Single Electron Transfer Mechanism in the Reaction of 1,3-Dithianyllithium and Alkyl Iodides[†,1]

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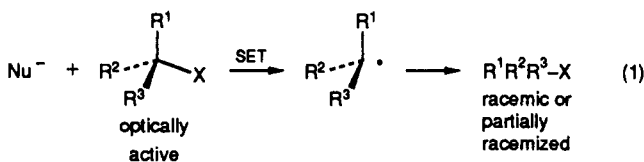
The reaction between 2-lithio-1,3-dithiane and optically active (*R*)-2-iodooctane was found to proceed with complete inversion of configuration. This result suggests that the S_N2 (rather than single electron transfer (SET)) mechanism is the preferred pathway for reaction between dithianyllithium and unhindered alkyl halides. When the neopentyl-type radical probe 5,5-dimethyl-6-iodo-1-hexene was used as the substrate halide, 6–11% cyclized alkylated product was obtained. This result suggests that when the S_N2 pathway is blocked, SET mechanisms become operative to some extent, at least with iodide as the halogen. The reaction of dithianyllithium and (*R*)-2-iodooctane and 5,5-dimethyl-6-iodo-1-hexene, with hexane as the solvent, proceeds under heterogeneous conditions to bring about complete racemization or cyclization of the respective iodide. These results demonstrate for the first time that 2-lithio-1,3-dithiane can act as electron donor in reactions initiated by electron transfer to alkyl iodides.

Introduction

The pioneering experiments that demonstrated the importance of single electron transfer (SET) mechanisms in the Grignard[2] and organocuprate[3] reactions have stimulated the search for related electron-transfer mechanistic pathways in many other organic reactions.[4] In this respect, Chung and Dunn,[5] and Juaristi et al.[6] examined the possible involvement of radical intermediates in the reactions of 1,3-dithianyllithium (1-Li) with alkyl halides. Both groups of researchers found no evidence for SET mechanisms because, for example, the reaction of 1-Li with 6-halo-1-hexenes 2 afforded the products expected from an S_N2 (rather than SET) mechanism. (Scheme I). Noting, however, that cyclization of the radical probe is always in competition with other pathways,[7,8] the question can be raised as to whether the cyclized product 4 does not form because coupling of the radical intermediates is much faster than cyclization ($k_1 \gg k_{cyclztn}$ in Scheme II). On this basis it was then decided to further explore the mechanism of the reaction of 1-Li with other more efficient radical probes.

A particularly attractive test is the one based on the stereochemical outcome of the reaction between the nucleophile and an optically active halide:[9] because racemization of the SET-derived radical should be extremely fast ($\sim 10^{13}$ s^{-1}), this pathway would be easily detected if present (eq 1).

$$Nu^- + \underset{\substack{\text{optically}\\\text{active}}}{R^2\text{---}\overset{R^1}{\underset{R^3}{\diagup}}X} \xrightarrow{SET} R^2\text{---}\overset{R^1}{\underset{R^3}{\diagup}}{}^{\bullet} \longrightarrow \underset{\substack{\text{racemic or}\\\text{partially}\\\text{racemized}}}{R^1R^2R^3\text{--}X} \quad (1)$$

On the other hand, one can ask whether SET will dominate when the S_N2 route is blocked. Indeed, the neopentyl-type probe 5 has been developed,[10] which not only prevents polar displacements but also cyclizes ca. 20 times faster than the primary hexenyl radical 2$^{\bullet}$ ($k_c = 2.2 \times 10^5$ s^{-1}, ref 11) when the corresponding radical is produced (eq 2).

The fundamental importance of mechanistic studies of this sort is augmented by the paucity of reports on carbon

