Tetrahedron 69 (2013) 8899–8903

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

$Y(OTf)_3$ catalyzed substitution dependent oxidative $C(sp^3)$–$C(sp^3)$ cleavage and regioselective dehydration of β-allyl-β-hydroxydithioesters: alternate route to α,β-unsaturated ketones and functionalized dienes

Sushobhan Chowdhury [a], Tanmoy Chanda [a], Ganesh Chandra Nandi [b], Suvajit Koley [a], B. Janaki Ramulu [a], S.K. Pandey [c], Maya Shankar Singh [a,*]

[a] Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi 221005, India
[b] Department of Chemistry, University of North Florida, 1 UNF Drive, Jacksonville, FL 32224, USA
[c] School of Chemistry and Biochemistry, Thapar University, Patiala 147004, India

ARTICLE INFO

Article history:
Received 22 June 2013
Received in revised form 18 July 2013
Accepted 30 July 2013
Available online 5 August 2013

Keywords:
Regioselective allylation
Yttrium(III)triflate
C–C activation and cleavage
Allylic isomerization
α,β-Unsaturated ketone
Selective dehydration
Functionalized diene

ABSTRACT

β-Allyl-β-hydroxydithioesters have been generated by the regioselective Grignard addition to the β-oxodithioesters. They have been successfully employed in selective $C(sp^3)$–$C(sp^3)$ bond cleavage to construct α,β-unsaturated ketone residues by the treatment of an emerging catalyst yttrium(III)triflate for the first time. On the other hand, hetaryl substituted β-allyl-β-hydroxydithioesters led to the useful diene precursors through selective dehydration under the similar conditions.

1. Introduction

The synthesis of important molecular structures has always been the primary motto of organic synthesis. The total synthesis of a molecule primarily needs the construction of the parts of its framework. The architectural strategy to achieve the frameworks includes fusion of small fragments to a large one or vice versa, i.e., the cleavage of fragments from a large skeleton until the access of the desired fragment residue becomes possible. Both ways are of equal synthetic importance. Fragmentation methodologies, especially, which are achieved by selective C–C bond activation, will certainly demand a prior significance due to the well-known inertness of the C–C bond. Tertiary alcohols in several cases have proven themselves suitable for C–C bond cleavage strategy. For this purpose, one established approach involves the β-alkyl elimination via an alkoxy-metal intermediate of various strained as well as unstrained tertiary alcohol analogues.[1,2] Further, transition-metal complexes have well been utilized for the purpose.[3] Namely, Kondo et al. have achieved β-allyl cleavage in open chain unstrained tertiary homoallyl alcohol employing Ru complexes as catalyst.[1a]

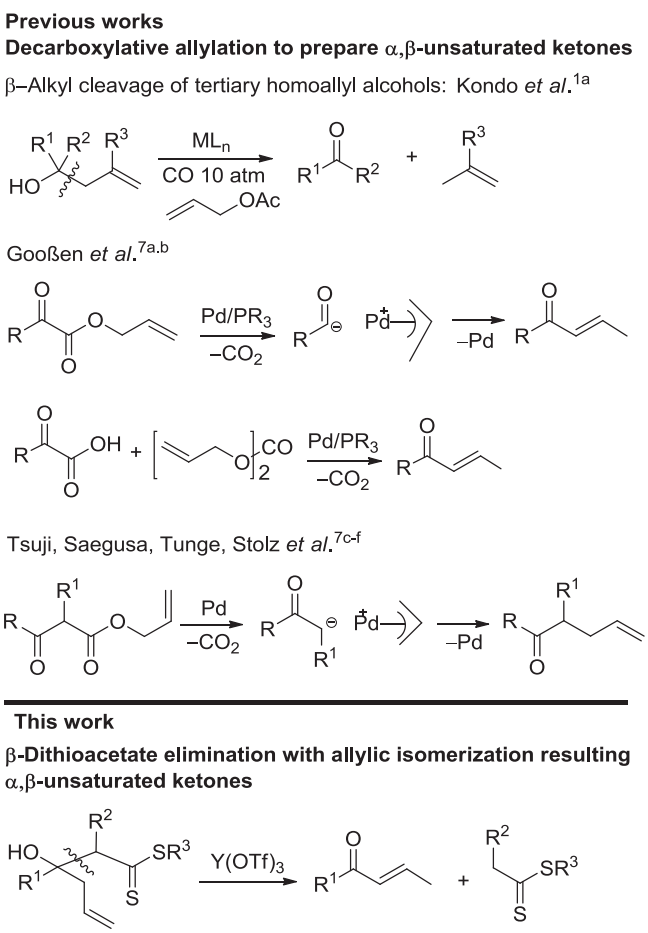
Rare-earth metal triflates are new type of Lewis acid catalysts, which are playing vital roles in various organic transformations.[4] Of them yttrium poses very specific coordination property by virtue of which its complexes like $Y(OTf)_3$ have become a well established catalyst in polymer science where it is mainly used to increase the stereoregularity of polymers.[5] In spite of its tremendous use in polymer, there exists only few examples of $Y(OTf)_3$ to catalyze traditional organic transformations.[4d–f] This time, we disclose the maiden example of selective cleavage of $C(sp^3)$–$C(sp^3)$ bond from β-allyl-β-hydroxydithioesters catalyzed by $Y(OTf)_3$. Furthermore, we have unveiled the highly selective dehydration in case of 2-thiophenyl and 2-furyl substituted β-allyl-β-hydroxydithioesters.

