FULL PAPER

A Metal-Free Synthesis of 2-Alkyl(or Aryl) Thiomethyl-2-cyclohexenones from Cyclic *Morita–Baylis–Hillman* Bromides

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Under mild conditions, an efficient and rapid *S*-allylation of thiols with cyclic *Morita–Baylis–Hillman* (*MBH*) bromides without the need of a transition-metal catalyst or an expensive additive is described herein. Treatment of the *MBH* bromides with various thiols or ethane-1,2-dithiol in the presence of Et_3N regioselectively affords the corresponding 2-alkyl(or aryl) thiomethyl-2-cyclohexenones or the perhydro benzo[1,4]dithiepinone, respectively, in moderate to good yields (40 – 73%). The reaction is rapid and carried out in THF at room temperature.

Keywords: Chemoselectivity, Nucleophilic substitution, Sulfur, Sulfur heterocycles, Allylic compounds, *S*-Allylation.

Introduction

Over the last decades, nucleophilic substitution reactions of allyl compounds have been developed very well. They are currently considered as a very important process and a powerful tool for the construction of new C–C and C–X (X = O, N, S, *etc.*) bonds that were widely used for the synthesis of a variety of interesting derivatives [1 – 4].

In organic synthetic reactions, the scope and applications of organosulfur chemistry have increased enormously since *S*-containing groups serve as important auxiliaries function in synthetic sequences [5]. Among them, allyl sulfides have acquired great importance as a class of useful scaffold in organic synthesis [6 – 8]. Indeed, they are used currently as valuable synthons for various organic transformations [9 – 11], including imidation and subsequent sigmatropic rearrangements [12] and thio-*Claisen* rearrangements [13].

They also serve as important synthetic intermediates in agricultural and pharmaceutical chemistry [14]. Over the last decades, the *Morita–Baylis–Hillman* (*MBH*) adducts [15 – 18] have been used for the synthesis of these compounds.

In the course of our study on the development of the chemistry of *MBH*, we have studied the behavior of cyclic *MBH* adducts with a large variety of nucleophiles [19]. We have previously reported the *S*-allylation of alkyl alcohols and thiols with 2-(hydroxymethyl)cyclohex-2-en-1-one in the presence of TsOH [20], as well as the behavior of cyclic *MBH* acetates with thiols in the presence of NaH in THF [21].

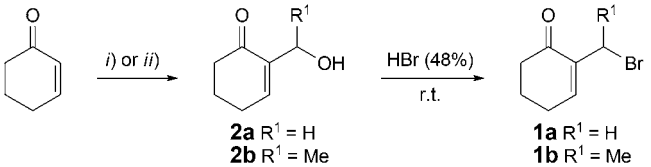
Moreover, we have reported a first DMAP-mediated Pd-free *Tsuji–Trost*-type reaction of cyclic and acyclic *MBH* alcohols as well as cyclic *MBH* acetates with active methylene compounds [22]. In 2016, we have described an efficient protocol for the synthesis of new series of γ-keto allyl phosphonates in good to excellent yields from the *MBH* acetates as starting materials in the presence of DMAP or imidazole, as promoters of the allylic nucleophilic substitution [23].

To the best of our knowledge, the *S*-allylation of thiols with cyclic *MBH* bromides **1a** and **1b** has not been extensively studied under catalyst-free conditions. Hence, we report in this paper an efficient method for the synthesis of various allyl sulfides **3a** – **3l** in mild conditions from the *MBH* bromides **1a** and **1b**.

Results and Discussion

The starting materials **1a** and **1b** were prepared in a two-step sequence according to previous reports. Indeed, allylic alcohols **2a** and **2b** were first prepared through the *MBH* reaction involving the cyclohex-2-enone [24][25],

Scheme 1. Synthesis of allyl bromides **1a** and **1b** from allyl alcohols **2a** and **2b**.



i) **2a**: HCHO, DMAP, THF/H_2O (60%). *ii*) **2b**: MeCHO, imidazole THF/H_2O (40%).