$$\text{5} \xrightarrow[-I^-]{e^-} \xrightarrow[3.6 \times 10^6 s^{-1}]{k =} \quad (2)$$
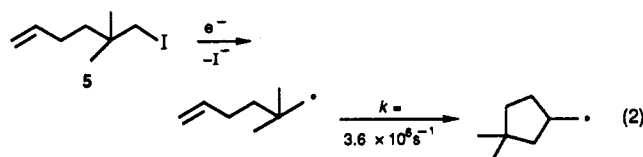
nucleophiles acting as electron donors in SET reactions[8] and the obvious need of a fuller understanding of the chemistry of 1,3-dithian-2-yllithium, which is such a widely used synthetic reagent.[12]
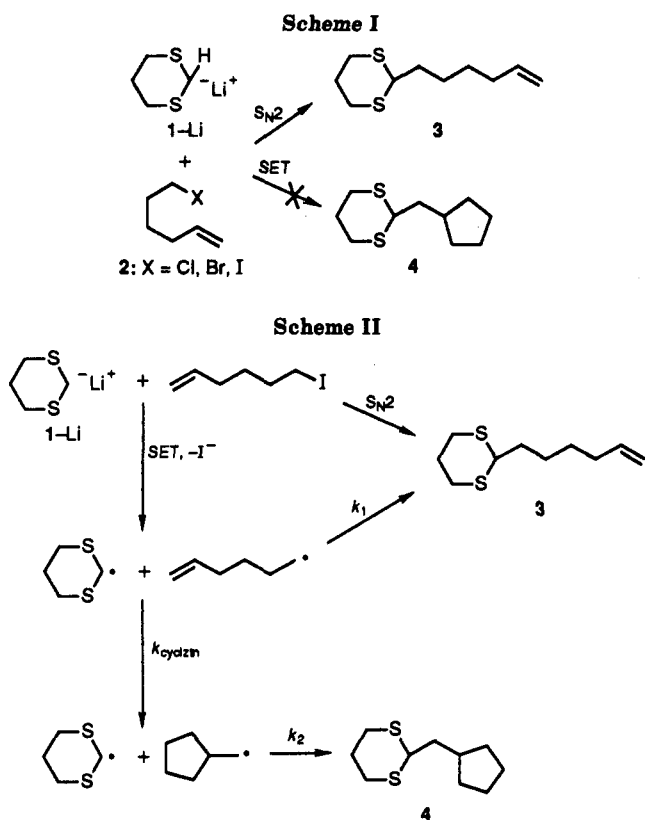
Results and Discussion

A. Examination of the Stereochemistry of the Reaction of 1,3-Dithianyllithium (1-Li) with Optically

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[†] Dedicated to Professor Andrew Streitwieser, Jr., with respect.
[‡] Extracted from the M.Sc. Thesis of H.A.J.-V., Instituto Politécnico Nacional, México, 1989. Present address: Department of Chemistry, Yale University, New Haven, CT 06511.
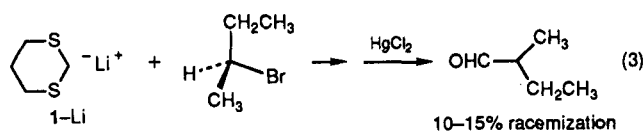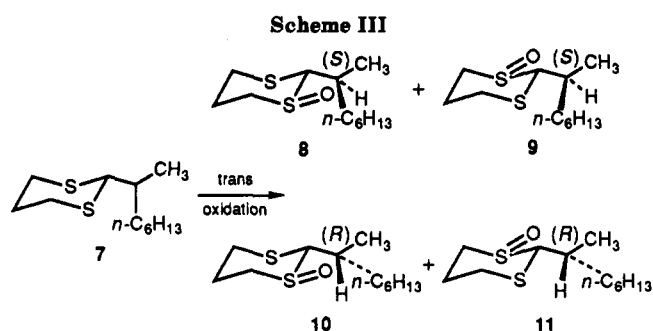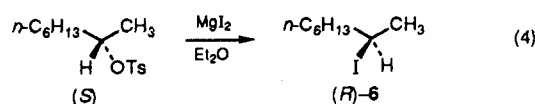
(1) Presented in part at the XXIV Congress of the Mexican Chemical Society: Juaristi, E.; Jiménez-Vázquez, H. A. *Rev. Soc. Quím. Méx.* **1988**, *32*, abstract 174.
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(4) See, for example: (a) San Filippo, J.; Silbermann, J.; Fagan, P. J. *J. Am. Chem. Soc.* **1978**, *100*, 4834–4842. (b) Kuivila, H. G.; Smith, G. F. *J. Org. Chem.* **1980**, *45*, 2918–2919. (c) Russell, G. A.; Jawdosiuk, M.; Makosza, M. *J. Am. Chem. Soc.* **1979**, *101*, 2355–2359. (d) Buncel, E.; Menon, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 3499–3507. (e) Kitching, W.; Olszowy, H.; Harvey, K. *J. Org. Chem.* **1981**, *46*, 2423–2424. (f) Guthrie, R. D.; Nutter, D. E. *J. Am. Chem. Soc.* **1982**, *104*, 7478–7482. (g) Bailey, W. F.; Gagnier, R. P.; Patricia, J. J. *J. Org. Chem.* **1984**, *49*, 2098–2107. (h) Bank, S.; Noyd, D. A. *J. Am. Chem. Soc.* **1973**, *95*, 8203–8205. (i) Ashby, E. C.; Bowers, J. S. *J. Am. Chem. Soc.* **1977**, *99*, 8504–8505. (j) Yamataka, H.; Fujimura, N.; Kawafuji, Y.; Hanafusa, T. *J. Am. Chem. Soc.* **1987**, *109*, 4305–4308. (k) Screttas, C. G.; Micha-Screttas, M. *J. Org. Chem.* **1978**, *43*, 1064–1071. (l) Ashby, E. C.; Goel, A. B. *Tetrahedron Lett.* **1981**, *22*, 1879–1880. (m) Ashby, E. C.; Coleman, D.; Gamasa, M. *J. Org. Chem.* **1987**, *52*, 4079–4085. (n) Ashby, E. C.; Goel, A. B. *Tetrahedron Lett.* **1981**, *22*, 1879–1880. (o) Ashby, E. C.; Coleman, D. *J. Org. Chem.* **1987**, *52*, 4554–4565. (p) Bordwell, F. G.; Harrelson, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 8112–8113. (q) Lund, T.; Lund, H. *Acta Chem. Scand.* **1986**, *B40*, 470–485. (r) Lexa, D.; Savéant, J.-M.; Su, K.-B.; Wang, D.-L. *J. Am. Chem. Soc.* **1988**, *110*, 7617–7625.
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(8) Ashby, E. C. *Acc. Chem. Res.* **1988**, *21*, 414–421.
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(12) (a) Seebach, D.; Corey, E. J. *J. Org. Chem.* **1975**, *40*, 231–237. (b) Gröbel, B. T.; Seebach, D. *Synthesis* **1977**, 357–402. (c) See, also: Hase, T. *Umpoled Synthons*; Wiley: New York, 1987.

