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Room-Temperature Metallation of 2-Substituted 1,3-Dithiane Derivatives and Subsequent Coupling with 2,3-Disubstituted Oxiranes

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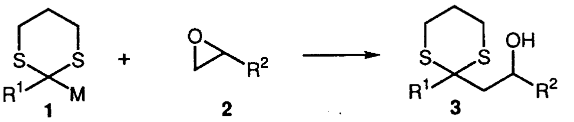
2-Substituted 1,3-dithiane derivatives, (*S*)-1-(*t*-butyldiphenylsiloxy)-2-(1,3-dithian-2-yl)propane (**9**), (*S*)-1-(*t*-butyldimethylsiloxy)-2-(1,3-dithian-2-yl)propane, 1-(*t*-butyldiphenylsiloxy)-2-(1,3-dithian-2-yl)-2-methylpropane, and 1,2-bis-(*t*-butyldiphenylsiloxy)-3-(1,3-dithian-2-yl)propane, were subjected to lithiation in THF with *n*-BuLi at room temperature (r.t.); the resulting anions reacted with 2,3-disubstituted oxirane, *trans*-2-methyl-3-(triphenylmethoxymethyl)oxirane (**22**), at r.t., giving the coupling products in satisfactory yield. On the other hand, the lithium salt formed in ether from (*S*)-2-(1,3-dithian-2-yl)-1-(4-methoxybenzyloxy)propane with *n*-BuLi at r.t. reacted with **22** at r.t. in the presence of hexamethylphosphoric triamide to afford the coupling product in moderate yield. In addition, a mixed organometallic reagent, *n*-BuLi / Bu_2Mg, was found to be an effective metallation reagent for **9** and the resulting anion reacted with **22** to afford the coupling product in good yield.

Corey and Seebach introduced in 1965[1] 2-lithio-1,3-dithiane derivatives as excellent acyl anion equivalents for carbon–carbon bond formation. Since then, many organic chemists have been using them in synthetic studies on natural products.[2] One of the representative examples is the coupling of 2-lithio-1,3-dithiane derivatives with oxiranes. In general, 2-lithio-1,3-dithiane itself and 2-substituted 2-lithio-1,3-dithiane derivatives **1** (M = Li, Eq. 1) react with monosubstituted oxiranes **2** to afford the coupling products **3** in satisfactory yield. Even in such a case, however, problems still remain: When anions are short-lived and/or oxiranes are relatively poor electrophiles, the coupling reaction is capricious.[3] Moreover, it has been considered that 2,3-disubstituted oxiranes **4** can not react efficiently with 2-substituted 2-lithio-1,3-dithiane derivatives **1** (M = Li, Eq. 2).[4] Therefore, such coupling reactions have scarcely attracted attention[5] and, to the best of our knowledge, have not been used in natural product syntheses. We now report in this full article[6] on the effective coupling reactions of 2-substituted 2-metallo-1,3-dithiane derivatives **1** with 2,3-disubstituted oxiranes **4** at room temperature (r.t.), providing the coupling products **5** in satisfactory yield. Compared with **3**, compound **5** includes an additional substituent, R^3, in its structure. Therefore, in the case of **5** having a partial structure (R^1 = Me-branched unit, R^3 = Me : Eq. 2), such as **A** (Eq. 3), it would be possible to obtain a sequential array of alternate Me and OH groups, such as **C**, via de-dithioacetalization (**A** to **B**) and reduction (**B** to **C**). This array is often found in the framework of natural products which are biogenetically synthesized from propionate units. In a following article[7] of this issue, a demonstration of this strategy will be described.



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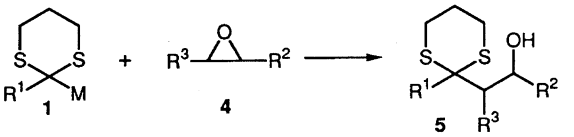

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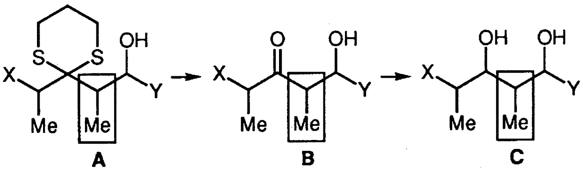

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Results and Discussion

Preparations of Substrates. The preparations of 2-substituted 1,3-dithiane derivatives and 2,3-disubstituted oxirane utilized in this study are summarized in Fig. 1. Chiral, Me-branched compounds (**9**, **10**, **11**, and **12**) were prepared as follows. Tritylation of methyl (*S*)-3-hydroxy-2-methylpropionate (**6**) followed by diisobutylaluminium hydride (DIBAH) reduction afforded **7**,[8] which was directly subjected to dithioacetalization with 1,3-propanedithiol in the presence of $BF_3 \cdot OEt_2$ to give, accompanied by spontaneous detritylation, **8**[9] in 88% overall yield from **6**. The optical purity of **8** was determined to be nearly 100% by ^{1}H NMR analysis of the (*R*)- and (*S*)-α-methoxy-α-(trifluoromethyl)phenylacetate (MTPA ester)[10] of **8**. Silylation of **8** with *t*-butylchlorodiphenylsilane (TBDPSCl) afforded **9**[11] in 98% yield. Silylation of **8** with *t*-butylchlorodimethylsilane (TBSCl) afforded **10** in 95% yield. A treatment of **8** with benzyl bromide

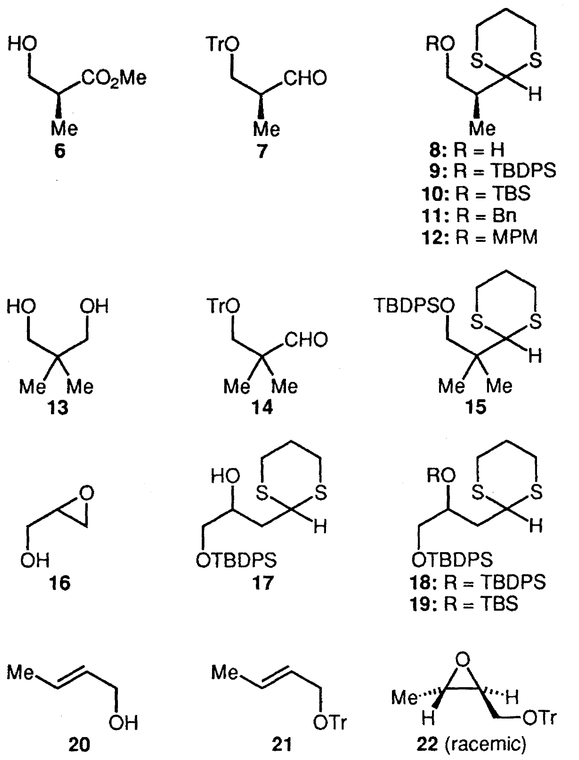
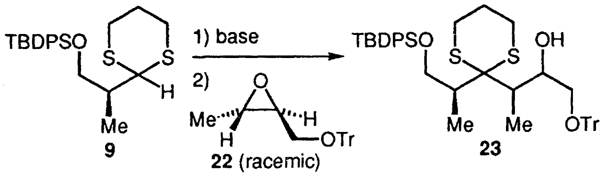


Fig. 1.

(BnBr) or 4-methoxybenzyl chloride (MPMCl) in the presence of NaH in DMF gave **11**[12] or **12** in 97 and 96% yields, respectively. 1-(*t*-Butyldiphenylsiloxy)-2-(1,3-dithian-2-yl)-2-methylpropane (**15**) was prepared from 2,2-dimethyl-1,3-propanediol (**13**) through aldehyde **14** by the following four steps: (1) trityl chloride (TrCl), NaH, THF, 0 °C, 3 h; (2) Swern oxidation; (3) 1,3-propanedithiol, $BF_3\cdot OEt_2$, CH_2Cl_2, 0 °C, 20 min, then MeOH, r.t., 0.5 h; (4) TBDPSCl, imidazole, DMF, r.t., 3 h, 48% overall yield. The racemic compounds **18** and **19**[13] were prepared from 2,3-epoxy-1-propanol (**16**) through **17**[13] via silylation (TBDPSCl, imidazole, CH_2Cl_2, r.t., 1 h, 88%), 1,3-dithiane addition (1,3-dithiane, *n*-BuLi, THF, −30 °C, 1 h) and silylation (to **18**: TBDPSCl, 4-dimethylaminopyridine (DMAP), DMF, 90 °C, 32 h, 89% for two steps. to **19**: TBSCl, DMAP, DMF, 90 °C, 32 h, 89% for two steps). The racemic *trans*-oxirane **22** was prepared from (*E*)-2-buten-1-ol (**20**) through **21** via tritylation (TrCl, Et_3N, CH_2Cl_2, 35 °C, 2 h, 61%) and epoxidation (3-chloroperbenzoic acid (*m*-CPBA), CH_2Cl_2, r.t., 3 h, 74%).

