C_6H_5CH_2CO_2Me$	1.0/2.5/2.5[d]	0°C(2 h), r.t.(4 h)	**1b**	85
8	*m*-$ClC_6H_4CO_2Et$	1.0/2.5/2.5[d]	0°C(2 h), r.t.(4 h)	**1c**	80
9	CH_3CO_2Et	1.0/4.0/4.0	0°C(2 h), r.t.(4 h)	**1d**	74
10	$CH_3CH_2CO_2Et$	1.0/4.0/4.0	0°C(2 h), r.t.(4 h)	**1e**	84
11	$CH_3CH_2CH_2CO_2Et$	1.0/4.0/4.0	0°C(2 h), r.t.(4 h)	**1f**	73
12	$CH_2{=}C(CH_3)CO_2Et$	1.0/4.0/4.0	0°C(2 h), r.t.(4 h)	**1g**	59
13	γ-Butyrolactone	1.0/4.0/4.0	0°C(2 h), r.t.(4 h)	**2**	62

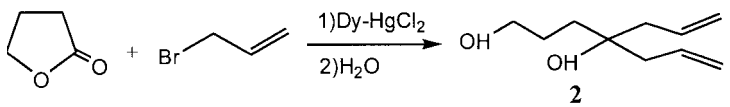
[a]All reactions of esters were carried out on a 2 mmol scale. Except in Entries 1 and 2, a catalytic amount of $HgCl_2$ was added in every other case.
[b]No $HgCl_2$ or $BF_3{\cdot}Et_2O$ was added.
[c]A catalytic amount of $BF_3{\cdot}Et_2O$ was added.
[d]One molar eq. of NaI was added.
[e]Isolated yields. The structures of all the products were confirmed by ^1H NMR and IR spectroscopy.
[f]75% of starting ethyl benzoate was recovered.



1

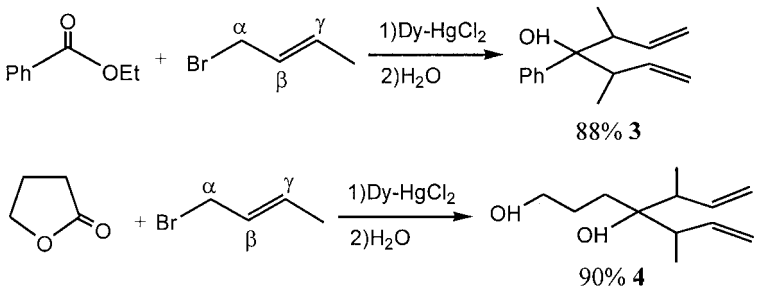
1a: R=C_6H_5; **1b**: R=$C_6H_5CH_2$; **1c**: R=*m*-ClC_6H_4; **1d**: R=CH_3
1e: R=CH_3CH_2; **1f**: R=$CH_3CH_2CH_2$; **1g**: R=$CH_2CHC(CH_3)$

Scheme 1.



2

Scheme 2.



Scheme 3.

This reaction is regioselective. An α,β-unsaturated ester (Entry 12) afforded a 1,2-addition product selectively, and no 1,4-addition product was found.

As shown in Scheme 3, the reactions of esters and crotyl bromide promoted by metallic dysprosium only gave γ-adduct products.

EXPERIMENTAL

Elemental analyses were performed by Perkin-Elmer 240C elemental analyzer. Infrared Spectra were recorded on an AVVATAR 360 FT-IR instrument. Nuclear magnetic resonance was recorded on a JNM-PMX 60 SI (60 MHz, JEOL) or a BRUKER (300 MHz).

The metallic dysprosium used in the reactions was prepared from a dysprosium ingot by carefully scraping with a rasp. THF was treated with sodium and distilled before use. Ethyl acetate and petroleum ether used in the flash column chromatography were distilled before use.

Reaction of Esters with Allyl Bromide and Metallic Dysprosium Powder

A mixture of ester (2 mmol), allyl bromide (5 mmol), dysprosium powder (5 mmol) (or 2 mmol of ester, 8 mmol of allyl bromide and 8 mmol of dysprosium powder), mercuric chloride (150 mg) and anhydrous THF (15 mL) was stirred at 0°C for 2 h and then at room temperature for 4 h. Then the reaction mixture was treated with 10 mL of saturated aqueous NH_4Cl and extracted with ether. The combined organic extracts were dried over magnesium sulfate. After the evaporation of ether, the residue was

purified by flash column chromatography, a mixture of petroleum ether and ethyl acetate being used as the elution solvent, and from which the products were isolated.

4-Phenyl-1,6-heptadiene-4-ol[3e] **(1a):** IR (neat) 3500 (br, O–H), 1630 (s, C=C), 910 (s, $CH=CH_2$) cm^{-1}. ^1H NMR($CDCl_3$, TMS) δ 2.21 (s, 1H, O$\underline{H}$), 2.48–2.74 (m, 4H, $2 \times C\underline{H}_2CH=CH_2$), 5.06–5.85 (m, 6H, $2 \times C\underline{H}=C\underline{H}_2$), 7.21–7.42 (m, 5H, $C_6\underline{H}_5$).

