Synthetic Methods

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Convergent Preparation of Enantiomerically Pure Polyalkylated Cyclopropane Derivatives**

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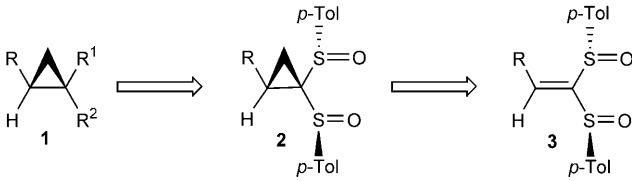
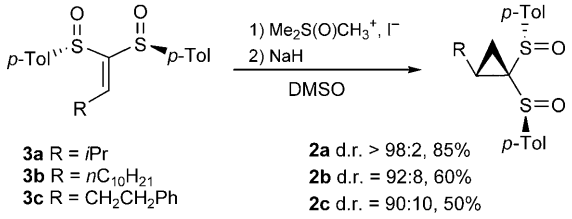
Cyclopropane is a basic structural element in a wide range of naturally occurring compounds,[1] and has been used as a versatile intermediate in the synthesis of more functionalized cyclic[2] and acyclic alkanes.[3] In the last few decades, most of the synthetic efforts have focused on the enantioselective synthesis of cyclopropanes,[4] however, new and more efficient methods for the preparation of these entities in enantiomerically enriched form are still evolving.[5] These methods can be divided into four types: the halomethylmetal-mediated cyclopropanation reaction,[6–8] the transition-metal-catalyzed decomposition of diazo compounds,[6] the nucleophilic addition/ring closure sequence, and the hydro- and carbometalation reaction of strained cyclopropene derivatives.[5a] All of these methods are among the most powerful and innovative approaches, but they usually lead to functionalized cyclopropanes. To prepare nonfunctionalized, enantiomerically enriched disubstituted cyclopropanes (95% *ee*), we successfully reported the (−)-sparteine-catalyzed enantioselective carbolithiation[9] of styrenyl derivatives which then undergo a 1,3-elimination reaction.[10] These reactions were restricted to aryl- and vinyl-substituted[10] cyclopropanes. To develop an even more general approach to the preparation of enantiomerically pure polyalkylated cyclopropanes (**1**; R, R^1, R^2 = alkyl groups), we envisaged subjecting **2** to a combination of two consecutive selective sulfoxide/lithium exchanges,[12] a transmetalation reaction, and then a reaction with an electrophile (Scheme 1). The sulfoxide/lithium exchange occurs when the reactive organometallic reagent reacts at the sulfur center of the sulfoxide, through an S_N2 process, to generate a more stable organometallic leaving group.[12f] Alkylidene bis(*p*-tolylsulfoxides)[12] (**3**) were recently used as highly versatile partners for asymmetric syntheses[13] in the context of radical chemistry,[14] polar Michael additions,[15] and the Michael-initiated ring closure reaction which is used herein as the key step for the preparation of cyclopropane **2**.[16]



Scheme 1. Retrosynthetic analysis for the preparation of enantiomerically pure polysubstituted cyclopropanes (**1**).

Indeed, when the sulfur ylide, generated in situ by deprotonation of trimethyloxosulfonium iodide with NaH in DMSO, was reacted with alkylidene bis(*p*-tolylsulfoxides) **3a–c** and corresponding bis(*p*-tolylsulfinyl)cyclopropanes **2a–c** were obtained in good to excellent diastereoisomeric ratios (Scheme 2). Each of the products **2b** and **2c** were easily separated by column chromatography on silica gel to obtain each diastereoisomer as a pure isomer. The absolute configuration of **2a** was determined by X-ray crystallographic analysis (see the Supporting Information) and by using the already established model.[16]



Scheme 2. Diastereoselective cyclopropanation reaction of alkylidene bis(*p*-tolylsulfoxides) (**3**).

When **2a** (R = *i*Pr) was treated at low temperature with *n*BuLi, a selective sulfoxide/lithium exchange took place to give the expected cyclopropyllithium species **5a**, which after methanolysis, afforded cyclopropane **6a** in excellent yield as a single diastereoisomer (Table 1, entry 1). An excess of *n*BuLi (routinely 3 equiv) was used for the exchange reaction to react with the *n*butyl-*p*-tolylsulfoxide formed in situ, thus avoiding protonation of **5a** by the acidic hydrogen atoms α to the sulfinyl group of the *n*butyl-*p*-tolylsulfoxide.[17]

The stereochemistry of the sulfoxide/lithium exchange was determined either by ^{1}H NMR spectroscopy (the coupling constant of the two cyclopropyl hydrogen atoms of **6b**,

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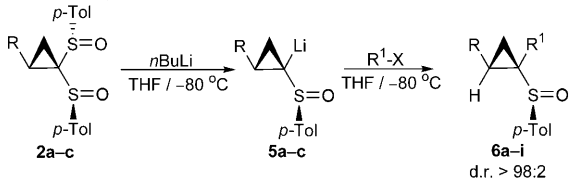
Table 1: Preparation of diastereoselectively pure cyclopropylsulfoxide derivatives **6a–j**