Preliminary Trial. We first selected **9** and **22** as dithiane and 2,3-disubstituted oxirane components, respectively (Eq. 4). One molar amount of *t*-BuLi in pentane was added at −78 °C to a solution of **9** in 10% hexamethylphosphoric triamide (HMPA) / THF (0.2 M for **9**)[14] (1 M = 1 mol dm^{-3}) and to this was added one molar amount of **22** in THF; the mixture was stirred at −78 °C for 1 d. However, only the starting materials were recovered. *n*-BuLi / *t*-BuONa complex, which was used for metallation of 2-substituted 1,3-dithiane derivatives by Lipshutz,[15] was of no effect on this coupling at −78 °C. These dissapointing results promoted us to investigate the metallation conditions using **9** as a substrate.



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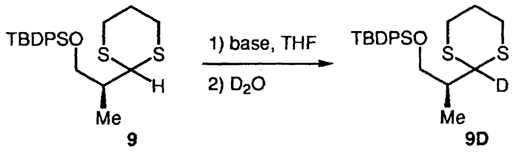
Metallation Conditions. Representative data obtained in THF by D_2O quenching are shown in Table 1. Metallation with *t*-BuLi / HMPA and *n*-BuLi / *t*-BuONa effectively occurred at −78 °C (Entries 1 and 2). Metallation with *n*-BuLi / HMPA moderately occurred at −78 °C (Entry 3). HMPA was needed for anion generation at −78 °C by using *n*-BuLi or *t*-BuLi as a base (Entries 1, 3, 4, and 5). These results suggest that the inertness of the reaction of Eq. 4 is due to the poor electrophilicity of **22**. We considered that it was necessary to raise the reaction temperature to overcome this problem. Using *n*-BuLi as a base, the temperature dependence in anion generation was examined (Entries 5, 6, 7, and 8). It was found that the anion of **9** was effectively generated at r.t. (20—25 °C) (Entry 8): 86% deuterium incorporation. Furthermore, we found that the anion was effectively generated within 5 min; D_2O quenching furnished 90% deuterium incorporation (Entry 9). The use of HMPA in metallation at r.t. was less satisfactory (Entries 9, 10, 11, and 12). The use of 1,2-dimethoxyethane (DME) or ether instead of THF caused a decrease in %D to 77 or 61, respectively, under the same conditions of Entry 9. This satisfactory result promoted us to reexamine the reaction of Eq. 4.

Table 1. Generation of the Anion of **9** and D_2O Quenching[a)]

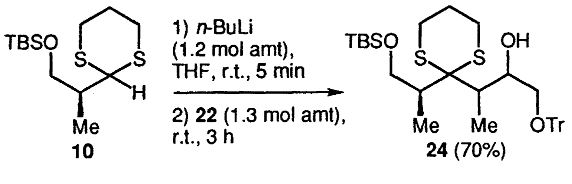


Entry	Base	Additive	Temp/°C	Time/min	%D[b)]
1	*t*-BuLi	HMPA	−78	5	82[c)]
2	*n*-BuLi / *t*-BuONa	None	−78	60	72
3	*n*-BuLi	HMPA	−78	5	46
4	*t*-BuLi	None	−78	60	0
5	*n*-BuLi	None	−78	60	0
6	*n*-BuLi	None	−40	60	32
7	*n*-BuLi	None	0	60	79
8	*n*-BuLi	None	r.t.	60	86[c)]
9	*n*-BuLi	None	r.t.	5	90[c)]
10	*n*-BuLi	HMPA	r.t.	5	14[d)]
11	*t*-BuLi	None	r.t.	5	54
12	*t*-BuLi	HMPA	r.t.	5	16[d)]

a) Base (1 molar amount for **9**) was added to a solution (0.2 M for **9**) of **9** in THF or 10% HMPA/THF at the specified temperature. After the specified time, D_2O was added and the mixture was worked up as usual. b) Determined by ^1H NMR analysis of the crude products. c) When 1.2 molar amounts of base was used, %D was>95. d) Contaminated with decomposed products.

Coupling Reaction of 9 and 22. To the anion generated in THF by the treatment of **9** with *n*-BuLi (one molar amount for **9**) at r.t. for 5 min was added oxirane **22** (one molar amount for **9**) in THF at r.t. After 3 h at r.t., the coupling product **23** was obtained in 61% isolated yield along with the recovered **9** (36%) and the recovered **22** (32%).[16] No regioisomeric coupling product other than **23** was obtained. Since oxirane **22** is racemic, the coupling product **23** consists of a 1 : 1 mixture of diastereomers.[17] When 1.2 molar amounts of *n*-BuLi and 1.3 molar amounts of **22** were used, the yield of **23** increased to 73%. When the coupling reaction was carried out at −40 or 0 °C after the anion of **9** had been generated at r.t., the yield of the coupling product **23** decreased to 10 or 46%, respectively, even though the reaction time was elongated to 1 d.

Scope and Limitations. Encouraged by this success, we next examined the coupling reactions of other 2-substituted 1,3-dithiane derivatives. Prior to examining the coupling reaction, we conducted deuterium incorporation experiments using **10**, **15**, and **18** with *n*-BuLi (one molar amount for each dithiane derivative) in THF at r.t. for 5 min. The %D was 86 for **10**, 71 for **15**, and 61 for **18**. The chiral compound **10** was subjected to coupling with **22** to afford **24** in 70% yield as a 1 : 1 mixture of diastereomers[17] (Eq. 5). Two molar amounts of dithiane components, **15** and **18**, were required to obtain coupling products **25** and **26** in satisfactory yields[17] (Eqs. 6 and 7). The coupling product **26** consisted of a 1.9 : 1 mixture of diastereomers; this result indicates that the racemic **18** distinguished the two enantiomers of **22** to some extents.



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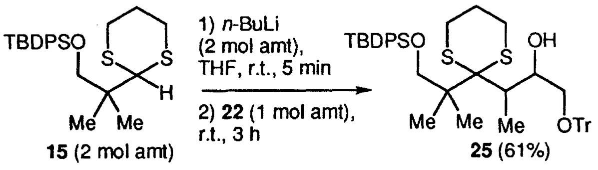

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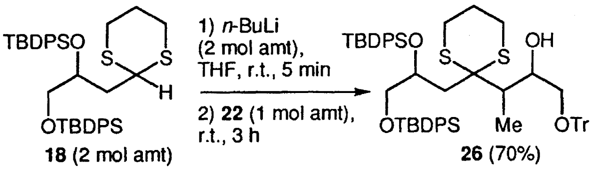

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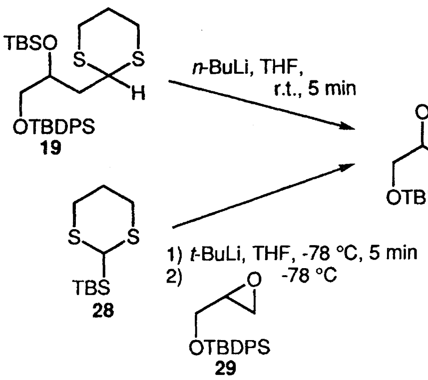
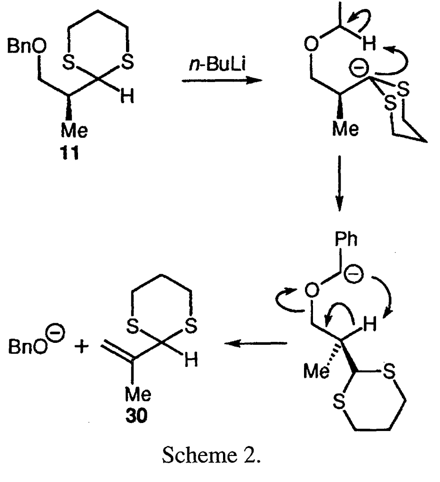
In the case of **19**, the requisite anion underwent a retro-Brook rearrangement[18] under our lithiation conditions (r.t.) and compound **27** was produced (Scheme 1). The structure of **27** was confirmed by a comparison of its ^{1}H NMR spectrum and TLC mobility with those of the product obtained from the coupling reaction of 2-(*t*-butyldimethylsilyl)-1,3-dithiane (**28**)[18] with oxirane **29**.[13] This undesirable retro-Brook rearrangement did not occur in other cases.