Scheme I

Scheme II

Scheme III

A.1. Reaction of 1-Li with (R)-6 in THF. The conditions described by Seebach[13] were chosen: the (R)-2-iodooctane was added to the dithianyllithium at -20 °C and the reaction mixture was stirred at this temperature for 72 h, and at ambient temperature for 24 additional hours. The ^{1}H NMR spectra of aliquots taken each 24 h showed that the reaction was complete (all starting iodide had been consumed) at the time of the first analysis. More relevant is the observation that the optical rotation of the isolated product was a constant, $[\alpha]^{28}_D = -8.7°$ ($c = 13$, ether), corresponding to inversion of configuration (eq 5). This result indicates also that under the reaction conditions no isomerization of the alkylated product takes place once it is formed.
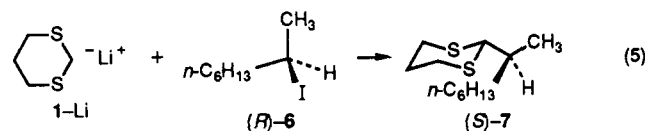
Active 2-Iodooctane (6). Some time ago, Seebach et al.[13] reported that the alkylation of lithiodithianes with (S)-bromobutane proceeds with over 85% degree of inversion (proportion of the S_N2 reaction with Walden inversion). Because the optical purity of the alkylated derivatives was measured on the hydrolyzed carbonyl compounds, the 10–15% racemization observed could have originated either during the alkylation or via the enolate of the derived aldehyde (eq 3).[13,14]

In order to obtain a quantitative estimate of the degree of inversion *at the alkylation step*, we prepared optically active (R)-2-iodooctane ((R)-6) from the precursor 2-octanol, which can be resolved via the brucine diastereomeric salts, according to the Ingersoll procedure.[15] Indeed, the tosylate of (S)-(+)-2-octanol afforded (R)-6, with almost complete inversion of configuration, when treated with magnesium iodide in ether[16] (eq 4). From the $[\alpha]^{28}_D = -43.9°$ (neat) measured for (R)-6, its optical purity was determined as 90%.[17]

Because the maximum rotation of 7 has not been described in the literature,[20] we first attempted to determine the optical purity of (S)-7 by recording its ^{1}H NMR spectrum in the presence of chiral Eu(hfc)$_3$ shift reagent. However, the poor Lewis basicity of the sulfur atoms in 7 did not allow for significant coordination with the europium, and as a consequence no useful lanthanide-induced shifts (LIS) were observed.