α,β-Unsaturated carbonyl groups are important structural units in a number of biologically active compounds, as well as ubiquitous structural motifs to various organic transformations. Some specific

* Corresponding author. Tel./fax: +91 (0)542 6702502; e-mail addresses: mssinghbhu@yahoo.co.in, mayashankarbhu@gmail.com (M.S. Singh).

0040-4020/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tet.2013.07.092

protocols for the synthesis of α,β-unsaturated ketones have been reported (Scheme 1).[6,7] In our protocol α,β-unsaturated ketones are generated after a sequence of chemical transformations within our β-allyl-β-hydroxydithioester precursor in a single stroke.

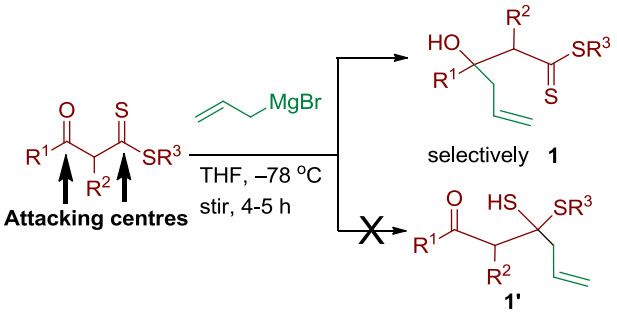


Scheme 1. Parallel comparison of previous works to this work.

2. Results and discussion

β-Oxodithioesters are not commercially sourced, and were synthesized by literature method[8a] in 70–80% yields, which are attractive synthetic scaffolds. Thanks to their dense number of reactive centers coupled with their ambident reactivity that can be exploited in sequential reactions or in cascade transformations into a range of useful products.[8] Moreover, it is always prone to show unorthodox behavior due to the presence of the dithioacetate group. Recently, our group has developed a number of synthetic strategies for the synthesis of various valuable heterocyclic scaffolds utilizing β-oxodithioesters as a key substrate.[9] Based on this initial vision, we became intrigued in scouting the use of β-oxodithioesters to prepare our target precursor. Masson and Thuillier[10] have prepared alkyl addition product from β-oxodithioesters by treating them with organometallic reagents.

Thus, following the same procedure when β-oxodithioesters are treated with allyl magnesium bromide, it led to selective addition on carbonyl carbon due to the preferable hard–hard interaction, providing *tert*-homoallylic alcohol adducts **1** exclusively. The alternative attack of allyl magnesium bromide could lead to **1′**, which was not observed even in trace during our investigations, thus, making the nucleophilic attack highly regioselective (Scheme 2).



Scheme 2. Regioselective addition of allyl magnesium bromide to β-oxodithioesters.

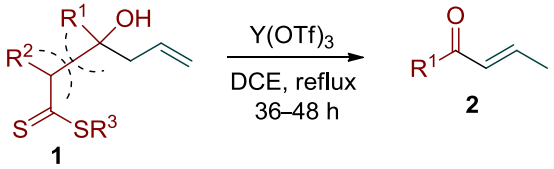
Various β-oxodithioesters derived from aryl, hetaryl, and aliphatic ketones were tolerated well under the reaction conditions to give homoallylic tertiary alcohols in moderate to good yields (Table 1). Adducts **1** have been characterized by spectral studies.

Table 1
Regioselective addition of allyl magnesium bromide to β-oxodithioesters to form **1**

Entry	R^1	R^2	R^3	Product **1**	Time (h)	Yield[a] (%)
1	C_6H_5	H	CH_3	**1a**	4.5	80
2	C_6H_5	CH_3	CH_3	**1b**	5	55
3	C_6H_5	H	$PhCH_2$	**1c**	5	58
4	2-ClC_6H_4	H	CH_3	**1d**	4	73
5	4-ClC_6H_4	H	CH_3	**1e**	5	75
6	2-BrC_6H_4	H	CH_3	**1f**	4.5	68
7	4-$CH_3C_6H_4$	H	CH_3	**1g**	5	70
8	2-Naphthyl	H	CH_3	**1h**	5	70
9	2-Thienyl	H	CH_3	**1i**	5	62
10	2-Furyl	H	CH_3	**1j**	4.5	63
11	CH_3	H	CH_3	**1k**	5	45
12	Isopropyl	H	CH_3	**1l**	5	42

[a] Isolated pure yields.