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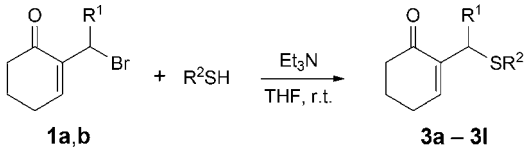
Scheme 2. Conversion of allyl bromides **1a** and **1b** into allyl sulfides **3a** – **3l**.



followed by their direct conversion into the corresponding allylic bromides **1a** and **1b** using aqueous 48% HBr (*Scheme 1*) [26].

It is noted that these allyl bromides **1a** and **1b** are of limited stability, particularly when neat. Therefore, they were prepared from the *MBH* alcohols **2a** and **2b** and then directly used without further purification. It is noteworthy that the chemistry of these derivatives has not been previously well developed. Indeed, only the ally bromide **1a** was first synthesized by *Handy et al.* [26] and its further dimerization was performed using a combination of Mn metal and $CuCl_2$. Moreover, the corresponding Sn and Zn reagents have also been prepared by the same research group and *in situ* involved in a *Barbier* reaction using various aldehydes [27]. In our part, we make our contribution by studying the behavior of compounds **1a** and **1b** toward a wide range of thiols as well as ethane-1,2-dithiol as a 1,4-bidentate nucleophile.

In our first attempt, a mixture of *MBH* bromide **1a** (4 mmol) and thiophenol (6 mmol) was carried out in THF without any additive. After stirring 1 h at room temperature, we observed a total conversion of the allylic bromide **1a** into the corresponding sulfide **3a** with a modest yield (45%), presumably because the presence of an acidic medium (HBr) may inhibit the progress of the reaction. Therefore, in order to improve this modest yield, we thought that a more efficient route would be implemented using Et_3N as a base to trap the excess of HBr formed in the reaction medium. Thus, we investigated the behavior of the bromide **1a** toward thiophenol in the presence of Et_3N (1.5 equiv.) as additive in THF as

Table. *S*-Allylation of thiols with the allyl bromides **1a** and **1b**

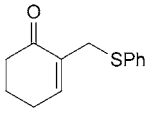
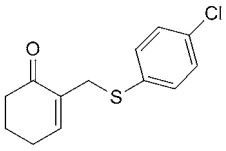
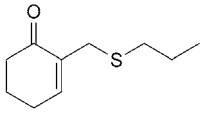
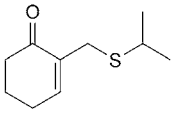
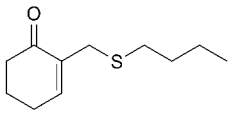
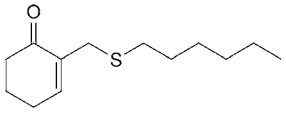
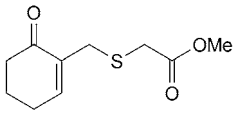
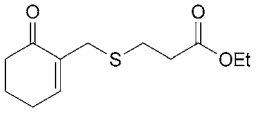
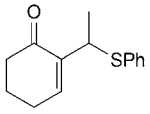
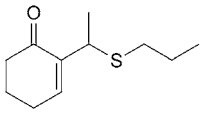
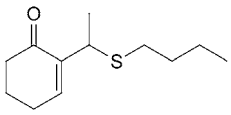
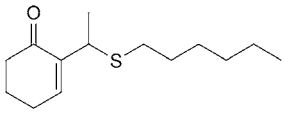
Entry	R^1	Thiol	Reaction time [h]	Product **3**		Yield [%]
1	H (**1a**)	PhSH	0.5	**3a** [21]		72
2	H (**1a**)	4-Cl–C_6H_4SH	0.5	**3b**		68
3	H (**1a**)	PrSH	0.5	**3c**		61
4	H (**1a**)	^{i}PrSH	0.5	**3d**		63
5	H (**1a**)	BuSH	0.5	**3e** [21]		70
6	H (**1a**)	$Me(CH_2)_5SH$	0.5	**3f** [21]		73

Table. (cont.)

Entry	R^1	Thiol	Reaction time [h]	Product **3**		Yield [%]
7	H (**1a**)	$MeOOCCH_2SH$	0.5	**3g** [21]		70
8	H (**1a**)	$EtOOC(CH_2)_2SH$	0.5	**3h**		65
9	Me (**1b**)	PhSH	4	**3i** [21]		52
10	Me (**1b**)	PrSH	4	**3j** [21]		54
11	Me (**1b**)	BuSH	4	**3k** [21]		40
12	Me (**1b**)	$Me(CH_2)_5SH$	4	**3l** [21]		55

solvent. Under these conditions and after 30 min, we have successfully observed a metal-free total conversion of the bromide **1a** into the corresponding *S*-allylation product **3a** in 72% yield (*Scheme 2*).