Scheme 1.

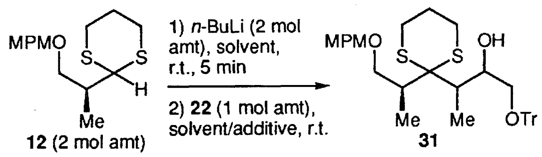
In contrast to the silyl protecting group series, some difficulties arose in coupling of the dithiane derivatives having the Bn and MPM protecting groups. The benzyl ether **11** was treated in THF with one molar amount of *n*-BuLi at r.t. for 5 min; the ^{1}H NMR spectrum and TLC of the crude products showed that one third of **11** decomposed into 2-isopropenyldithiane (**30**) (Scheme 2). This can probably be explained by the mechanism shown in Scheme 2. The dithianide anion generated from **11** and *n*-BuLi abstracts the benzylic hydrogen; the resulting phenylmethanide anion abstracts the methine hydrogen and benzyl alkoxide departs to leave 2-isopropenyldithiane (**30**).[19]

To overcome this problem, we considered that the MPM ether **12** would resist being abstracted the benzylic hydrogen because of the electron-donating nature of the *p*-methoxy substituent. This turned out to be the case. MPM ether **12** was treated in THF with one molar amount of *n*-BuLi at r.t. for 5 min; D_2O quenching furnished 73% deuterium incorporation. Only a trace amount of **30** was observed. In contrast to the TBDPS ether **9** (vide supra), the lithium salt from **12** was more effectively generated in DME (%D = 79) and in ether (%D = 86). On the basis of these results, the coupling reaction of **12** with **22** was investigated. Representative data are given in Table 2. When the anion generated from **12** (two molar amounts for **22**) in THF was treated with oxirane **22**, the desired coupling product **31**[17] was obtained in only 27% yield (Entry 1). The presence of HMPA increased the



Scheme 2.

Table 2. Coupling of the MPM Ether **12** with **22**[a)]

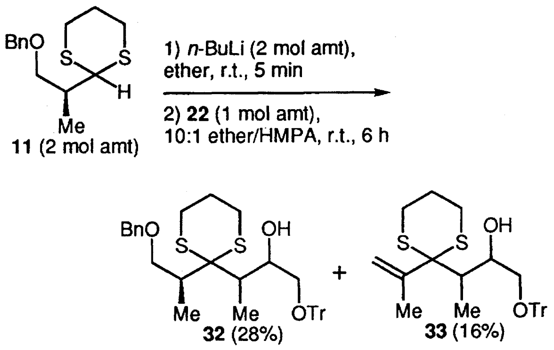


Entry	Solvent	Solvent/Additive	Time/h	Yield/%
1	THF	THF/None	24	27
2	THF	THF/HMPA	6	39
3	Ether	Ether/None	16	Trace
4	Ether	Ether/TMEDA	6	Trace
5	Ether	Ether/HMPA	6	53

a) *n*-BuLi (2 molar amounts for **22**) was added to a solution (0.2 M for **12**) of **12** (2 molar amounts for **22**) in the specified solvent at r.t. After 5 min, **22** in the specified solvent with or without an additive was added and the mixture was stirred at r.t. for the specified time.

yield of **31** to 39% (Entry 2). The coupling was next carried out in ether; but a trace amount of **31** was obtained (Entry 3). Finally, we were delighted to find that coupling in ether occurred in the presence of HMPA, giving **31** in 53% yield (Entry 5).

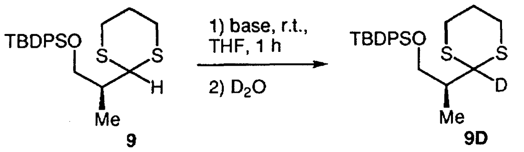
Under the same reaction conditions, the coupling of the benzyl ether **11** with oxirane **22** was carried out; however, the desired coupling product **32**[17] was obtained in only 28% yield along with the olefin product **33**[17] in 16% yield (Eq. 8). The yield of **32** could not be improved despite considerable effort.



(8)

Generation of Anion with *n*-BuLi / Bu$_2$Mg. During the course of our synthetic studies on biscembranoids,[20] we found that *n*-BuLi / Bu$_2$Mg complex (Bu$_2$Mg consisting of *n*-Bu : *s*-Bu = 1 : 1, Aldrich) was an effective anion generator for the Ito–Kodama cyclization and/or the Biellmann-type reaction,[21] which are coupling reactions of phenylthio-stabilized allylic anions with oxiranes. We anticipated that this mixed reagent would stabilize the anions generated from 1,3-dithiane derivatives.[22,23] We first investigated the metallation conditions using **9** as a substrate. The complex, pre-mixed with a variety of ratio of *n*-BuLi and Bu$_2$Mg, was added at r.t. to a solution of **9** in THF. After 1 h, D$_2$O was added and the crude mixture was analyzed by ^{1}H NMR. Relevant data are shown in Table 3. An increase in the ratio of Bu$_2$Mg / *n*-BuLi decreased %D (Entries 2, 3, 4, and 5). Bu$_2$Mg alone did not generate an anion (Entry 6).

Table 3. Generation of the Anion of **9** and D$_2$O Quenching[a)]



Entry	Base	%D[b)]
1	*n*-BuLi	86
2	*n*-BuLi/Bu$_2$Mg (0.25)[c)]	85
3	*n*-BuLi/Bu$_2$Mg (0.50)[c)]	74
4	*n*-BuLi/Bu$_2$Mg (0.75)[c)]	67
5	*n*-BuLi/Bu$_2$Mg (1.00)[c)]	62
6	Bu$_2$Mg	0

a) Base (1 molar amount for **9**) was added to a solution of **9** in THF (0.2 M for **9**) at r.t. After 1 h, D$_2$O was added and the mixture was worked up as usual. b) Determined by ^{1}H NMR analysis of the crude products. c) Bu$_2$Mg in heptane (molar amount indicated in parenthesis) was added to *n*-BuLi (1 molar amount for **9**) in hexane at r.t.; this mixed reagent was used as a base.

Next, we investigated the anion lifetime at r.t. As we would expect, the data shown in Fig. 2 indicate that the anion generated with *n*-BuLi / Bu$_2$Mg was long-lived at r.t.; %D reached to 85 over 1 h and was unchangeable after 6 h when a 4 : 1 ratio of *n*-BuLi / Bu$_2$Mg was used. In contrast, %D gradually decreased from 86 (1 h) to 67 (6 h) in the case of the anion generated with only *n*-BuLi. It should be noted that when Bu$_2$Mg (0.25—1.00 molar amounts for **9**) was added to the anion generated by a treatment of **9** with only *n*-BuLi (one molar amount for **9**) for 5 min, %D (6 h) was also 85. This result clearly shows that Bu$_2$Mg works

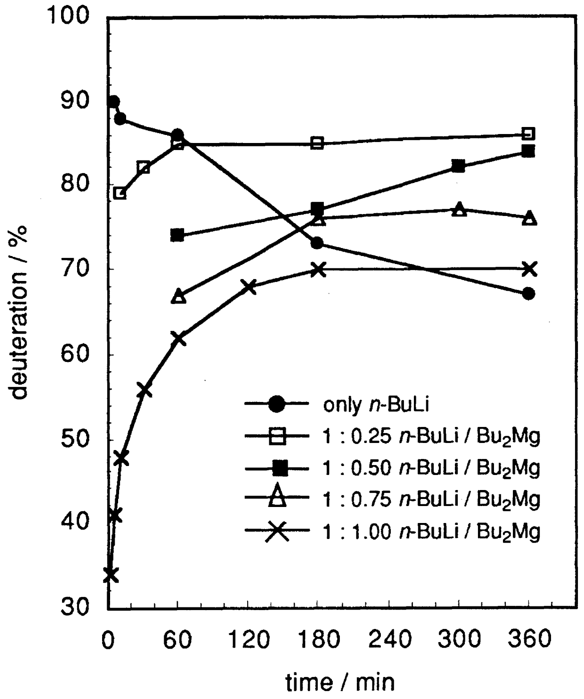


Fig. 2. Time course in the generation and the lifetime of the anion derived from **9** with a variety of ratio of *n*-BuLi / Bu$_2$Mg.

very well to lengthen the lifetime of the anion whatever the real active species are.