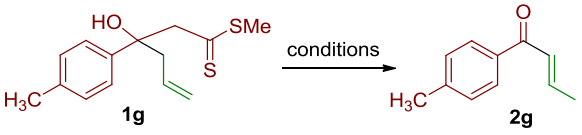
To execute our motto of selective C–C cleavage we employed various transition and rare earth metal catalysts, of them $Y(OTf)_3$ ends up with satisfactory results in successful execution of our project. When β-allyl-β-hydroxydithioesters **1** were treated with $Y(OTf)_3$ in dry dichloroethane at reflux, $Y(OTf)_3$ selectively activates and cleaves the $C(sp^3)$–$C(sp^3)$ bond eliminating dithioacetate moiety with a subsequent conversion of the terminal double bond to the non-terminal one, resulting the α,β-unsaturated ketones **2** in 50–70% yields (Scheme 3, Table 3).



Scheme 3. Synthesis of α,β-unsaturated ketones **2**.

Initially, a solution of methyl-3-hydroxy-3-(*p*-tolyl)hex-5-enedithioate **1g** (1.0 mmol) in dry 1,2-dichloroethane (DCE) was treated with 5 mol % of $Y(OTf)_3$ at reflux for 40 h, which provided the expected product **2g** in 70% yield. Being lured by the obtained results, we went for the optimization of reaction conditions including catalysts, solvents, and temperature, and the results are summarized in Table 2. Ultimately, optimal condition was identified as 5 mol % of $Y(OTf)_3$ in refluxing DCE (Table 2, entry 6). Blank reaction did not give the desired product and therefore proved the catalytic efficacy of $Y(OTf)_3$ (Table 2, entry 11).

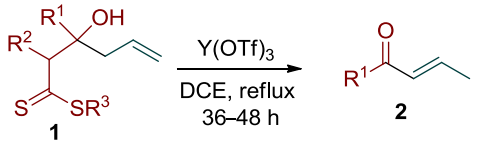
Table 2
Optimization of reaction conditions[a]



Entry	Catalyst (mol %)	Solvent[b]	Temp	Yield[c] (%)
1	$Sc(OTf)_3$ (5)	DCE	Reflux	60
2	$Zn(OTf)_2$ (5)	DCE	Reflux	20
3	$CuBr_2$ (5)	DCE	Reflux	Trace
4	$In(OTf)_3$ (5)	DCE	Reflux	55
5	$Pd(OAc)_2$ (5)	DCE	Reflux	—
6	$Y(OTf)_3$ (5)	DCE	Reflux	70
7	$Y(OTf)_3$ (2)	DCE	Reflux	61
8	$Y(OTf)_3$ (10)	DCE	Reflux	63
9	$Y(OTf)_3$ (5)	Toluene	Reflux	60
10	$Y(OTf)_3$ (5)	THF	Reflux	64
11	None	DCE	Reflux	—

[a] Reaction of adduct **1g** (1.0 mmol) with various catalysts.
[b] 10 mL of each solvents were used.
[c] Isolated pure yields.

Table 3
Substrate scope for the synthesis of **2**

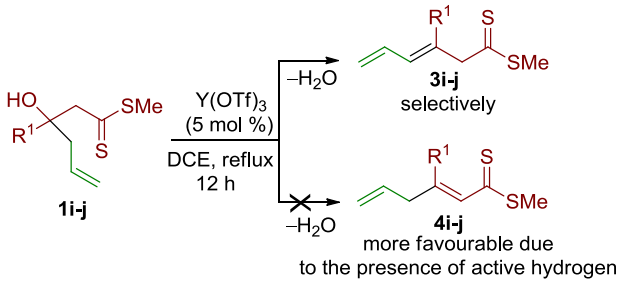


Entry	R^1	R^2	R^3	Product	Time (h)	Yield[a] (%)
1	C_6H_5	H	CH_3	**2a**	48	65
2	C_6H_5	CH_3	CH_3	**2a**	48	50
3	C_6H_5	H	CH_2Ph	**2a**	48	55
4	2-ClC_6H_4	H	CH_3	**2d**	48	60
5	4-ClC_6H_4	H	CH_3	**2e**	48	62
6	2-BrC_6H_4	H	CH_3	**2f**	48	58
7	4-$CH_3C_6H_4$	H	CH_3	**2g**	40	70
8	2-Naphthyl	H	CH_3	**2h**	48	—[b]
9	CH_3	H	CH_3	**2k**	36	—[c]
10	Isopropyl	H	CH_3	**2l**	40	—[c]

[a] Isolated pure yields.
[b] No reaction and **1h** remained unconsumed.
[c] Decomposition of starting material.

Under the optimized reaction conditions, the scope of **1** for the synthesis of α,β-unsaturated ketones **2** was investigated. Both electron-rich and electron-deficient substituents attached to the phenyl rings could be smoothly transformed into the desired product **2** (Table 3). β-Allyl-β-hydroxydithioesters with aliphatic R^1 groups provided only trace amount of products **2k**–**l** with several very close spots on the TLC plate, which could not be isolated (Table 3, entries 9 and 10). As the aliphatic dithioesters are not too heat stable and so the case may be for their Grignard adducts also. Therefore, it can be assumed that due to prolonged heating β-allyl-β-hydroxydithioesters with aliphatic R^1 groups may undergo some sort of decomposition to give complex TLC pattern.