4-Benzyl-1,6-heptadiene-4-ol[3e] **(1b):** IR (neat) 3450 (br, O–H), 1630 (s, C=C), 905 (s, $CH=CH_2$) cm^{-1}. ^1H NMR(CCl_4, HMDS) δ 1.37 (s, 1H, O$\underline{H}$), 2.07 (d, 4H, $2 \times C\underline{H}_2CH=CH_2$), 2.57 (s, 2H, $C_6H_5C\underline{H}_2$), 4.67–6.13 (m, 6H, $2 \times C\underline{H}=C\underline{H}_2$), 6.93–7.17 (m, 5H, $C_6\underline{H}_5$).

***m*-Chlorophenyl-1,6-heptadiene-4-ol**[3e] **(1c):** IR (neat) 3530 (br, O–H), 1630 (s, C=C), 910 (s, $CH=CH_2$) cm^{-1}. ^1H NMR(CCl_4, HMDS) δ 1.97 (s, 1H, O$\underline{H}$), 2.30–2.53 (m, 4H, $2 \times C\underline{H}_2CH=CH_2$), 4.67–5.87 (m, 6H, $2 \times C\underline{H}=C\underline{H}_2$), 6.93–7.27 (m, 4H, $C_6\underline{H}_4$).

4-Methyl-1,6-heptadiene-4-ol[3e] **(1d):** IR (neat) 3350 (br, O–H), 1630 (s, C=C), 910 (s, $CH=CH_2$) cm^{-1}. ^1H NMR(CCl_4, HMDS) δ 1.03 (s, 3H, $C\underline{H}_3$), 1.43 (s, 1H, O$\underline{H}$), 2.10 (d, 4H, $2 \times C\underline{H}_2CH=CH_2$), 4.70–6.10 (m, 6H, $2 \times C\underline{H}=C\underline{H}_2$).

4-Ethyl-1,6-heptadiene-4-ol[3e] **(1e):** IR (neat) 3350 (br, O–H), 1630 (s, C=C), 910 (s, $CH=CH_2$) cm^{-1}. ^1H NMR(CCl_4, HMDS) δ 0.70–1.03 (t, 3H, $CH_2C\underline{H}_3$), 1.33 (q, 2H, $C\underline{H}_2CH_3$), 1.57 (s, 1H, O$\underline{H}$), 2.10 (d, 4H, $2 \times C\underline{H}_2CH=CH_2$), 4.70–6.07 (m, 6H, $2 \times C\underline{H}=C\underline{H}_2$).

4-*n*-Propyl-1,6-heptadiene-4-ol[10] **(1f):** IR (neat) 3350 (br, O–H), 1630 (s, C=C), 910 (s, $CH=CH_2$) cm^{-1}. ^1H NMR(CCl_4, HMDS) δ 0.73–1.40 (m, 7H, $C\underline{H}_2C\underline{H}_2C\underline{H}_3$), 1.10 (s, 1H, O$\underline{H}$), 2.10 (d, 4H, $2 \times C\underline{H}_2CH=CH_2$), 4.67–6.0 (m, 6H, $2 \times C\underline{H}=C\underline{H}_2$).

4-(1-Methylvinyl)-1,6-heptadiene-4-ol[11] **(1 g):** IR (neat) 3450 (br, O–H), 1630 (s, C=C), 900 (s, $C=CH_2$) cm^{-1}. ^1H NMR(CCl_4, HMDS) δ 1.57 (s, 1H, O$\underline{H}$), 1.63 (s, 3H, $C\underline{H}_3$), 2.20 (d, 4H, $2 \times C\underline{H}_2CH=CH_2$), 4.63–5.97 (m, 8H, $2 \times C\underline{H}=C\underline{H}_2$, $C(CH_3)=C\underline{H}_2$).

4-Allyl-6-heptene-1,4-diol[3e] **(2):** IR (neat) 3300 (br, O–H), 1630 (s, C=C), 905 (s, $C=CH_2$) cm^{-1}. ^1H NMR(CCl_4, HMDS) δ 1.37–1.70 (m, 4H, $C\underline{H}_2C\underline{H}_2$), 2.13 (d, 4H, $2 \times C\underline{H}_2CH=CH_2$), 3.47 (t, 2H, $C\underline{H}_2OH$), 3.90 (s, 2H, $2 \times O\underline{H}$), 4.70–6.10 (m, 6H, $2 \times C\underline{H}=C\underline{H}_2$).