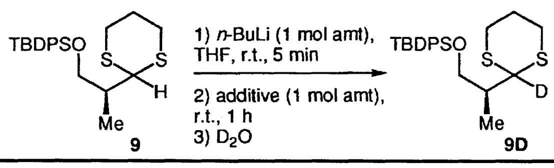
Coupling Reaction of 9 and 22. To the anion, generated in THF by the treatment of **9** (one molar amount) with a premixed reagent of one molar amount of *n*-BuLi and 0.25 molar amounts of Bu_2Mg at r.t. for 1 h, was added **22** (one molar amount) in THF; the mixture was stirred at r.t. for 3 h, giving **23** in 71% yield[16] (Eq. 4). When 1.2 molar amounts of *n*-BuLi, 0.3 molar amounts of Bu_2Mg, and 1.3 molar amounts of **22** were used, the yield of **23** increased to 85%.[16] This result was superior to that of the aforementioned coupling using only *n*-BuLi.

Generation of Anion with Other Additives. Having found conditions that afforded the coupling product in good yield, we proceeded to examine other additives in the expectation that they would exhibit the same effect on the coupling and mechanistic insight into the real active species of 2-metallo-1,3-dithiane derivatives would be gained. The lithium salt of **9** was generated using *n*-BuLi at r.t. for 5 min; then, the additive was added at r.t. After 1 h, D_2O was added and the crude mixture was analyzed by ^1H NMR. The data are given in Table 4. Among the additives used, *n*-BuMgCl, $MgBr_2$, and Et_2Zn exhibited an acceptable anion lifetime (Entries 2, 3, and 6). The coupling of these 2-metallo-1,3-dithiane derivatives with oxirane **22**, however, gave the adduct in less than 10% yield. Furthermore, each Bu_2Mg, *n*-BuMgCl, *n*-BuLi / Et_2Zn, and Et_2Zn did not generate an anion of **9** and each Bu_2Mg, *n*-BuMgCl, and Et_2Zn did not react with oxirane **22**. According to these facts, it seems that the magnesium ate complex would be an active species.[24]

Conclusions

2-Substituted 1,3-dithiane derivatives, **9**, **10**, **15**, and **18**, were effectively lithiated in THF with *n*-BuLi at r.t. for 5 min and the resulting anions reacted with 2,3-disubstituted oxirane **22** at r.t. to afford the coupling products in satisfactory yields. On the other hand, the MPM ether **12** was lithiated in ether and the derived anion reacted with **22** in the presence of HMPA to afford the coupling product in moderate yield. In addition, a mixed organometallic reagent, *n*-BuLi / Bu_2Mg, was found to be an effective metallation reagent for **9**, and the resulting anion reacted with **22** to afford the coupling product in good yield. The results presented in this article would broaden the synthetic usefulness of 1,3-dithiane chemistry.

Table 4. Transmetallation of Lithiated **9** and D_2O Quenching[a)]



Entry	Additive (solvent)	%D[b)]
1	Bu_2Mg (heptane)	85
2	*n*-BuMgCl (THF)	89
3	$MgBr_2$ (THF)[c,d)]	66
4	(*i*-PrO)$_3$TiCl (THF)[e)]	40[f)]
5	$ZnCl_2$ (ether)[g)]	37[f)]
6	Et_2Zn (hexane)	77

a) *n*-BuLi (1 molar amount for **9**) was added to a solution (0.2 M for **9**) of **9** in THF at r.t. After 5 min, the specified additive (1 molar amount for **9**) was added and the mixture was stirred at r.t. for 1 h. D_2O was added and the mixture was worked up as usual. b) Determined by ^1H NMR analysis of the crude products. c) To a suspension of $MgBr_2$ (1 molar amount for **9**) in THF was added at r.t. the lithiated **9** prepared as above. After 1 h, D_2O was added and the mixture was worked up as usual. d) Ref. 14g e) Ref. 22b. f) Contaminated with decomposed products. g) Ref. 22f.

Experimental

The melting points were determined on a micro hot-stage Yanaco MP-S3 and were uncorrected. Optical rotations were measured on JASCO DIP-360 photoelectric polarimeters in chloroform, unless otherwise noted. IR spectra were recorded on a JASCO FT IR-200 spectrometer (neat, 25 °C) and ^1H NMR spectra were on a JEOL GSX270 or a JEOL LAMBDA300 spectrometer in $CDCl_3$ at 25 °C using TMS as an internal standard, unless otherwise noted. Mass spectra (EI) were recorded on a JEOL GCmate mass spectrometer. Silica-gel TLC and column chromatography were performed on a Merck TLC 60F-254 and a Fuji-Davison BW-820MH, respectively. Air- and/or moisture-sensitive reactions were carried out under an atmosphere of argon with oven-dried glassware. In general, the organic solvents were purified and dried by appropriate procedures, and evaporation and concentration were carried out under reduced pressure below 30 °C, unless otherwise noted.

(*S*)-2-(1,3-Dithian-2-yl)-1-propanol (8). To a stirred solution of methyl (*S*)-3-hydroxy-2-methylpropionate (**6**) (5.36 g, 45.4 mmol) in dry CH_2Cl_2 (50 ml) were added at 0 °C triethylamine (9.50 ml, 68.2 mmol), DMAP (277 mg, 2.27 mmol), and TrCl (13.3 g, 47.7 mmol) successively. After 16 h at r.t., ethanol (20 ml) was added and the mixture was stirred at r.t. for 1 h. Saturated aqueous NH_4Cl was added and the mixture was extracted with CH_2Cl_2. The extracts were washed with saturated aqueous NaCl, dried, and concentrated. A portion (2.53 g) of the residual crystals (16.4 g) was dissolved in dry CH_2Cl_2 (30 ml) and cooled to −78 °C. To this was slowly added 0.95 M DIBAH in hexane (7.76 ml, 7.37 mmol) and the mixture was stirred at −78 °C for 25 min. To this were added 1,3-propanedithiol (1.50 ml, 14.0 mmol) and $BF_3 \cdot OEt_2$ (1.76 ml, 14.0 mmol) and the mixture was stirred at −78 °C for 10 min and gradually warmed to r.t. for a period of 1 h. MeOH was added and the mixture was stirred at r.t. for a while. After neutralization with 10 M aqueous NaOH, potassium sodium tartrate·$4H_2O$ (6.20 g, 22.1 mmol) in water (20 ml) was added and the mixture was separated. The aqueous layer was extracted with ether and the combined organic layers were concentrated and the residue was chromatographed on silica gel (100 g) with 5 : 1 $CHCl_3$–ethyl acetate to afford **8**[9] (1.10 g, 88%) as a colorless syrup: $R_f = 0.25$ (3 : 1 hexane–ethyl acetate); $[\alpha]^{26}_{D}+6.2$, $[\alpha]^{26}_{435}+8.5$ (*c* 1.07); ^1H NMR (270 MHz, $CHCl_3 = 7.26$) $\delta = 1.11$ (3H, d, $J = 7.1$ Hz), 1.72 (1H, t, $J = 6.2$ Hz), 1.78—1.95 (1H, m), 2.03—2.18 (2H, m), 2.81—3.00 (4H, m), 3.65—3.73 (2H, m), and 4.30 (1H, d, $J = 5.4$ Hz). Found: C, 47.01; H, 8.10%. Calcd for $C_7H_{14}OS_2$: C, 47.15; H, 7.91%.

(*S*)-α-Methoxy-α-(trifluoromethyl)phenylacetate of 8. To a stirred solution of **8** (4.5 mg, 0.0252 mmol) in dry CH_2Cl_2 (0.5 ml) were added at r.t. triethylamine (0.0176 ml, 0.126 mmol), DMAP (3.1 mg, 0.0252 mmol), and (*S*)-α-methoxy-α-(trifluoromethyl)-phenylacetyl chloride (0.0057 ml, 0.030 mmol). After 0.5 h, water was added and the mixture was extracted with hexane. The extracts were washed with saturated aqueous NaCl, dried, and concentrated.

The crude residue was analyzed by ^{1}H NMR spectrum: $R_f = 0.72$ (3 : 1 hexane–ethyl acetate); ^{1}H NMR (270 MHz) $\delta = 1.12$ (3H, d, $J = 7.0$ Hz), 1.75—1.95 (1H, m), 2.03—2.16 (1H, m), 2.23—2.40 (1H, m), 2.67—2.91 (4H, m), 3.57 (3H, s), 4.07 (1H, d, $J = 6.4$ Hz), 4.29 (1H, dd, $J = 11.4$, 6.0 Hz), 4.45 (1H, dd, $J = 11.4$, 7.0 Hz), and 7.30—7.62 (5H, m).