Interestingly, when R^1 groups became 2-thiophenyl and 2-furyl, instead of α,β-unsaturated ketones **2** selectively less favorable dehydrated diene products **3** were obtained in 92–95% yields within 12 h under the similar reaction conditions (Scheme 4). This is entirely different from the dehydrated product **4** obtained by Masson and Thuillier where more favorable dehydration occurred by the participation of active α-hydrogen from β-allyl-β-hydroxydithioesters.[10] A blank reaction in the absence of $Y(OTf)_3$ was also carried out, which did not give the trace of dehydrated product even after 24 h of reflux, suggesting catalytic efficacy, excellent site



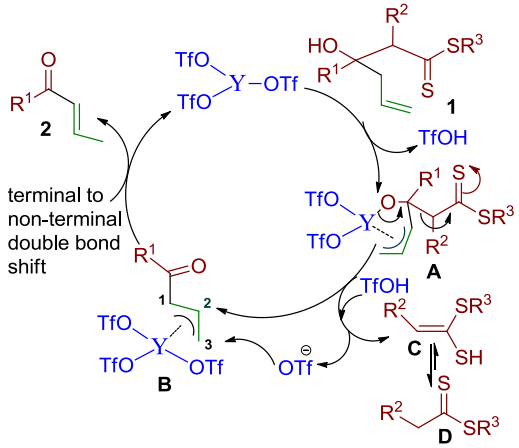
3i: R^1=2-thienyl (92%); **3j:** R^1=2-furyl (95%)

Scheme 4. Selective dehydration of adducts **1i**–**j**.

selectivity and regioselectivity of $Y(OTf)_3$. The products **3** were characterized as dienes by their spectral studies (NMR and mass). Further transformations by using the diene residue as precursor is under the way and will be coming shortly.

To gain some insights into the mechanism of the reaction process, we have accumulated some experimental results like (i) methyl-3-hydroxy-2-methyl-3-phenylhex-5-enedithioate (R^2=CH_3, Table 3, entry 2) and 3-hydroxy-3-phenyl-hex-5-enedithioic acid benzyl ester (R^3=$PhCH_2$, Table 3, entry 3) also led to the formation of the desired products (50–55%), which support the eliminating part to be dithioacetate. (ii) Methyl-3-hydroxy-3-(naphthalen-2-yl)hex-5-enedithioate did not furnish the desired compound (Table 3, entry 8), which accounts for the formation of a congested intermediate that could not accommodate the naphthyl group into the intermediate and the precursor remained unconsumed even after 48 h. It also shows the specific coordination property of $Y(OTf)_3$ as Lewis acid to drive the reaction in such a complicated catalytic pathway. (iii) Insertion of allyl group and elimination of dithioacetate signifies that it also is not merely a retro aldol reaction. (iv) Precursors with 2-thiophenyl and 2-furyl substitution did not led to the product proving the channelizing of the reaction through different intermediate. The available lone pair of the heteroatom, which can coordinate with the yttrium drives the reaction through different intermediate.

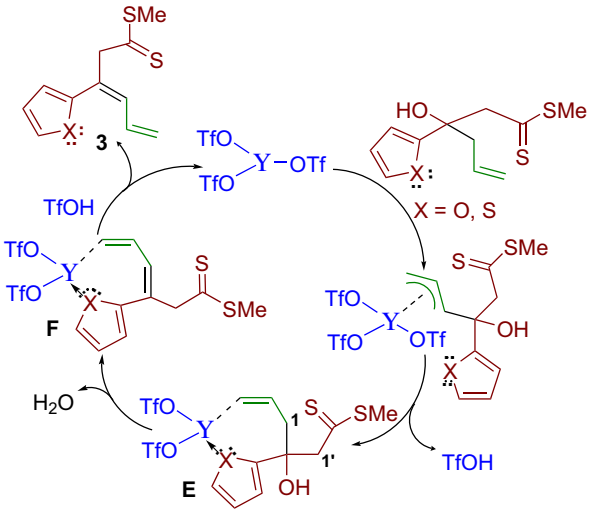
Therefore, after a careful study of the open literature[11] and taking into consideration the entire outcome, a plausible mechanism for the formation of **2** is outlined in Scheme 5. A cyclic mechanism for the catalytic activity of $Y(OTf)_3$ has been postulated in accordance with Ru, Pd, and Rh catalysis. We believe that the first step is the addition of $Y(OTf)_3$ to adduct **1** to form an alkoxy-metal complex **A**, which is stabilized due to delocalization of the allylic double bond over three centers forming a metal-3-center-2-electron bond [$Y(\eta^3$–CH_2–CH–CH_2)].[11b] Complex **A** undergoes



Scheme 5. Plausible mechanism for the formation of α,β-unsaturated ketones **2**.

selective C–C cleavage releasing dithioacetate moiety **D** to give complex **B**. Finally, complex **B** undergoes shift of the terminal double bond to thermodynamically more stable non-terminal double bond yielding the desired product **2** and releases the parent catalyst $Y(OTf)_3$ completing the catalytic cycle.