In order to demonstrate the scope and the limitation of this rapid and efficient synthetic methodology, we investigated the behavior of a variety of thiols under the above conditions (Et_3N in THF at room temperature) toward the *MBH* bromides **1a** and **1b**. Our results, listed in the *Table*, showed the total conversion of the *MBH* bromides **1a** and **1b** into the corresponding allyl sulfides **3a** – **l** in modest to good yields ranging from 40% to 73% (*Scheme 2*, *Table*, *Entries 1 – 12*).

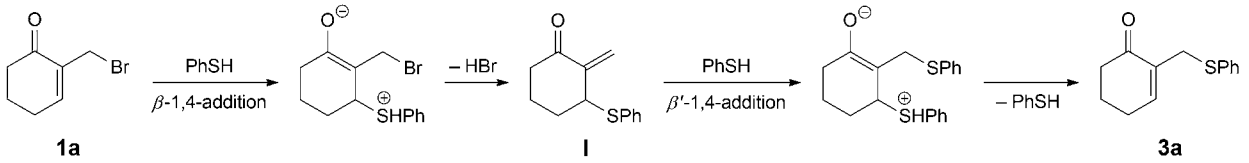
Under the above optimized reaction conditions, we have observed that the six-membered allylic bromide **1a** rapidly reacted with primary thiols (*Scheme 2*, *Table*, *Entries 1 – 8*) affording, within 30 min, in 61 – 73% yields, the corresponding allyl sulfides **3a** – **3h**. This allylation reaction also worked with the six-membered bromide **1b** but the latter is less reactive than its homologous compound **1a**, presumably as it is slightly hindered at the α-allyl bromide C-atom bearing a Me group. The corresponding sulfides **3i** – **3l** were obtained within 4 h, in 40 – 55% moderate yields (*Scheme 2*, *Table*, *Entries 9 – 12*).

We believe that the reaction mechanism starts with a conjugate addition of a thiol onto the *Michael* acceptor **1a**, followed by the elimination of HBr, affording the intermediate **I**. Subsequent second β′-conjugate addition of a thiol onto the intermediate **I**, then elimination of a molecule of thiol, provides the allyl sulfide **3a**, which is therefore the result of two consecutive S_N2' reactions through a one-pot addition–elimination sequence[1]) (*Scheme 3*).

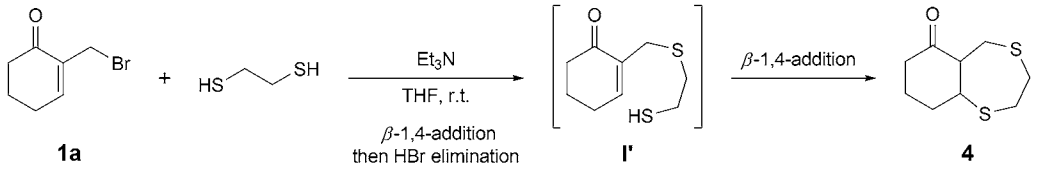
However, when 1 equiv. of ethane-1,2-dithiol, as a 1,4-bidentate nucleophile, was left to react with the allyl bromide **1a**, under the previous conditions, we have obtained, *via* a one-pot two-step sequence, the perhydrobenzo[1,4]-dithiepinone **4** in 50% overall yield (*Scheme 4*).

[1]) Regarding the reaction mechanism, one of the referee suggested that the tertiary amine Et_3N could have two roles: it could also act as a catalyst for the reaction in a similar manner than in the *MBH* reactions, giving initially the 1,4-addition product, and neutralizing HBr.

Scheme 3. Proposed mechanism for the conversion of **1a** into **3a**.



Scheme 4. Proposed mechanism for the conversion of **1a** into 1,4-dithiepine derivative **4**.



We believe that, in this study, the reaction mechanism starts with a β-conjugate addition of the thiol onto the *Michael* acceptor **1a**, followed by the elimination of HBr, yielding the intermediate **I′**. The latter subsequently reacts in an intramolecular β'-conjugate addition onto the cyclic enone subunit, to finally afford the bicyclic 1,4-dithiepine derivative **4** (*Scheme 4*).