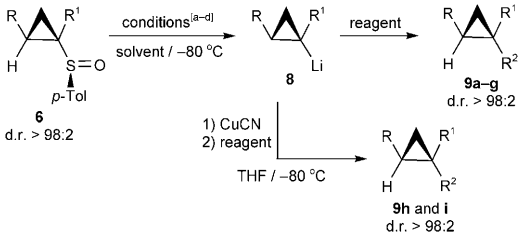
Entry[a]	Substrate, R	R^1X	R^1	d.r.[b]	Yield [%][c]
1	**2a**, *i*Pr	MeOH	H	>98:2(**6a**)	80
2	**2b**, $nC_{10}H_{21}$	MeOH	H	>98:2(**6b**)	70
3	**2a**, *i*Pr	CH_3I	CH_3	>98:2(**6c**)	70
4	**2a**, *i*Pr	$PhCH_2Br$	$PhCH_2$	>98:2(**6d**)	60
5	**2a**, *i*Pr	CH_2CHCH_2Br	CH_2CHCH_2	>98:2(**6e**)	60
6	**2a**, *i*Pr	*n*BuI	*n*Bu	>98:2(**6f**)	65
7	**2b**, $nC_{10}H_{21}$	CH_3I	CH_3	>98:2(**6g**)	65
8	**2b**, $nC_{10}H_{21}$	*n*BuI	*n*Bu	>98:2(**6h**)	65
9	**2c**, $PhCH_2CH_2$	CH_3I	CH_3	>98:2(**6i**)	60
10	**2b**, $nC_{10}H_{21}$	CH_2O	CH_2OH	>98:2(**6j**)	70

[a] See experimental section. [b] Determined from the crude reaction mixture by using ^{1}H NMR spectroscopy; only one diastereoisomer was detected. [c] Yield of product isolated after purification by column chromatography.

$J = 4.5$ Hz, corresponds to a *trans* relationship) or by X-ray crystallographic analysis of sulfone **7b** (see the Supporting Information), which is obtained after oxidation of the sulfinyl group. Our mechanistic hypothesis is based on the more hindered *syn*-selective sulfoxide/lithium exchange as it results in the release of strain. This assumption was corroborated by obtaining a 1:1 mixture of diastereoisomers when the more sterically demanding *t*BuLi was used, instead of *n*BuLi, for the sulfoxide/lithium exchange. If the lithiation initially occurred *trans* to the cyclopropane substituent, then subsequent alkylation would occur with inversion of configuration; to rule out the possibility, we compared the stereochemical outcome of the reactions run with H_2O and CH_3I. Indeed, the stereochemical outcome for the reaction of the classical sp^3 carbon center with an appended α-lithiosulfoxide group may be dependent on the electrophile; electrophiles containing oxygen atoms (H_2O, D_2O, and CH_2O) react with such sp^3 centers in THF with retention of configuration whereas CH_3I reacts with inversion.[18] In the case of cyclopropyl lithiosulfoxide **5**, MeOH and CH_3I react with retention of configuration (Table 1, entries 2 and 3; **6b** and **6c** have the same stereochemistry as determined by X-ray crystallographic analyses). The stereochemistry of other reaction products was assigned by analogy. Various electrophiles could be added to the reaction mixture and in all cases the disubstituted cyclopropyl sulfoxides were obtained as a single diastereoisomer (Table 1, entries 3–10). The next step, namely the second sulfoxide/lithium exchange was then investigated (Table 2). The sulfoxide/metal exchange is known to proceed with retention of configuration at the carbon center,[19] and since the lithiated cyclopropyl species are configurationally stable[20] the diastereoisomerically pure cyclopropyl sulfoxides (**6**) were transformed into the corresponding *cis*-lithiated cyclopropyl species (**8**) and then into enantiomerically pure products (*cis*-**9a–c**) after hydrolysis. Indeed, this stereochemical outcome was verified when cyclopropyl sulfoxide **6d** was treated with *n*BuLi (2 equiv) at −80 °C in THF and **6h** was treated with *t*BuLi (1 equiv) at −80 °C in THF (Table 2, entries 1 and 3). Similar results were obtained when **6g** was treated with *i*PrMgCl at room temperature in THF (Table 2, entry 2) or with *t*BuLi (1 equiv) at −80 °C in toluene (Table 2, entry 4). In all cases, the reaction proceeded smoothly and led to the expected *cis*-dialkylated cyclopropanes **9a–e** after hydrolysis; the products were isolated in good yields as a single isomer.

As expected, when the exchange was run in THF, the resulting basic tertiary organometallic species **8** rapidly reacted by deprotonating the solvent; therefore, conditions for additional alkylation reactions of **8** were found to work best in a nonbasic solvent such as toluene (Table 2, entry 4). In this case, the addition of MeOD led to the corresponding deuteriocyclopropane **9d** in 80% yield as single isomer. In addition, when **6j** was subjected to the sulfoxide/lithium exchange and subsequent hydrolysis, the corresponding (2-decylcyclopropyl)methanol[21] **9e** was isolated in greater than 97% *ee* (Table 2, entry 5, determined after correlation with an authentic sample).