In case of β-allyl-β-hydroxydithioesters with hetaryl R^1 groups due to possible chelation of yttrium between available lone pair on the heteroatom of the heteroaryl groups of **1i–j** and terminal carbon of its allyl group in complex **E** may play an important role in preventing the formation of alkoxy-metal complex intermediate responsible for dithioacetate elimination. However, complex **E**, which is highly susceptible for dehydration undergoes selective C-1 hydrogen elimination rather than C-1′ hydrogen to give complex **F**. Finally, complex **F** takes up one molecule of TfOH to come back to the parent catalyst with the formation of dehydrated product diene **3** completing the catalytic cycle. A mechanistic model is presented to understand in detail the results obtained (Scheme 6).



Scheme 6. Plausible mechanism for the selective dehydration of adducts **1i–j**.

3. Conclusions

In summary, we have established a successful synthetic operation on β-allyl-β-hydroxydithioesters generated from β-oxodithioesters. The described protocol is highly substitution dependent to give α,β-unsaturated ketones through the selective $C(sp^3)$–$C(sp^3)$ bond cleavage with allylic isomerization for the aromatic substitutions and dienes via a selective dehydration in case of hetaryl substitution, in the presence of $Y(OTf)_3$. The detailed mechanistic aspects of the discussed methodology and its tolerance to substituted allyl groups or their higher analogues are currently the subject matter of our further investigation.

4. Experimental section

4.1. General method

The commercially available allyl magnesium bromide (Grignard reagent) and yttrium triflate were used as received without any further purification. β-Oxodithioesters were prepared following the literature procedure. Thin-layer chromatography (TLC) was performed using silica gel 60 F_{254} precoated plates. Column chromatography was performed with 100–200 mesh silica gel. Infrared (IR) spectra are measured in KBr, and wavelengths (ν) are reported in cm^{-1}. ^1H and ^{13}C NMR spectra were recorded on NMR spectrometers operating at 300 and 75.5 MHz, respectively. Chemical shifts (δ) are given in parts per million (ppm) using the residue solvent peaks as reference relative to TMS. Coupling constant (J) values are given in Hertz. Mass spectra were recorded using electrospray ionization (ESI) mass spectrometry. The melting points are uncorrected.

4.2. General procedure for the synthesis of 3-hydroxy-hex-5-enedithioic acid esters (Grignard adducts) (1a–l)

To a solution of β-oxodithioester (1.0 mmol) in 6 mL of dry THF, 10 mL of allyl magnesium bromide (1 M ethereal solution) was added dropwise at −78 °C. The mixture was stirred for the stipulated period of time. After completion of the reaction (monitored by TLC), the reaction mixture was quenched by the addition of ammonium chloride solution followed by extraction with ethyl acetate (2×10 mL). The organic layer was dried over anhydrous Na_2SO_4 and was then evaporated in vacuo. The crude residue was purified by column chromatography over silica gel using increasing amounts of ethyl acetate in *n*-hexane to afford pure Grignard adducts β-allyl-β-hydroxydithioesters **1**.

*4.2.1. 3-Hydroxy-3-phenyl-hex-5-enedithioic acid methyl ester (**1a**).* Yellow oil. ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 7.38–7.35 (m, 2H, Ar), 7.30–7.11 (m, 3H, Ar), 5.79–5.65 (m, 1H, olefinic CH), 5.08–5.00 (m, 3H, OH and olefinic CH_2), 3.72 (d, J=15 Hz, 1H, CH_2), 3.33 (d, J=14.7 Hz, 1H, CH_2), 2.68–2.48 (m, 2H, CH_2), 2.38 (s, 3H, SMe); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 235.6 (thiocarbonyl), 143.9, 132.8, 132.6, 127.3, 126.1, 126.0, 125.0, 124.7, 118.5, 117.9, 76.0, 60.1, 47.5, 19.6; IR (KBr, ν_{max}, cm^{-1}): 3400, 3073, 2913, 1446, 1196, 1062, 917, 841, 701, 591.

*4.2.2. 3-(2-Chlorophenyl)-3-hydroxy-hex-5-enedithioic acid methyl ester (**1d**).* Yellow oil. ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 7.66 (d, J=7.8 Hz, 1H, Ar), 7.24 (t, J=6.4 Hz, 1H, Ar), 7.17–7.06 (m, 2H, Ar), 5.77–5.63 (m, 1H, olefinic CH), 5.07–4.94 (m, 3H, OH and olefinic CH_2), 4.44 (d, J=14.7 Hz, 1H, CH_2), 3.35 (d, J=14.4 Hz, 1H, CH_2), 3.07–3.00 (m, 1H, CH_2), 2.80–2.73 (m, 1H, CH_2), 2.37 (s, 3H, SMe); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 235.9 (thiocarbonyl), 140.2, 132.7, 130.4, 129.8, 129.6, 128.0, 126.1, 118.4, 117.6, 76.6, 57.3, 43.2, 19.7; IR (KBr, ν_{max}, cm^{-1}): 3378, 3073, 2914, 1430, 1187, 1035, 917, 842, 758, 595; HRMS: m/z=286.0253 (M^+). Found: 287.0185 (M^++1).