Conclusions

In summary, we have developed a rapid and efficient protocol for the synthesis of allyl sulfides **3a** – **3l** from the reaction of a variety of thiols onto the corresponding cyclic *MBH* bromides **1a** and **1b** in moderate to good yields. Mild and metal-free catalyzed reaction conditions are the attractive features of this synthetic methodology. We believe these functionalized allyl sulfides would be of much importance in organic chemistry.

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Supplementary Material

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/hlca.201600136.

Experimental Part

General

Anal. thin-layer chromatography (TLC): precoated SiO_2 *60* F_{254} plates; visualization by UV light (254 nm). Flash chromatography (FC): SiO_2 *60* and a gradient solvent system (petroleum ether (PE)/Et_2O as eluent). M.p.: *Electrothermal 9100* apparatus; uncorrected. IR Spectra: *IFS 66v/S* spectrometer; $\tilde{\nu}$ in cm^{-1}. ^{1}H- and ^{13}C-NMR spectra: *Bruker AC-300* spectrometer, 300 and 75 MHz, resp., in $CDCl_3$; δ in ppm rel. to Me_4Si as internal standard, J in Hz. HR-ESI-MS: *Autospec Ultima* micromass mass spectrometer at 70 eV; in m/z.

Typical Procedure for the Preparation of Sulfur Compounds (**3a** – **l**)

To a soln. of allyl bromides (4 mmol) **1a** or **1b** in THF were added 6 mmol of Et_3N and a soln. of thiol (6 mmol) in THF (2 ml). The mixture was stirred at r.t., then quenched with H_2O, and extracted with CH_2Cl_2 (3 × 10 ml). The combined org. layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The resulting residue was purified by FC on silica gel (PE/Et_2O), affording compounds **3a** – **3l** or **4**.

2-[(Phenylsulfanyl)methyl]cyclohex-2-en-1-one (**3a**) [21]. Yield: 72%. Yellow oil. IR ($CHCl_3$): 1680, 1590, 1480, 1440. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.31 – 7.17 (*m*, 5 H); 6.76 (*t*, *J* = 4.0, 1 H); 3.70 – 3.69 (*d*, *J* = 3, 2 H); 2.46 – 2.41 (*m*, 2 H); 2.32 – 2.26 (*m*, 2 H); 1.99 – 1.92 (*m*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 198.0; 147.0; 136.1; 135.2; 130.2; 128.8; 126.4; 38.3; 32.6; 26.0; 22.8. EI-MS: 53 (46), 79 (55.4), 81 (98), 110 (54.5), 185 (36.6), 218 ($C_{13}H_{14}OS$, M^+, 100).

2-{[(4-Chlorophenyl)sulfanyl]methyl}cyclohex-2-en-1-one (**3b**). Yield: 68%. Yellow oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.25 – 7.22 (*m*, 4 H); 6.77 (*t*, *J* = 3.5, 1 H); 3.68 (*d*, *J* = 3, 2 H); 2.48 – 2.43 (*m*, 2 H); 2.35 – 2.30 (*m*, 2 H); 2.02 – 1.93 (*m*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 197.7; 147.4; 134.9; 134.6; 132.4; 131.5; 128.9; 38.2; 32.8; 26.0; 22.8. EI-MS: 53 (73), 81 (100), 108 (44), 144 (14), 252 ($C_{13}H_{13}ClOS$, M^+, 94).

2-[(Propylsulfanyl)methyl]cyclohex-2-en-1-one (**3c**). Yield: 61%. Yellow oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.92 (*t*, *J* = 3.0, 1 H); 3.30 (*d*, *J* = 3, 2 H); 2.48 – 2.41 (*m*, 6 H); 2.05 – 1.97 (*m*, 2 H); 1.63 – 1.56 (*m*, 2 H); 1.00 – 0.95 (*m*,

3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 198.2; 146.5; 136.4; 38.2; 34.2; 29.9; 26.0; 23.0; 22.7; 13.4. EI-MS: 82 (90), 110 (100), 141 (89), 184 ($C_{10}H_{16}OS$, M^+, 55).