It was then deemed necessary to incorporate in 7 a functionality that would complex to Eu(hfc)$_3$, so that signals for the enantiomers could be resolved. Of course, such modification of the substrate should not alter the ratio of configurations at the center of chirality present in 7. The obvious decision was made to oxidize the dithiane ring to a monosulfoxide derivative with sodium periodate. This reaction proceeds in high yield, leaving untouched the chirality center of interest. In addition, it is known that 2-substituted 1,3-dithianes are oxidized stereoselectively to afford the trans product.[21]

In the present system, oxidation of 7 creates *two* new stereogenic centers, and therefore a maximum of eight stereoisomers can be expected. Because of the observed exclusive formation of the trans sulfoxides, the number of possible stereoisomers is reduced to four (Scheme III). Complete inversion of configuration in the reaction of 1-Li with *optically pure* (R)-6 is predicted to yield diastereo-

(13) Seebach, D.; Steinmüller, D.; Demuth, F. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 620–621.
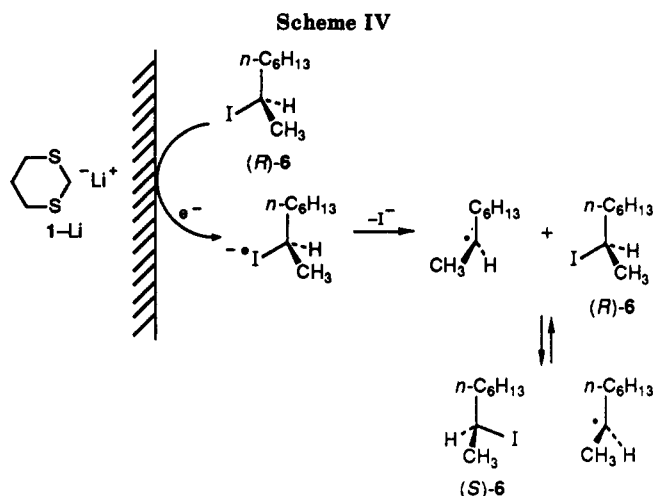
(14) Seebach, D. Personal communication.

(15) Ingersoll, A. W. *Org. React.* **1962**, *2*, 376–414.

(16) Place, P.; Roumestant, M. L.; Gore, J. *Bull. Soc. Chim. Fr.* **1976**, 169–176.

(17) From the rotation data reported by Hoffmann[18] for 2-iodooctane, $\alpha = 64.2°$, the maximum specific rotation was estimated by dividing this value by its density:[19] $[\alpha]_D = 64.2/1.322 = 48.6°$.

(18) Hoffmann, M. R. *J. Chem. Soc.* **1964**, 1249–1251.

(19) *Handbook of Chemistry and Physics*; Chemical Rubber Co.: New York, 1967.

(20) Starting from the *S* iodide, Seebach's group obtained (R)-7 with $[\alpha]_D = +8.3°$ ($c = 13$, ether);[13,14] however, the optical purity of these compounds was not ascertained.

(21) (a) Cook, M. J.; Tonge, A. P. *Tetrahedron Lett.* **1973**, 849–850. (b) Carey, F. A.; Dailey, O. D.; Hernández, O.; Tucker, J. R. *J. Org. Chem.* **1976**, *41*, 3975–3978. It is interesting to speculate that the regioselectivity found in this reaction originates from a stereoelectronic effect: $n_S \rightarrow \sigma^*_{C-S(O)}$ hyperconjugation makes difficult the oxidation of the second sulfur in the ring.

Scheme IV

Scheme V[a]

[a] (a) $SOCl_2$, Py; (b) Na/Et_2O; (c) CrO_3/H_2SO_4, acetone; (d) KOH, $EtBr/DMSO$; (e) 2 × LDA, $CH_3I/HMPA$; (f) $LiAlH_4$, Et_2O; (g) PPh_3, I_2/Py.

Scheme VI

meric sulfoxides **8** and **9** exclusively (Scheme III).