*4.2.3. 3-Hydroxy-3-p-tolylhex-5-enedithioic acid methyl ester (**1g**).* Yellow oil. ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 7.25 (s, 2H, Ar), 7.09 (d, J=4.8 Hz, 2H, Ar), 5.80–5.66 (m, 1H, olefinic CH), 5.09–5.03 (m, 2H, olefinic CH_2), 4.77 (s, 1H, OH), 3.73 (d, J=15.3 Hz, 1H, CH_2), 3.34 (d, J=15 Hz, 1H, CH_2), 2.66–2.48 (m, 5H, CH_2 and SMe), 2.30 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 235.0 (thiocarbonyl), 141.8, 136.3, 133.8, 133.7, 128.8, 125.7, 118.6, 76.7, 60.8, 48.2, 21.2, 20.2; IR (KBr, ν_{max}, cm^{-1}): 3423, 2920, 2851, 1412, 1261, 1020, 814, 463; MS: m/z (%)=249 (25), 201 (55), 168 (90), 119 (100).

4.3. General procedure for the synthesis of but-2-en-1-ones (2a–l)

A solution of β-allyl-β-hydroxydithioester **1** (1.0 mmol) in dichloroethane (10 mL) was degassed for 15 min by continuous purging of ultrapure argon. To this solution 5 mol % of $Y(OTf)_3$ was added and the mixture was refluxed for the stipulated period of time. After completion of the reaction (monitored by TLC), the reaction mixture was diluted with EtOAc (10 mL) followed by addition of water (20 mL). The organic layer was dried over anhydrous Na_2SO_4 and then was evaporated in vacuo. The crude residue was purified by column chromatography over silica gel using increasing amounts of ethyl acetate in *n*-hexane as eluent to afford pure but-2-en-1-ones **2**.

*4.3.1. 1-Phenyl-but-2-en-1-one (**2a**).* Beige oil. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 7.91 (d, J=7.8 Hz, 2H, Ar), 7.55–7.43 (m, 3H, Ar), 7.11–7.03 (m, 1H, olefinic CH), 6.89 (d, J=15.3 Hz, 1H, olefinic CH), 2.00 (d, J=6.6 Hz, 3H, Me); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 190.7 (carbonyl), 145.0, 137.8, 133.3, 132.5, 128.4, 127.4, 125.2, 119.1, 18.5; IR (KBr, ν_{max}, cm^{-1}): 2925, 1682, 1448, 1218, 755, 691.

*4.3.2. 1-(2-Chlorophenyl)-but-2-en-1-one (**2d**).* Dark oil. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 7.41–7.26 (m, 4H, Ar), 6.77–6.65 (m, 1H, olefinic CH), 6.47 (dd, J=14.4, 1.2 Hz, 1H, olefinic CH), 1.96 (dd, J=5.4, 1.2 Hz, 3H, Me); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 194.2 (carbonyl), 147.9, 138.9, 131.9, 130.9, 130.0, 128.9, 126.5, 18.5; HRMS: m/z=180.0342 (M^+). Found: 181.0423 (M^++1).

*4.3.3. 1-(4-Chlorophenyl)-but-2-en-1-one (**2e**).* Dark oil. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 7.86 (d, J=8.1 Hz, 2H, Ar), 7.42 (d, J=8.4 Hz, 2H, Ar), 7.12–7.04 (m, 1H, olefinic CH), 6.86 (dd, J=14.1, 1.2 Hz, 1H, olefinic CH), 2.00 (dd, J=5.7, 1.2 Hz, 3H, Me); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 189.3 (carbonyl), 145.6, 138.9, 136.1, 129.8, 128.7, 126.9, 18.6.

*4.3.4. 1-(2-Bromophenyl)-but-2-en-1-one (**2f**).* Beige oil. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 7.62–7.58 (m, 1H, Ar), 7.40–7.26 (m, 3H, Ar), 6.74–6.64 (m, 1H, olefinic CH), 6.46 (d, J=15.3 Hz, 1H, olefinic CH), 1.97 (d, J=6.6 Hz, 3H, Me); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 195.1 (carbonyl), 148.4, 140.9, 133.2, 131.8, 131.0, 128.7, 127.0, 119.2, 18.6; IR (KBr, ν_{max}, cm^{-1}): 2932, 2858, 1660, 1293, 1024, 764; MS: m/z (%)=202 (80), 185 (90), 183 (100), 138 (30), 102 (67).