(*R*)-*α*-Methoxy-*α*-(trifluoromethyl)phenylacetate of 8. This was prepared from **8** and (*R*)-*α*-methoxy-*α*-(trifluoromethyl)phenylacetyl chloride as described above: $R_f = 0.72$ (3 : 1 hexane–ethyl acetate); ^{1}H NMR (270 MHz) $\delta = 1.12$ (3H, d, $J = 7.0$ Hz), 1.75—1.95 (1H, m), 2.00—2.15 (1H, m), 2.25—2.40 (1H, m), 2.67—2.91 (4H, m), 3.57 (3H, s), 4.07 (1H, d, $J = 6.4$ Hz), 4.33 (1H, dd, $J = 11.4$, 6.8 Hz), 4.39 (1H, dd, $J = 11.4$, 6.3 Hz), and 7.30—7.62 (5H, m).

(*S*)-1-(*t*-Butyldiphenylsiloxy)-2-(1,3-dithian-2-yl)propane (9). To a stirred solution of **8** (1.74 g, 9.76 mmol) in dry CH_2Cl_2 (40 ml) were added at r.t. imidazole (997 mg, 14.6 mmol) and TBDPSCl (3.05 ml, 11.7 mmol). After 1 h at r.t., water was added and the mixture was separated. The aqueous layer was extracted with CH_2Cl_2 and the combined organic layers were concentrated. The residue was chromatographed on silica gel (150 g) with 20 : 1 hexane–ethyl acetate to afford **9** (3.97 g, 98%) as a colorless syrup: $R_f = 0.74$ (10 : 1 hexane–ethyl acetate); $[\alpha]_D^{28} -2.8$, $[\alpha]_{435}^{28} -10.4$ (*c* 0.86); ^{1}H NMR (270 MHz) $\delta = 1.06$ (9H, s), 1.08 (3H, d, $J = 6.8$ Hz), 1.75—1.94 (1H, m), 2.05—2.22 (2H, m), 2.75—2.99 (4H, m), 3.62 (1H, dd, $J = 10.0$, 6.2 Hz), 3.75 (1H, dd, $J = 10.0$, 6.8 Hz), 4.41 (1H, d, $J = 5.0$ Hz), 7.33—7.46 (6H, m), and 7.65—7.72 (4H, m). Found: C, 66.14; H, 7.77%. Calcd for $C_{23}H_{32}OSiS_2$: C, 66.29; H, 7.74%.

(*S*)-1-(*t*-Butyldimethylsiloxy)-2-(1,3-dithian-2-yl)propane (10). To a stirred solution of **8** (421 mg, 2.36 mmol) in dry DMF (6.0 ml) were added at r.t. imidazole (289 mg, 4.25 mmol) and TBSCl (427 mg, 2.83 mmol). After 0.5 h at r.t., water was added and the mixture was extracted with 1 : 1 hexane–ethyl acetate. The extracts were washed with saturated aqueous NaCl, dried, and concentrated. The residue was chromatographed on silica gel (70 g) with 1 : 1 hexane–$CHCl_3$ to afford **10** (656 mg, 95%) as a colorless syrup: $R_f = 0.77$ (10 : 1 hexane–ethyl acetate); $[\alpha]_D^{28}$ 0.0, $[\alpha]_{435}^{28} -5.4$ (*c* 0.95); ^{1}H NMR (270 MHz, $CHCl_3 = 7.26$) $\delta = 0.00$ (6H, s), 0.84 (9H, s), 1.00 (3H, d, $J = 6.8$ Hz), 1.70—1.88 (1H, m), 1.92—2.11 (2H, m), 2.70—2.93 (4H, m), 3.47 (1H, dd, $J = 9.6$, 6.0 Hz), 3.62 (1H, dd, $J = 9.6$, 7.0 Hz), and 4.25 (1H, d, $J = 4.8$ Hz). Found: C, 53.22; H, 9.70%. Calcd for $C_{13}H_{28}OSiS_2$: C, 53.37; H, 9.65%.

(*S*)-1-Benzyloxy-2-(1,3-dithian-2-yl)propane (11). To a stirred solution of **8** (885 mg, 4.96 mmol) in dry DMF (12 ml) was added at 0 °C NaH (179 mg, 7.46 mmol). After 45 min at 0 °C, BnBr (0.768 ml, 6.46 mmol) was added at 0 °C and the mixture was stirred at 0 °C for 1.5 h. Saturated aqueous NH_4Cl was added and the mixture was extracted with 1 : 1 hexane–ethyl acetate. The extracts were washed with saturated aqueous NaCl, dried, and concentrated. The residue was chromatographed on silica gel (90 g) with 20 : 1 hexane–ethyl acetate to afford **11**[12] (1.29 g, 97%) as a colorless syrup: $R_f = 0.41$ (10 : 1 hexane–ethyl acetate); $[\alpha]_D^{27} -7.5$, $[\alpha]_{435}^{27} -20.8$ (*c* 1.06); ^{1}H NMR (270 MHz) $\delta = 1.11$ (3H, d, $J = 7.1$ Hz), 1.74—1.94 (1H, m), 2.05—2.31 (2H, m), 2.80—3.01 (4H, m), 3.42 (1H, dd, $J = 9.2$, 5.8 Hz), 3.60 (1H, dd, $J = 9.2$, 7.1 Hz), 4.36 (1H, d, $J = 4.4$ Hz), 4.53 (2H, s), and 7.25—7.38 (5H, m). Found: C, 62.88; H, 7.57%. Calcd for $C_{14}H_{20}OS_2$: C, 62.64; H, 7.51%.

(*S*)-2-(1,3-Dithian-2-yl)-1-(4-methoxybenzyloxy)propane (12). To a stirred solution of **8** (1.17 g, 6.56 mmol) in dry DMF (7.0 ml) was added at 0 °C NaH (221 mg, 9.21 mmol). After 45 min at 0 °C, MPMCl (1.16 ml, 8.56 mmol) was added at 0 °C and the mixture was stirred at 0 °C for 1.5 h. Saturated aqueous NH_4Cl was added and the mixture was extracted with 1 : 1 hexane–ethyl acetate. The extracts were washed with saturated aqueous NaCl, dried, and concentrated. The residue was chromatographed on silica gel (150 g) with 10 : 1 hexane–ethyl acetate to afford **12** (1.89 g, 96%) as a colorless syrup: $R_f = 0.44$ (8 : 1 hexane–ethyl acetate); $[\alpha]_D^{27} -10.3$, $[\alpha]_{435}^{27} -26.6$ (*c* 0.97); ^{1}H NMR (270 MHz) $\delta = 1.09$ (3H, d, $J = 7.0$ Hz), 1.75—1.94 (1H, m), 2.05—2.29 (2H, m), 2.78—3.01 (4H, m), 3.38 (1H, dd, $J = 9.2$, 6.2 Hz), 3.57 (1H, dd, $J = 9.2$, 7.0 Hz), 3.81 (3H, s), 4.35 (1H, d, $J = 4.2$ Hz), 4.45 (2H, s), 6.88 (2H, d, $J = 8.6$ Hz), and 7.27 (2H, d, $J = 8.6$ Hz). Found: C, 60.38; H, 7.62%. Calcd for $C_{15}H_{22}O_2S_2$: C, 60.36; H, 7.43%.