3,5-Dimethyl-4-Phenyl-1,6-heptadiene-4-ol (3): IR (neat) 3500 (br, O–H), 1630 (s, C=C), 910 (s, $CH=CH_2$) cm^{-1}. ^1H NMR($CDCl_3$, HMDS) δ 0.70–1.00 (m, 6H, $2 \times C\underline{H}_3$), 1.50 (br, 1H, O$\underline{H}$), 2.33–2.97 (m, 2H, $2 \times C\underline{H}CH=CH_2$), 4.67–6.00 (m, 6H, $2 \times C\underline{H}=C\underline{H}_2$), 7.00–7.30 (m, 5H, $C_6\underline{H}_5$). Anal. Calcd. for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.55; H, 9.30.

6-Methyl-4-(1-butene-3-yl)-7-heptene-1,4-diol (4): IR (neat) 3400 (br, O–H), 1630 (s, C=C), 910 (s, $C=CH_2$) cm^{-1}. ^1H NMR($CDCl_3$, TMS)

δ 0.97 (d, 6H, $2 \times C\underline{H}_3$), 1.37–1.70 (m, 4H, $C\underline{H}_2C\underline{H}_2$), 2.00–2.27 (m, 2H, $2 \times C\underline{H}CH{=}CH_2$), 2.50 (br, 2H, $2 \times O\underline{H}$), 3.47 (t, 2H, $C\underline{H}_2OH$), 4.67–6.10 (m, 6H, $2 \times C\underline{H}{=}C\underline{H}_2$). Anal. Calcd. for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.88; H, 11.03.

ACKNOWLEDGMENTS

We thank the National Natural Science Foundation of China (project No. 29872008) for financial support.

REFERENCES

1. (a) *Handbook on the Physics and Chemistry of Rare Earths*; Gschneider, K.A., Eyring, L., Eds.; North Holland Publishing Co.: Amsterdam, 1982; (b) Marks, T.J.; Ernst, R.D. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F.G.A., Abel, E.W., Eds.; Pergamon Press: Oxford, 1982; Vol.3, p 173; (c) Marks, T.J. Prog. Inorg. Chem. **1978**, *24*, 51; (d) Tsutsui, M.; Ely, N.; Dubois, R. Acc. Chem. Res. **1976**, *9*, 217; (e) Yamamoto, Y.; Asao, N. Chem. Rev. **1993**, *93*, 2207 and references cited therein.
2. (a) Imamoto, T.; Hatanaka, Y.; Tawarayama, Y.; Yokoyama, M. Tetrahedron Lett. **1981**, *22*, 4987; (b) Imamoto, T.; Kusumoto, T.; Tawarayama, Y.; Sugiura, Y.; Mita, T.; Hatanaka, Y.; Yokoyama, M. J. Org. Chem. **1984**, *49*, 3904.
3. (a) Molander, G.A.; Harris, C.R. Chem. Rev. **1996**, *96*, 307 and references cited therein; (b) Namy, J.L.; Souppe, J.; Kagan, H.B. Tetrahedron Lett. **1983**, *24*, 765; (c) Souppe, J.; Danon, L.; Namy, J.L.; Kagan, H.B. J. Organometal. Chem. **1983**, *250*, 227; (d) Gao, X.; Wang, X.; Cai, R.F.; Wei, J.D.; Wu, S.H. Acta Chimica Sinica **1993**, *51*, 1139; (e) Gao, X.; Zeng, J.; Zhou, J.Y.; Wu, S.H. Acta Chimica Sinica **1993**, *51*, 1191.
4. (a) Deacon, G.B.; Tuong, T.D. J. Organometal. Chem. **1981**, *205*, C4; (b) Fukagama, T.; Fujiwara, Y.; Yokoo, K.; Taniguchi, H. Chem. Lett. **1981**, *120*, 1771.
5. Zhang, M.F.; Jia, Y.; Zhou, J.Y.; Wu, S.H. Heteroatom Chem. **1998**, *9*, 475.
6. Bardshiri, E.; Simpson, T.J.; Scott, A.I.; Shishido, K. J. Chem. Soc. Perkin Trans I **1984**, *8*, 1765.
7. Hochstrasser, D.F.; Patchornick, A.; Merril, C.R. US 159,847, 1988. (C.A. 1989, *111*:191011).

8. Kong, D.Y.; Li, H.T.; Lu, S.Q.; Lei, X.H. Acta Pharmaceutica Sinica **1990**, *25*(5), 349.
9. (a) Barluenga, J.; Florez, J.; Yus, M. Synthesis **1983**, *5*, 378; (b) Gaudemar, M. Bull. Soc. Chim. Fr. **1962**, *5*, 974; (c) Mikhailov, B.M.; Bubnov, Y.N.; Tsyban, A.V.; Grigoryan, M.S. J. Organometal Chem. **1978**, *154*, 131.
10. Wilde, J.; Eggerer, H. Eur. J. Biochem. **1994**, *221*, 463.
11. Snowden, R.L.; Linder, S.M.; Muller, B.L.; Schulte-Elte, K.H. Helv. Chim. Acta **1987**, *70*, 1858.

Received in the UK June 29, 2001