In the event, exposure of the sulfoxides obtained by oxidation of optically active **7** to 0.4 equiv of $Eu(hfc)_3$ showed only two diastereomeric products in the ^{13}C NMR spectrum.[22,23] Since our optically active iodide consisted of 95% (*R*)-**6** and 5% (*S*)-**6** (see above) and the spectroscopic result indicates that the *R* products **10** and **11** do not exceed 5%, we conclude that the alkylation of dithianyllithium proceeds with complete inversion, i.e., there is *no manifestation of a SET mechanism in the reaction of 1-Li with a secondary iodide.*[24] This result is in full agreement with the observations recorded with primary halides.[5,6]

A.2. Reaction of 1-Li with (R)-6 in Hexane. It has been suggested that electron-transfer mechanisms compete more effectively with the S_N2 mechanism in less effective cation-solvating media.[25] For this reason it was then decided to carry out the reaction between 2-lithio-1,3-dithiane (1-Li) and (*R*)-2-iodooctane in hexane at –20 °C. As it turned out, the organolithium reagent was not soluble under these conditions, and, not surprisingly, the crude product gave no indication of formation of **7** (by ^1H NMR spectroscopy). This apparent blank experiment provided nevertheless a most unusual result: *the recovered iodide was optically inactive!*

The explanation we propose for this observation is as follows: electron transfer is facilitated by the heterogeneous surface lattice,[26] which probably also helps to stabilize the dithianyl radicals that are generated. A chain reaction[27-30] could then be responsible for a rapid race-

mization of the 2-iodooctane (Scheme IV).

B. Examination of Products in the Reaction of 1-Li with 5,5-Dimethyl-6-iodo-1-hexene (5). As indicated in the Introduction, the polar S_N2 displacement mechanism is essentially blocked with this neopentyl-type iodide. Can SET pathways become now dominant?

Synthesis of 5,5-Dimethyl-6-iodo-1-hexene (5). Initially we prepared **5** according to the method described by Ashby et al;[30] however, the overall yield we achieved starting from allyl chloride was a meager 1.5% (Ashby et al. obtained 13.3% yield starting from 4-bromo-1-butene; two steps less). Because this route also involves a not so trivial generation of a tertiary Grignard reagent, it was decided to explore the alternative route shown in Scheme V. This sequence involves reproducible reactions and affords the desired iodide in 15.2% overall yield.

The reactions between 2-lithio-1,3-dithiane (generated from 1,3-dithiane with 1 equiv of *n*-BuLi at –20 °C) and the alkyl halide **5** were carried out under nitrogen, adding the anion to the substrate via cannula, and stirring the reaction mixture for 90 min at –20 °C and then for 2 h at ambient temperature, afterwhich D_2O was added in order to verify the formation of 1-Li when 1,3-dithiane was recovered.

B.1. Reaction in THF. The ^1H NMR spectrum of the crude product showed mostly starting materials; deuteration of the 1,3-dithiane exceeded 80%, which confirms the presence of 1-Li in the reaction medium. Nevertheless, vapor-phase chromatography (VPC) analysis indicated the formation of several products (ca. 13) in very small

(22) ^1H NMR spectra of sulfoxides 8–11 (prepared from racemic iodide 6) were not sufficiently resolved even in the presence of 0.5 equiv of $Eu(hfc)_3$; much better results were achieved from ^{13}C NMR analysis (compare Figures 1a and 1b).

(23) The most useful signals are the ones that correspond to C(6). In the spectrum of the racemic material (Figure 1b), signals at 62.37, 61.50, and 61.11 (br) ppm are observed. The broad signal at 61.11 ppm apparently corresponds to two stereoisomers. In the spectrum of the optically active material (Figure 1c), only the two lower field signals are present.

(24) According to these arguments, the optical purity of our dithiane 7 is 90%; therefore, its maximum $[\alpha]_D$ = –9.7° (neat), assuming linearity in α vs c.