2-{[(1-Methylethyl)sulfanyl]methyl}cyclohex-2-en-1-one (**3d**). Yield: 63%. Yellow oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.95 (*t*, *J* = 4.5, 1 H); 3.33 (*d*, *J* = 1.1, 2 H); 2.92 – 2.81 (*m*, 1 H); 2.48 – 2.40 (*m*, 4 H); 2.05 – 199 (*m*, 2 H); 1.27 – 1.24 (*m*, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 197.8; 146.8; 136.3; 38.3; 35.0; 28.6; 26.0; 23.3; 22.9. EI-MS: 53 (46), 79 (69), 82 (75), 110 (100), 141 (24), 184 ($C_{10}H_{16}OS$, M^+, 52).

2-[(Butylsulfanyl)methyl]cyclohex-2-en-1-one (**3e**) [21]. Yield: 70%. Yellow oil. IR ($CHCl_3$): 1662. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.91 (*t*, *J* = 4.0, 1 H); 3.30 – 3.29 (*d*, *J* = 3, 2 H); 2.49 – 2.38 (*m*, 6 H); 2.05 – 1.97 (*m*, 2 H); 1.61 – 1.51 (*m*, 2 H); 1.45 – 1.33 (*m*, 2 H); 0.91 (*t*, *J* = 4.0, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 198.1; 146.5; 136.5; 38.4; 32.0; 31.5; 30.1; 26.0; 23.0; 22.0; 13.6. EI-MS: 53 (63), 82 (97), 110 (100), 141 (60), 198 ($C_{11}H_{18}OS$, M^+, 33).

2-[(Hexylsulfanyl)methyl]cyclohex-2-en-1-one (**3f**) [21]. Yield: 73%. Yellow oil. IR: 1673. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.91 (*t*, *J* = 4.2, 1 H); 3.29 (*d*, *J* = 3, 2 H); 2.48 – 2.41 (*m*, 6 H); 2.07 – 1.97 (*m*, 2 H); 1.61 – 1.52 (*m*, 2 H); 1.39 – 1.25 (*m*, 6 H); 0.88 (*t*, *J* = 7.5, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 198.1; 146.6; 136.5; 38.4; 32.3; 31.5; 30.3; 29.7; 28.6; 26.1; 23.0; 22.8; 14.0. HR-ESI-MS: 249.1284 ([*M* + Na]$^+$, $C_{13}H_{22}NaOS^+$; calc. 249.1289).

Methyl {[(6-Oxocyclohex-1-en-1-yl)methyl]sulfanyl}acetate (**3g**). Yield: 70%. Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.96 (*t*, *J* = 3, 1 H); 3.74 (*s*, 3 H); 3.40 (*d*, *J* = 0.9, 2 H); 3.19 (*s*, 2 H); 2.49 – 2.42 (*m*, 4 H); 2.07 – 1.98 (*m*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 198.2; 170.9; 147.9; 135.3; 52.2; 38.2; 32.9; 30.4; 25.9; 22.9. EI-MS: 53 (20), 79 (40), 109 (13), 141 (100), 155 (21), 214 ($C_{10}H_{14}O_3S$, M^+, 16).

Ethyl 3-{[(6-Oxocyclohex-1-en-1-yl)methyl]sulfanyl}propanoate (**3h**). Yield: 65%. Yellow oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.94 (*t*, *J* = 3, 1 H); 4.12 (*q*, *J* = 9, 2 H); 3.32 (*d*, *J* = 3, 2 H); 2.76 – 2.71 (*m*, 2 H); 2.62 – 2.60 (*m*, 2 H); 2.46 – 2.44 (*m*, 4 H); 2.06 – 1.99 (*m*, 2 H); 1.27 (*t*, *J* = 6, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 198.2; 171.9; 147.1; 136.1; 60.6; 38.0; 34.3; 30.2; 26.8; 25.8; 22.7; 13.8. EI-MS: 82 (54), 110 (63), 141 (100), 197 (20), 242 ($C_{12}H_{18}O_3S$, M^+, 19).