1-(*t*-Butyldiphenylsiloxy)-2-(1,3-dithian-2-yl)-2-methylpropane (15). To a stirred solution of 2,2-dimethyl-1,3-propanediol (**13**) (2.00 g, 19.2 mmol) in dry THF (20 ml) was added at 0 °C NaH (461 mg, 19.2 mmol). After 45 min at 0 °C, TrCl (5.35 g, 19.2 mmol) was added at 0 °C and the mixture was stirred at 0 °C for 3 h. MeOH was added and the mixture was stirred at r.t. for 1 h. Saturated aqueous NH_4Cl was added and the mixture was extracted with ethyl acetate. The extracts were washed with saturated aqueous NaCl, dried, and concentrated. The residue was chromatographed on silica gel (100 g) with 8 : 1 hexane–ethyl acetate to afford colorless crystals (5.70 g, 85%) [$R_f = 0.25$ (8 : 1 hexane–ethyl acetate); ^{1}H NMR (270 MHz) $\delta = 0.89$ (6H, s), 2.04 (1H, br s), 2.92 (2H, s), 3.36 (2H, br s), and 7.15—7.43 (15H, m)]. A solution of DMSO (12.5 ml, 176 mmol) in dry CH_2Cl_2 (30 ml) was added at −78 °C to a stirred solution of oxalyl dichloride (7.70 ml, 88.3 mmol) in dry CH_2Cl_2 (230 ml). After 0.5 h at −78 °C, a solution of the above crystals (15.3 g, 44.0 mmol) in dry CH_2Cl_2 (45 ml) was added; the resulting suspension was stirred at −78 °C for 1 h. After the addition of triethylamine (36.8 ml, 264 mmol), the mixture was gradually warmed to r.t. for a period of 1 h. The reaction mixture was quenched with water and extracted with CH_2Cl_2. The extracts were washed with saturated aqueous NaCl, dried, and concentrated to afford **14** (14.3 g, 94%) as pale yellow crystals [$R_f = 0.47$ (10 : 1 hexane–ethyl acetate); ^{1}H NMR (270 MHz) $\delta = 1.07$ (6H, s), 3.15 (2H, s), 7.19—7.43 (15H, m), and 9.48 (1H, s)]. To a suspension of **14** (14.2 g, 41.1 mmol) and molecular sieves 3A powder (MS 3AP) (2.1 g) in CH_2Cl_2 (110 ml) were added at 0 °C $BF_3 \cdot OEt_2$ (2.58 ml, 21.0 mmol) and 1,3-propanedithiol (6.61 ml, 65.8 mmol). After 20 min at 0 °C, MeOH (140 ml) was added and the mixture was stirred at r.t. for 0.5 h. Triethylamine was added and the mixture was filtered with Celite. The filter cake was washed with CH_2Cl_2 and the combined filtrate and the washings were concentrated. The residue was chromatographed on silica gel twice (500 g with 3 : 1 hexane–ethyl acetate and 120 g with 10 : 1 $CHCl_3$–ethyl acetate) to afford a pale yellow syrup (4.90 g, 62%). To a stirred solution of this syrup (1.20 g, 6.24 mmol) in dry DMF (6.0 ml) were added at 0 °C imidazole (767 mg, 11.3 mmol) and TBDPSCl (1.95 ml, 7.50 mmol). After 3 h at r.t., water was added and the mixture was extracted with 1 : 1 hexane–ethyl acetate. The extracts were washed with saturated aqueous NaCl, dried, and concentrated. The residue was chromatographed on silica gel (90 g) with 2 : 1 hexane–$CHCl_3$ to afford **15** (2.59 g, 96%) as colorless crystals: $R_f = 0.67$ (20 : 1 hexane–ethyl acetate); mp 59—60 °C; ^{1}H NMR (270 MHz, $CHCl_3 = 7.26$) $\delta = 1.07$ (9H, s), 1.09 (6H, s), 1.73—1.90 (1H, m), 2.03—2.14 (1H, m), 2.83—2.95 (4H, m), 3.55 (2H, s), 4.39 (1H, s), 7.33—7.47 (6H, m), and 7.65—7.75 (4H, m). Found: C, 66.92; H, 8.03%. Calcd for $C_{24}H_{34}OSiS_2$: C, 66.92; H, 7.96%.

1,2-Bis(*t*-butyldiphenylsiloxy)-3-(1,3-dithian-2-yl)propane (18). To a stirred solution of **17**[13] (1.63 g, 3.77 mmol) in dry

DMF (50 ml) were added at r.t. DMAP (1.15 g, 9.41 mmol) and TBDPSCl (1.96 ml, 7.54 mmol). After 16 h at 90 °C, DMAP (1.15 g, 9.41 mmol) and TBDPSCl (2.45 ml, 9.42 mmol) were added and the mixture was stirred at 90 °C for 16 h. Water was added and the mixture was extracted with 1 : 1 hexane–ethyl acetate. The extracts were washed with saturated aqueous NaCl, dried, and concentrated. The residue was chromatographed on silica gel (100 g) with 20 : 1 hexane–ethyl acetate to afford **18** (2.34 g, 93%) as a colorless syrup: $R_f = 0.53$ (20 : 1 hexane–ethyl acetate); ^{1}H NMR (270 MHz, $CHCl_3 = 7.26$) $\delta = 1.00$ (9H, s), 1.03 (9H, s), 1.70—1.88 (1H, m), 1.92—2.07 (2H, m), 2.17 (1H, ddd, $J = 14.0, 8.6, 4.6$ Hz), 2.47—2.75 (4H, m), 3.50 (1H, dd, $J = 10.0, 5.2$ Hz), 3.56 (1H, dd, $J = 10.0, 3.2$ Hz), 3.96 (1H, dd, $J = 8.6, 5.8$ Hz), 4.05—4.15 (1H, m), 7.25—7.45 (12H, m), and 7.50—7.68 (8H, m). Found: C, 69.88; H, 7.49%. Calcd for $C_{39}H_{50}O_2Si_2S_2$: C, 69.80; H, 7.51%.

***trans*-2-Methyl-3-(triphenylmethoxymethyl)oxirane (22).** To a stirred solution of **20** (998 mg, 13.8 mmol) in dry CH_2Cl_2 (10 ml) were added at r.t. triethylamine (3.86 ml, 27.7 mmol) and TrCl (4.05 g, 14.5 mmol). After 2 h at 35 °C, saturated aqueous $NaHCO_3$ was added and the mixture was extracted with CH_2Cl_2. The extracts were washed with saturated aqueous NaCl, dried, and concentrated. The residue was recrystallized from 20 : 1 hexane–ethyl acetate to afford **21** (2.65 g, 61%) as colorless crystals [$R_f = 0.52$ (20 : 1 hexane–ethyl acetate); mp 74—76 °C (not recrystallized); ^{1}H NMR (270 MHz) $\delta = 1.72$ (3H, d with a small long-range coupling, $J = 6.2, 1.2$ Hz), 3.53 (2H, d with a small long-range coupling, $J = 5.2, 1.2$ Hz), 5.59 (1H, dt with a small long-range coupling, $J = 15.0, 5.2, 1.2$ Hz), 5.75 (1H, dq with a small long-range coupling, $J = 15.0, 6.2, 1.2$ Hz), and 7.16—7.49 (15H, m)]. To a stirred solution of **21** (7.85 g, 25.0 mmol) in dry CH_2Cl_2 (70 ml) was added at 0 °C *m*-CPBA (5.33 g, 30.9 mmol). After 3 h at r.t., saturated aqueous $NaHCO_3$ was added and the mixture was extracted with CH_2Cl_2. The extracts were concentrated and the residue was dissolved in ether (30 ml). To this was added at 0 °C 1 M aqueous NaOH (100 ml). After 1 h at 0 °C, the mixture was separated and the aqueous layer was extracted with ether. The combined organic layers were washed with saturated aqueous NaCl, dried, and concentrated. The residue was recrystallized from 8 : 1 hexane–ethyl acetate to afford **22** (6.11 g, 74%) as colorless crystals: $R_f = 0.48$ (10 : 1 hexane–ethyl acetate); mp 115—116 °C; ^{1}H NMR (270 MHz) $\delta = 1.30$ (3H, d, $J = 5.0$ Hz), 2.86—2.94 (2H, m), 3.14 (1H, dd, $J = 10.2, 5.2$ Hz), 3.28 (1H, dd, $J = 10.2, 3.0$ Hz), 7.18—7.35 (9H, m), and 7.43—7.48 (6H, m). Found: C, 83.59; H, 6.57%. Calcd for $C_{23}H_{22}O_2$: C, 83.61; H, 6.71%.

Representative Procedure for Generation of the Anion of 9 and D_2O Quenching. Method 1 (Table 1, Entry 9). To a stirred solution of **9** (35.7 mg, 0.0857 mmol) in dry THF (0.40 ml) was added at r.t. 1.53M *n*-BuLi in hexane (0.0560 ml, 0.0857 mmol). After 5 min at r.t., the red solution was quenched by the addition of D_2O (0.25 ml). The mixture was stirred at r.t. for 5 min and to this was added saturated aqueous NH_4Cl. The mixture was extracted with hexane and the extracts were washed with saturated aqueous NaCl, dried, and concentrated. %D was determined by ^{1}H NMR analysis of the crude products.

Method 2 (Table 3, Entry 2). Bu_2Mg in heptane (1.0 M, 0.0207 ml, 0.0207 mmol; *n*-Bu : *s*-Bu = 1 : 1, Aldrich) was added at r.t. to a solution of 1.54 M *n*-BuLi in hexane (0.0538 ml, 0.0828 mmol). This mixed reagent was added at r.t. to a stirred solution of **9** (34.5 mg, 0.0828 mmol) in dry THF (0.45 ml). After 1 h at r.t., the red solution was quenched by the addition of D_2O (0.25 ml). The mixture was stirred at r.t. for 5 min and to this was added saturated aqueous NH_4Cl. The mixture was extracted with hexane and the extracts were washed with saturated aqueous NaCl, dried, and concentrated. %D was determined by ^{1}H NMR analysis of the crude products.