*4.3.5. 1-p-Tolyl-but-2-en-1-one (**2g**).* Beige oil. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 7.83 (d, J=8.1 Hz, 2H, Ar), 7.24 (d, J=8.0 Hz, 2H, Ar), 7.10–7.00 (m, 1H, olefinic CH), 6.90 (d, J=15.9 Hz, 1H, olefinic CH), 2.41 (s, 3H, benzylic CH_3), 1.98 (s, 3H, Me); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 190.2 (carbonyl), 144.4, 143.3, 135.2, 129.1, 128.6, 127.4, 21.6, 18.5; IR (KBr, ν_{max}, cm^{-1}): 2924, 2854, 1722, 1458, 1097, 815; MS: m/z=161 (M^++1).

4.4. General procedure for the synthesis of dienes (3i–j)

A solution of β-allyl-β-hydroxydithioesters **1i** and **1j** (1.0 mmol) in dichloroethane (10 mL) was degassed for 15 min by continuous purging of ultrapure argon. To this solution 5 mol % of $Y(OTf)_3$ was added and the mixture was refluxed for the stipulated period of time. After completion of the reaction (monitored by TLC), the reaction mixture was diluted with EtOAc (10 mL) followed by addition of water (20 mL). The organic layer was dried over anhydrous Na_2SO_4 and then evaporated in vacuo. The crude residue was purified by column chromatography over silica gel using *n*-hexane as eluent to afford dienes **3i–j**.

*4.4.1. 3-Thiophen-2-yl-hexa-3,5-dienedithioic acid methyl ester (**3i**).* Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 7.14 (dd, J=9.9, 4.2 Hz, 2H, Ar), 6.95 (d, J=5.2 Hz, 1H, Ar), 6.79–6.72 (m, 2H, olefinic CH_2), 5.45 (d, J=14.4 Hz, 1H, olefinic CH), 5.30 (d, J=7.8 Hz, 1H, olefinic CH), 4.32 (s, 2H, CH_2), 2.58 (s, 3H, SMe); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 234.7 (thiocarbonyl), 145.1, 132.3, 129.8, 127.5, 126.7, 125.6, 124.5, 124.4, 120.1, 52.1, 20.1 (SMe); MS: m/z=239 (M^+–1).

*4.4.2. 3-Furan-2-yl-hexa-3,5-dienedithioic acid methyl ester (**3j**).* Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 7.37 (s, 1H, Ar), 6.92–6.75 (m, 2H, Ar), 6.40 (dd, J=11.7, 2.4 Hz, 2H, olefinic CH_2), 5.47 (d, J=16.8 Hz, 1H, olefinic CH), 5.31 (d, J=9.3 Hz, 1H, olefinic CH), 4.21 (s, 2H, CH_2), 2.58 (s, 3H, SMe); ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 235.1 (thiocarbonyl), 142.3, 142.2, 133.9, 132.2, 127.7, 125.3, 120.2, 111.5, 107.6, 50.1, 20.1 (SMe); IR (KBr, ν_{max}, cm^{-1}): 2922, 1655, 1440, 1230, 1018; MS: m/z=223 (M^+–1).

Acknowledgements

We gratefully acknowledge the generous financial supports from the Council of Scientific and Industrial Research (CSIR), the Department of Science and Technology (DST), and University Grants Commission (UGC), New Delhi.

Supplementary data

Supplementary data (IR, ^{1}H and ^{13}C NMR, and HRMS spectra) are available. Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2013.07.092.