2-[1-(Phenylsulfanyl)ethyl]cyclohex-2-en-1-one (**3i**) [21]. Yield: 52%. Yellow oil. IR: 1670. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.34 – 7.19 (*m*, 5 H); 6.85 (*t*, *J* = 3, 1 H); 4.46 (*q*, *J* = 7.1, 1 H); 2.42 (*t*, *J* = 7.5, 2 H); 2.35 – 2.29 (*m*, 2 H); 1.97 – 1.9 (*m*, 2 H); 1.34 (*d*, *J* = 7.1, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 197.3; 145.7; 140.4; 135.0; 135.5; 128.6; 126.9; 39.0; 38.4; 25.9; 22.6; 20.8. HR-ESI-MS: 255.0814 ([*M* + Na]$^+$, $C_{14}H_{16}NaOS^+$; calc. 255.0819).

2-[1-(Propylsulfanyl)ethyl]cyclohex-2-en-1-one (**3j**) [21]. Yield: 54%. Yellow oil. IR: 1670. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.07 (*t*, *J* = 4.2, 1 H); 4.02 (*q*, *J* = 7, 1 H); 2.49 – 2.39 (*m*, 6 H); 2.04 – 1.95 (*m*, 2 H); 1.61 – 1.51 (*m*, 2 H); 1.35 (*d*, *J* = 7, 3 H); 0.96 (*t*, *J* = 7.5, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 197.7; 145.1; 141.8; 38.6; 35.8; 33.6; 26.1; 22.9; 22.8; 21.4; 13.5. HR-ESI-MS: 221.0971 ([*M* + Na]$^+$, $C_{11}H_{18}NaOS^+$; calc. 221.0976).

2-[1-(Butylsulfanyl)ethyl]cyclohex-2-en-1-one (**3k**) [21]. Yield: 40%. Yellow oil. IR: 1672.02. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.03 (*t*, *J* = 4.2, 1 H); 4.04 (*q*, *J* = 7.0, 1 H); 2.49 – 2.42 (*m*, 6 H); 2.04 – 1.97 (*m*, 2 H); 1.56 – 1.51 (*m*, 2 H); 1.43 – 1.39 (*m*, 2 H); 1.34 (*d*, *J* = 7.0, 3 H); 0.89 (*t*, *J* = 7.5, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 197.8; 145.2; 141.8; 38.9; 35.8; 31.6; 31.2; 26.1; 22.8; 22.1; 21.7; 13.7. HR-ESI-MS: 235.1127 ([*M* + Na]$^+$, $C_{12}H_{20}NaOS^+$; calc. 235.1133).

2-[1-(Hexylsulfanyl)ethyl]cyclohex-2-en-1-one (**3l**) [21]. Yield: 55%. Yellow oil. IR: 1674. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.03 (*t*, *J* = 4.2, 1 H); 4.05 (*q*, *J* = 7.1, 1 H); 2.48 – 2.41 (*m*, 6 H); 2.04 – 1.95 (*m*, 2 H); 1.59 – 1.49 (*m*, 2 H); 1.37 – 1.24 (*m*, 6 H); 1.33 (*d*, *J* = 7.0, 3 H); 0.88 (*t*, *J* = 7.5, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 197.5; 144.9; 142.0; 38.6; 36.0; 31.7; 31.5; 29.6; 28.7; 26.1; 22.9; 22.5; 21.5; 14.0. HR-ESI-MS: 263.1440 ([*M* + Na]$^+$, $C_{14}H_{24}NaOS^+$; calc. 263.1445).

Typical Procedure for the Preparation of Sulfur Compound (**4**)

To a soln. of allyl bromide (4 mmol) **1a** in THF were added 4 mmol of Et_3N and a soln. of ethane-1,2-dithiol (4 mmol) in THF (2 ml). Following the previous procedure for compounds **3a** – **3l**, the compound **4** was obtained pure.

Octahydro-6*H*-1,4-benzodithiepin-6-one (**4**) [21]. Yield: 50%. White solid. M.p. 150 – 152 °C. IR ($CHCl_3$): 1710, 1410. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.32 – 2.66 (*m*, 8 H); 2.53 – 1.64 (*m*, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 209.1; 207.9; 60.4; 55.4; 50.2; 50.0; 42.0; 40.6; 39.4; 37.5; 37.0; 33.4; 33.3; 33.0; 25.4; 23.0. EI-MS: 97 (22.3), 110 (54.1), 174 (16.9), 202 ($C_9H_{14}OS_2$, M^+, 100).

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