Method 3 (Table 4, Entry 1). To a stirred solution of **9** (30.7 mg, 0.0737 mmol) in dry THF (0.45 ml) was added at r.t. 1.54 M *n*-BuLi in hexane (0.0478 ml, 0.0737 mmol). After 5 min at r.t., 1.0 M Bu_2Mg in heptane (0.0737 ml, 0.0737 mmol) was added at r.t. and the red solution was stirred at r.t. for 1 h. D_2O (0.50 ml) was added at 0 °C and the mixture was stirred at r.t. for 5 min; to this was added saturated aqueous NH_4Cl. The mixture was extracted with hexane and the extracts were washed with saturated aqueous NaCl, dried, and concentrated. %D was determined by ^{1}H NMR analysis of the crude products.

(2*R*,3*R*)- and (2*S*,3*S*)-3-{2-[(*S*)-2-(*t*-Butyldiphenylsiloxy)-1-methylethyl]-1,3-dithian-2-yl}-1-(triphenylmethoxy)-2-butanol (23). Method 1. To a stirred solution of **9** (31.5 mg, 0.0756 mmol) in dry THF (0.35 ml) was added at r.t. 1.56 M *n*-BuLi in hexane (0.0581 ml, 0.0906 mmol). After 5 min at r.t., a solution of **22** (32.5 mg, 0.0984 mmol) in dry THF (0.20 ml) was added. A red color once faded away, but soon returned. After 3 h at r.t., saturated aqueous NH_4Cl was added and the mixture was extracted with hexane. The extracts were washed with saturated aqueous NaCl, dried, and concentrated. The residue was chromatographed on silica gel (3 g) with 15 : 1 hexane–ethyl acetate to afford **23** (41.2 mg, 73%: a 1 : 1 mixture of diastereomers) as colorless crystals.

Method 2. Bu_2Mg in heptane (1.0 M, 0.0222 ml, 0.0222 mmol) was added at r.t. to a solution of 1.56 M *n*-BuLi in hexane (0.0570 ml, 0.0889 mmol). This mixed reagent was added at r.t. to a stirred solution of **9** (30.9 mg, 0.0742 mmol) in dry THF (0.35 ml) and the mixture was stirred at r.t. for 1 h. To this red-colored solution was added a solution of **22** (31.9 mg, 0.0965 mmol) in dry THF (0.20 ml). After 3 h at r.t., saturated aqueous NH_4Cl was added and the mixture was extracted with hexane. The extracts were washed with saturated aqueous NaCl, dried, and concentrated. The residue was chromatographed on silica gel (3 g) with 15 : 1 hexane–ethyl acetate to afford **23** (47.1 mg, 85%: a 1 : 1 mixture of diastereomers) as colorless crystals.

23: $R_f = 0.36$ (10 : 1 hexane–ethyl acetate); mp 37—40 °C (not recrystallized); ^{1}H NMR (270 MHz) $\delta = 0.75$ (3H/2, d, $J = 7.0$ Hz), 0.85 (3H/2, d, $J = 7.0$ Hz), 1.06 and 1.07 (each 9H/2, each s), 1.30 (3H/2, d, $J = 7.0$ Hz), 1.34 (3H/2, d, $J = 7.0$ Hz), 1.70—1.95 (2H, m), 2.00—2.20 (1H, m), 2.37—2.95 (7H, m), 3.18 (1H, dd, $J = 9.0, 6.4$ Hz), 3.68 (1H/2, dd, $J = 8.8, 8.8$ Hz), 3.70 (1H/2, dd, $J = 8.8, 8.8$ Hz), 4.22 (1H/2, dd, $J = 8.8, 3.0$ Hz), 4.29 (1H/2, dd, $J = 8.8, 3.0$ Hz), 4.73 (1H, br m), and 7.17—7.76 (25H, m). Found: C, 73.75; H, 7.55%. Calcd for $C_{46}H_{54}O_3SiS_2$: C, 73.95; H, 7.28%.

(2*R*,3*R*)- and (2S,3S)-3-{2-[(*S*)-2-(*t*-Butyldimethylsiloxy)-1-methylethyl]-1,3-dithian-2-yl}-1-(triphenylmethoxy)-2-butanol (24). To a stirred solution of **10** (23.0 mg, 0.0786 mmol) in dry THF (0.35 ml) was added at r.t. 1.61 M *n*-BuLi in hexane (0.0586 ml, 0.0943 mmol). After 5 min at r.t., a solution of **22** (33.7 mg, 0.102 mmol) in dry THF (0.20 ml) was added. A red color once faded away, but soon returned. After 3 h at r.t., saturated aqueous NH_4Cl was added and the mixture was extracted with hexane. The extracts were washed with saturated aqueous NaCl, dried, and concentrated. The residue was chromatographed on silica gel (4 g) with 15 : 1 hexane–ethyl acetate to afford **24** (34.2 mg, 70%: a 1 : 1 mixture of diastereomers) as a colorless syrup: $R_f = 0.31$ (15 : 1 hexane–ethyl acetate); ^{1}H NMR (270 MHz, $CHCl_3 = 7.26$) $\delta = -0.02$, -0.01, 0.00, and 0.01 (each 3H/2, each s), 0.83 (9H+3H/2, s including d), 0.87 (3H/2, d, $J = 7.0$ Hz), 1.18 (3H/2, d, $J = 7.2$ Hz), 1.21 (3H/2, d, $J = 7.2$ Hz), 1.70—2.00 (2H, m), 2.10—2.25 (1H, m), 2.25—2.45

(1H, m), 2.55—2.85 (5H, m), 2.88 (1H, dd, $J = 9.0$, 7.0 Hz), 3.15 (1H/2, dd, $J = 9.0$, 1.6 Hz), 3.18 (1H/2, dd, $J = 9.0$, 1.6 Hz), 3.49 (1H, dd, $J = 9.4$, 8.2 Hz), 3.60 (1H, dd, $J = 9.4$, 8.2 Hz), 4.07—4.15 (1H, m), 4.70 (1H, br m), and 7.10—7.45 (15H, m). Found: C, 69.66; H, 7.97%. Calcd for $C_{36}H_{50}O_3SiS_2$: C, 69.40; H, 8.09%.

(2*R,3*R**)-(±)-3-{2-[2-(*t*-Butyldiphenylsiloxy)-1,1-dimethylethyl]-1,3-dithian-2-yl}-1-(triphenylmethoxy)-2-butanol (25).** To a stirred solution of **15** (39.1 mg, 0.0908 mmol) in dry THF (0.45 ml) was added at r.t. 1.61 M *n*-BuLi in hexane (0.0564 ml, 0.0908 mmol). After 5 min at r.t., a solution of **22** (15.0 mg, 0.0454 mmol) in dry THF (0.20 ml) was added. A red color once faded away, but soon returned. After 3 h at r.t., saturated aqueous NH_4Cl was added and the mixture was extracted with hexane. The extracts were washed with saturated aqueous NaCl, dried, and concentrated. The residue was chromatographed on silica gel (4 g) with 15 : 1 hexane–ethyl acetate to afford **25** (21.1 mg, 61%) as colorless crystals: $R_f = 0.31$ (10 : 1 hexane–ethyl acetate); mp 54—55 °C (not recrystallized); ^{1}H NMR (270 MHz) $\delta = 1.03$ (3H, d, $J = 7.0$ Hz), 1.07 (9H, s), 1.30 (3H, s), 1.34 (3H, s), 1.65—1.88 (2H, m), 2.34 (1H, q, $J = 7.0$ Hz), 2.26—2.78 (5H, m), 3.03 (1H, dd, $J = 9.0$, 5.8 Hz), 3.18 (1H, dd, $J = 9.0$, 7.4 Hz), 3.84 and 3.90 (each 1H, ABq, $J = 9.0$ Hz), 4.55 (1H, br m), and 7.16—7.70 (25H, m). Found: C, 73.88; H, 7.38%. Calcd for $C_{47}H_{56}O_3SiS_2$: C, 74.16; H, 7.42%.