References and notes

1. (a) Kondo, T.; Kodoi, K.; Nishinaga, E.; Okada, T.; Morisaki, Y.; Watanabe, Y.; Mitsudo, T. *J. Am. Chem. Soc.* **1998**, *120*, 5587 and references therein; (b) Weaver, J. D.; Recio, A.; Grenning, A. J.; Tunge, J. A. *Chem. Rev.* **2011**, *111*, 1846.
2. (a) Matsumura, S.; Maeda, Y.; Nishimura, T.; Uemura, S. *J. Am. Chem. Soc.* **2003**, *125*, 8862; (b) Matsuda, T.; Shigeno, M.; Murakami, M. *J. Am. Chem. Soc.* **2007**, *129*, 12086; (c) Seiser, T.; Roth, O. A.; Cramer, N. *Angew. Chem., Int. Ed.* **2009**, *48*, 6320; (d) Seiser, T.; Cramer, N. *J. Am. Chem. Soc.* **2010**, *132*, 5340; (e) Bunel, E.; Burger, B. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 976.
3. (a) Hegedus, L. S. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, UK, 1995; Vol. 12; (b) Bishop, K. C. *Chem. Rev.* **1976**, *76*, 461; (c) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245; (d) Jennings, P. W.; Johnson, L. L. *Chem. Rev.* **1994**, *94*, 2241.
4. (a) Zhang, C. X.; Dong, J. C.; Cheng, T. M.; Li, T. T. *Tetrahedron Lett.* **2001**, *42*, 461; (b) Kobayashi, S. *Lanthanides: Chemistry and Use in Organic Synthesis*; Springer: Berlin, Germany, 1999; p 63; (c) Sun, L.; Gao, C.; Zhou, W.; Wei, Y. *Indian J. Chem., Sect. B* **2008**, *47*, 481; (d) De, S. K. *Tetrahedron Lett.* **2004**, *45*, 2339; (e) Wang, Y.; Onozawa, S. Y.; Kunioka, M. *Green Chem.* **2003**, *5*, 571; (f) Jha, M.; Enaohwo, O.; Guy, S. *Tetrahedron Lett.* **2011**, *52*, 684.
5. (a) Ray, B.; Isobe, Y.; Matsumoto, K.; Habaue, S.; Okamoto, Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2004**, *37*, 1702; (b) Biswas, C. S.; Patel, V. K.; Vishwakarma, N. K.; Mishra, A. K.; Saha, S.; Ray, B. *Langmuir* **2010**, *26*, 6775; (c) Biswas, C. S.; Vishwakarma, N.; Patel, V. K.; Mishra, A. K.; Saha, S.; Ray, B. *Langmuir* **2012**, *28*, 7014 and references therein.
6. (a) Clayden, J.; Greeves, N.; Warren, S.; Wothers, P. *Organic Chemistry*; Oxford University: Oxford, UK, 2001; (b) Stefanoni, M.; Luparia, M.; Porta, A.; Zanoni, G.; Vidari, G. *Chem.—Eur. J.* **2009**, *15*, 3940; (c) Egi, M.; Yamaguchi, Y.; Fujiwara, N.; Akai, S. *Org. Lett.* **2008**, *10*, 1867 and references therein.
7. (a) Rodriguez, N.; Manjolinho, F.; Grunberg, M. F.; Gooßen, L. J. *Chem.—Eur. J.* **2011**, *17*, 13688 and references therein; (b) Manjolinho, F.; Grunberg, M. F.; Rodriguez, N.; Gooben, L. J. *Eur. J. Org. Chem.* **2012**, 4680; (c) Tsuji, J.; Yamada, T.; Minami, I.; Yuhara, M.; Nisar, M.; Shimizu, I. *J. Org. Chem.* **1987**, *52*, 2988 and references therein; (d) Tsuda, T.; Chujo, Y.; Nishi, S.-I.; Tawara, K.; Saegusa, T. *J. Am. Chem. Soc.* **1980**, *102*, 6381; (e) Waetzig, S. R.; Tunge, J. A. *J. Am. Chem. Soc.* **2007**, *129*, 14860; (f) Levine, S. R.; Krout, M. R.; Stoltz, B. M. *Org. Lett.* **2009**, *11*, 289 and references therein.
8. (a) Samuel, R.; Asokan, C. V.; Suma, S.; Chandran, P.; Retnamma, S.; Anabha, E. R. *Tetrahedron Lett.* **2007**, *48*, 8376; (b) Peruncheralathan, S.; Khan, T. A.; Ila, H.; Junjappa, H. *J. Org. Chem.* **2005**, *70*, 10030; (c) Roy, A.; Nandi, S.; Ila, H.; Junjappa, H. *Org. Lett.* **2001**, *3*, 229.
9. Recent papers: (a) Nandi, G. C.; Samai, S.; Singh, M. S. *J. Org. Chem.* **2010**, *75*, 7785; (b) Nandi, G. C.; Samai, S.; Singh, M. S. *J. Org. Chem.* **2011**, *76*, 8009; (c) Chowdhury, S.; Nandi, G. C.; Samai, S.; Singh, M. S. *Org. Lett.* **2011**, *13*, 3762; (d) Nandi, G. C.; Singh, M. S.; Ila, H.; Junjappa, H. *Eur. J. Org. Chem.* **2012**, 967; (e) Verma, R. K.; Verma, G. K.; Raghuvanshi, K.; Singh, M. S. *Tetrahedron* **2011**, *67*, 584; (f) Verma, R. K.; Verma, G. K.; Shukla, G.; Nagaraju, A.; Singh, M. S. *ACS Comb. Sci.* **2012**, *14*, 224; (g) Verma, G. K.; Verma, R. K.; Singh, M. S. *RSC Adv.* **2013**, *3*, 245; (h) Singh, M. S.; Nagaraju, A.; Verma, G. K.; Shukla, G.; Verma, R. K.; Srivastava, A.; Raghuvanshi, K. *Green Chem.* **2013**, *15*, 954; (i) Janaki Ramulu, B.; Chanda, T.; Chowdhury, S.; Nandi, G. C.; Singh, M. S. *RSC Adv.* **2013**, *3*, 5345.
10. Masson, S.; Thuillier, A. *Tetrahedron Lett.* **1982**, *23*, 4087.
11. (a) Stanlake, L. J. E.; Schafer, L. L. *Organometallics* **2009**, *28*, 3990; (b) Casey, C. P.; Tunge, J. A.; Fagan, M. A. *J. Organomet. Chem.* **2002**, *663*, 91 and references therein; (c) Duchateau, R.; van Wee, C. T.; Teuben, J. H. *Organometallics* **1996**, *15*, 2291.