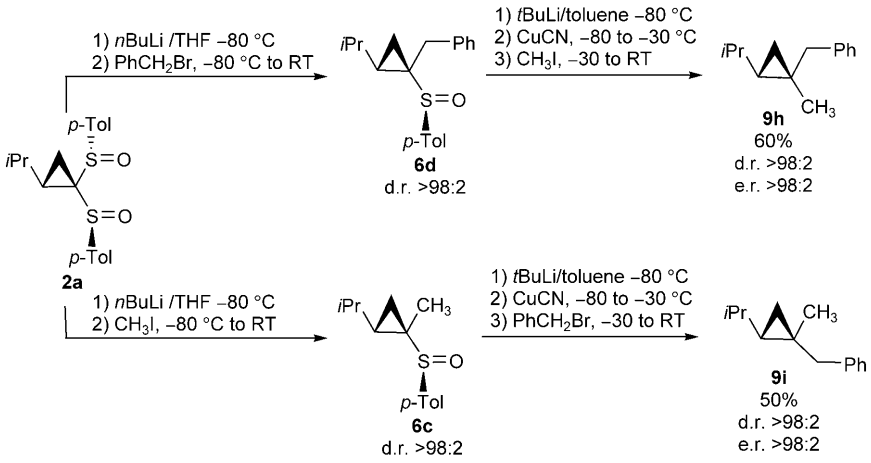
Table 2: Preparation of Enantiomerically enriched 1,2-di- and 1,2,2′-trisubstituted cyclopropane derivatives **9a–i**



Entry	Substrate, R	R^1	Reagent	R^2	d.r.[f]	Yield [%][g]
1[a]	**6d**, *i*Pr	$PhCH_2$	H_2O	H	>98:2(**9a**)	70
2[b]	**6g**, $nC_{10}H_{21}$	CH_3	H_2O	H	>98:2(**9b**)	80
3[c]	**6h**, $nC_{10}H_{21}$	*n*Bu	H_2O	H	>98:2(**9c**)	82
4[d]	**6g**, $nC_{10}H_{21}$	CH_3	CH_3OD	D	>98:2(**9d**)	80
5[d]	**6j**, $nC_{10}H_{21}$	CH_2OH	H_2O	H	>98:2(**9e**)	50
6[d]	**6g**, $nC_{10}H_{21}$	CH_3	*n*PrCHO	CH(OH)Pr[h]	> 98:2(**9f**)	60
7[d]	**6i**, $PhCH_2CH_2$	CH_3	*p*-TolylSO$_3$S-*p*-Tolyl	*S*-Tol	>98:2(**9g**)	82
8[e]	**6d**, *i*Pr	$PhCH_2$	CH_3I	CH_3	>98:2(**9h**)	60
9[e]	**6c**, *i*Pr	CH_3	$PhCH_2Br$	$PhCH_2$	>98:2(**9i**)	50

[a] *n*BuLi in THF was used for the exchange. [b] *i*PrMgCl in THF at RT was used for the exchange. [c] *t*BuLi in THF was used for the exchange. [d] *t*BuLi in toluene was used for the exchange. [e] After the exchange, a Li to copper transmetalation with CuCN was performed for the alkylation reaction. [f] Determined on the crude reaction mixture by ^{1}H NMR spectroscopy. [g] Yield of isolated product after purification by column chromatography. [h] A 1:1 mixture of isomers is formed; isomeric at the carbinol center.

Stereo- and enantiomerically pure cyclopropyl lithium species **8** could also react with several electrophiles, such as an aldehyde (Table 2, entry 6) or *S*-*p*-tolyl-4-methylbenzenethiosulfonate (Table 2, entry 7). However, when less reactive electrophiles were used, such as alkyl halides, tertiary cyclopropyl lithium species **8** was not nucleophilic enough in toluene (addition of THF would lead to a protonation of the tertiary alkyl lithium species as previously stated),[22] necessitating a transmetalation to the organocopper species. The transmetalation of a cyclopropyl metal species to the cyclopropyl copper species occurs with retention of configuration,[23] and cyclopropyl copper species are configurationally stable;[24] thus subjecting **6d** and **c** to modified conditions including transmetalation and subsequent addition of alkyl halides as electrophiles (Table 2, entries 8 and 9) led to alkylated cyclopropane derivatives **9h** and **9i** respectively with retention configuration. This methodology leads to the preparation of the two diastereo- and enantiomerically pure trisubstituted cyclopropyl derivatives from the same precursor. As shown in Scheme 3, permutation of the electrophiles introduced after each of the two sulfoxide/lithium exchange reactions allows the formation of the two diastereoisomers (**9h** and **i**), which have different absolute configurations at the quaternary centers.



Scheme 3. Independent preparation of the two diastereo- and enantiomerically pure cyclopropanes.

In conclusion, selective sulfoxide/lithium exchange reactions lead to the unique preparation of diastereo- and enantiomerically pure polyalkylated cyclopropanes. This new reaction allows the independent formation of both diastereoisomers from a common starting material. Additional studies are now ongoing in our research group to extend this methodology to more functionalized substrates.

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