(2*R,3*R**)-(±)-3-(2-{2,3-Bis[(*R**)- and (*S**)-*t*-butyldiphenylsiloxy]propyl}-1,3-dithian-2-yl)-1-(triphenylmethoxy)-2-butanol (26).** To a stirred solution of **18** (73.0 mg, 0.109 mmol) in dry THF (0.60 ml) was added at r.t. 1.61 M *n*-BuLi in hexane (0.0676 ml, 0.109 mmol). After 5 min at r.t., a solution of **22** (18.0 mg, 0.0545 mmol) in dry THF (0.20 ml) was added. A red color once faded away but soon returned. After 3 h at r.t., saturated aqueous NH_4Cl was added and the mixture was extracted with hexane. The extracts were washed with saturated aqueous NaCl, dried, and concentrated. The residue was chromatographed on silica gel (15 g) with 15 : 1 hexane–ethyl acetate to afford **26** (38.2 mg, 70%: a 1.9 : 1 mixture of diastereomers) as colorless crystals. These diastereomers could be separated by silica-gel column chromatography and analytical data of each diastereomer were obtained.

One Diastereomer of 26: $R_f = 0.39$ (12 : 1 hexane–ethyl acetate); mp 58—60 °C (not recrystallized); ^{1}H NMR (270 MHz, $CHCl_3 = 7.26$) $\delta = 0.85$ (3H, d, $J = 6.8$ Hz), 0.98 (9H, s), 1.00 (9H, s), 1.65—1.91 (2H, m), 1.96 (1H, d, $J = 4.0$ Hz), 2.10—2.18 (1H, m), 2.20 (1H, dd, $J = 15.8$, 5.2 Hz), 2.34 (1H, dd, $J = 15.8$, 5.2 Hz), 2.45—2.72 (4H, m), 2.95 (1H, dd, $J = 9.0$, 5.8 Hz), 3.12 (1H, dd, $J = 9.0$, 7.0 Hz), 3.52 (1H, dd, $J = 10.2$, 5.2 Hz), 3.59 (1H, dd, $J = 10.2$, 4.2 Hz), 4.35 (1H, m), 4.55 (1H, m), and 7.17—7.77 (35H, m). Found: C, 74.24; H, 7.17%. Calcd for $C_{62}H_{72}O_4Si_2S_2$: C, 74.35; H, 7.25%.

the Other Diastereomer of 26: $R_f = 0.35$ (12 : 1 hexane–ethyl acetate); mp 57—59 °C (not recrystallized); ^{1}H NMR (270 MHz) $\delta = 0.80$ (9H, s), 0.94 (9H, s), 0.98 (3H, d, $J = 6.8$ Hz), 1.72—1.88 (2H, m), 2.04—2.25 (2H, m), 2.36—2.48 (1H, m), 2.50 (1H, d, $J = 2.8$ Hz), 2.57—2.85 (4H, m), 2.91 (1H, dd, $J = 8.6$, 4.0 Hz), 3.13 (1H, dd, $J = 8.6$, 8.6 Hz), 3.34 (1H, dd, $J = 9.2$, 7.6 Hz), 3.47 (1H, dd, $J = 9.2$, 4.2 Hz), 4.34 (1H, m), 4.82 (1H, m), and 7.13—7.75 (35H, m). Found: C, 74.15; H, 7.30%. Calcd for $C_{62}H_{72}O_4Si_2S_2$: C, 74.35; H, 7.25%.

(2*R*,3*R*)- and (2*S*,3*S*)-3-{2-[(*S*)-2-(4-Methoxybenzyloxy)-1-methylethyl]-1,3-dithian-2-yl}-1-(triphenylmethoxy)-2-butanol (31). To a stirred solution of **12** (37.7 mg, 0.126 mmol) in dry ether (0.40 ml) was added at r.t. 1.53 M *n*-BuLi in hexane (0.0826 ml, 0.126 mmol). After 5 min at r.t., a solution of **22** (20.9 mg, 0.0633 mmol) in HMPA (0.020 ml) and dry ether (0.20 ml) was added. A yellow color changed to a red color. After 6 h at r.t., saturated aqueous NH_4Cl was added and the mixture was extracted with hexane. The extracts were washed with saturated aqueous NaCl, dried, and concentrated. The residue was chromatographed on silica gel (10 g) with 6 : 1 hexane–acetone to afford **31** (21.0 mg, 53%: a 1 : 1 mixture of diastereomers) as a colorless syrup: $R_f = 0.33$ (5 : 1 hexane–acetone); ^{1}H NMR (270 MHz) $\delta = 0.85$ (3H/2, d, $J = 6.8$ Hz), 0.93 (3H/2, d, $J = 6.8$ Hz), 1.28 (3H/2, d, $J = 6.8$ Hz), 1.31 (3H/2, d, $J = 6.8$ Hz), 1.71—2.07 (2H, m), 2.15—2.30 (1H, m), 2.45—2.99 (7H, m), 3.21 (1H, dd, $J = 8.6$, 6.2 Hz), 3.42 (1H/2, dd, $J = 9.0$, 8.2 Hz), 3.50 (1H/2, dd, $J = 9.0$, 9.0 Hz), 3.79 (3H, s), 4.06 (1H, dd, $J = 9.0$, 3.0 Hz), 4.41 and 4.47 (each 1H/2, ABq, $J = 8.6$ Hz), 4.43 and 4.49 (each 1H/2, ABq, $J = 8.6$ Hz), 4.70—4.83 (1H, m), 6.85 (2H, d, $J = 8.6$ Hz), and 7.17—7.48 (17H, m). Found: C, 72.26; H, 7.15%. Calcd for $C_{38}H_{44}O_4S_2$: C, 72.57; H, 7.05%.

(2*R*,3*R*)- and (2*S*,3*S*)-3-{2-[(*S*)-2-Benzyloxy-1-methylethyl]-1,3-dithian-2-yl}-1-(triphenylmethoxy)-2-butanol (32) and (2*R,3*R**)-(±)-3-(2-Isopropenyl-1,3-dithian-2-yl)-1-(triphenylmethoxy)-2-butanol (33).** To a stirred solution of **11** (33.0 mg, 0.123 mmol) in dry ether (0.40 ml) was added at r.t. 1.53 M *n*-BuLi in hexane (0.0804 ml, 0.123 mmol). After 5 min at r.t., a solution of **22** (20.3 mg, 0.0614 mmol) in HMPA (0.040 ml) and dry ether (0.35 ml) was added. A yellow color changed to a red color. After 6 h at r.t., saturated aqueous NH_4Cl was added and the mixture was extracted with ethyl acetate. The extracts were washed with saturated aqueous NaCl, dried, and concentrated. The residue was chromatographed on silica gel (8 g) with 6 : 1 hexane–acetone to afford **32** (10.3 mg, 28%: a 1 : 1 mixture of diastereomers) and **33** (4.7 mg, 16%) as colorless syrups.

32: $R_f = 0.34$ (6 : 1 hexane–acetone); ^{1}H NMR (270 MHz) $\delta = 0.85$ (3H/2, d, $J = 7.0$ Hz), 0.93 (3H/2, d, $J = 7.0$ Hz), 1.27 (3H/2, d, $J = 7.0$ Hz), 1.33 (3H/2, d, $J = 7.0$ Hz), 1.77—2.06 (2H, m), 2.15—2.28 (1H, m), 2.46—3.00 (7H, m), 3.21 (1H, dd, $J = 8.8$, 6.0 Hz), 3.45 (1H/2, dd, $J = 8.8$, 8.0 Hz), 3.54 (1H/2, dd, $J = 8.8$, 8.8 Hz), 4.10 (1H, dd, $J = 8.8$, 2.8 Hz), 4.49 and 4.53 (each 1H/2, ABq, $J = 11.8$ Hz), 4.50 and 4.55 (each 1H/2, ABq, $J = 11.8$ Hz), 4.66—4.83 (1H, m), and 7.17—7.49 (20H, m). Found: C, 74.43; H, 7.00%. Calcd for $C_{37}H_{42}O_3S_2$: C, 74.21; H, 7.07%.

33: $R_f = 0.43$ (6 : 1 hexane–acetone); ^{1}H NMR (270 MHz) $\delta = 0.88$ (3H, d, $J = 6.8$ Hz), 1.76—1.95 (1H, m), 1.90 (3H, s), 1.96—2.08 (1H, m), 2.16 (1H, q, $J = 6.8$ Hz), 2.41 (1H, d, $J = 2.8$ Hz), 2.62 (2H, ddd, $J = 14.2$, 4.0, 4.0 Hz), 2.82—2.98 (3H, m), 3.24 (1h, dd, $J = 8.6$, 6.2 Hz), 4.63 (1H, br), 5.39 (1H, d, $J = 1.6$ Hz), 5.57 (1H, d, $J = 1.6$ Hz), 7.17—7.33 (9H, m), and 7.40—7.47 (6H, m). Found: C, 73.11; H, 7.01%. Calcd for $C_{30}H_{34}O_2S_2$: C, 73.43; H, 6.98%.

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