(25) Kuivila, H. G.; Alnajjar, M. S. *J. Am. Chem. Soc.* **1982**, *104*, 6146–6147.
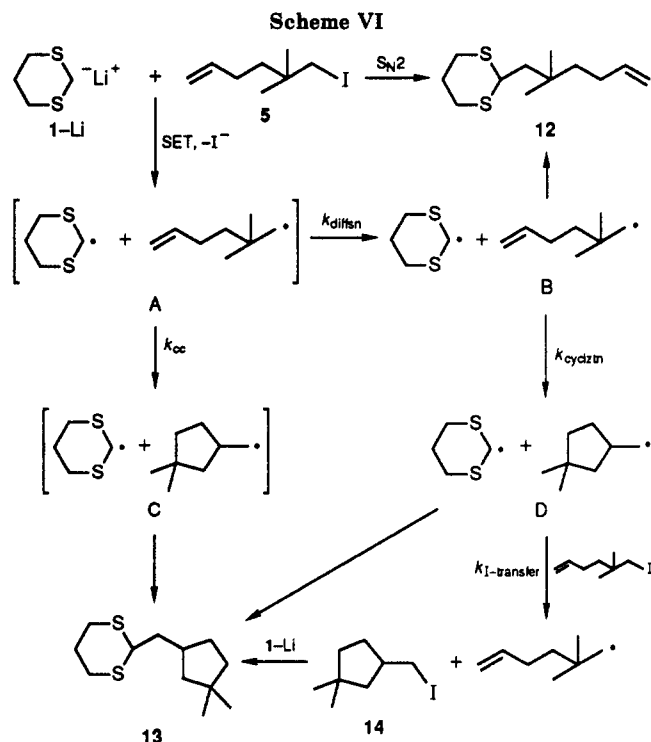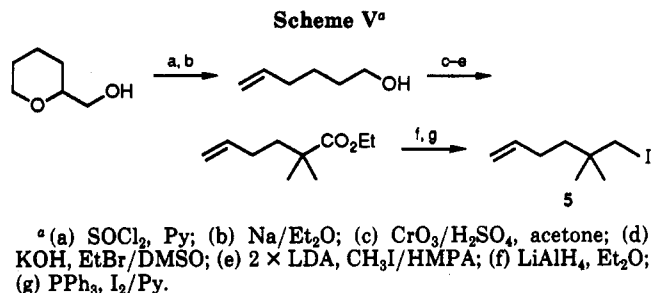
(26) This phenomenon is well known in metal surfaces, see; for example: Garst, J. F.; Swift, B. L. *J. Am. Chem. Soc.* **1989**, *111*, 241–250.

(27) Newcomb, M.; Sanchez, R. M.; Kaplan, J. *J. Am. Chem. Soc.* **1987**, *109*, 1195–1199.

(28) Newcomb, M.; Curran, D. P. *Acc. Chem. Res.* **1988**, *21*, 206–214.

(29) Ashby, E. C.; Wenderoth, B.; Pham, T. N. *J. Org. Chem.* **1984**, *49*, 4505–4509.

(30) Ashby, E. C.; De Priest, R. N.; Goel, A. B.; Wenderoth, B.; Pham, T. N. *J. Org. Chem.* **1984**, *49*, 3545–3556.
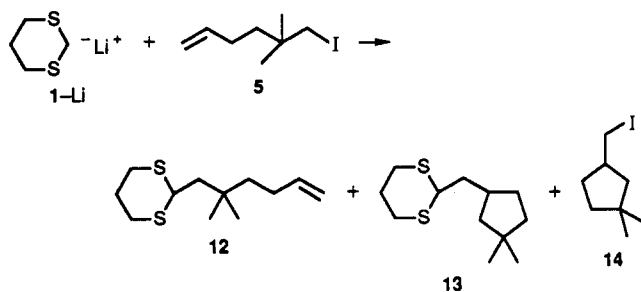
Table I. Main Products Obtained in the Reactions of 1-Li
and 5[a]

solvent	temp (°C)	% yield		
		12	13	14
THF	-20 → 25	1.7	6	
THF–TMEDA	-20 → 25	2.5	11	
hexane	0 → 25			86

[a] VPC yields of the crude reaction products.

amounts (ca. 14% combined yield, relative to the peak of recovered iodide 5). The most abundant of these products was obtained in 6% yield (VPC) and could be purified and identified (^{1}H and ^{13}C NMR and high resolution mass spectrum) as 13, *the product expected from a SET mechanism*. The second most important product (1.7% by VPC) could be separated and characterized as 12, the product expected from an S_N2 mechanism or from coupling of intermediate radicals as shown in Scheme VI.

The rest of the products were obtained in very small amounts (<1%) and could not be separated or identified satisfactorily.[31] Because some loss of 1,3-dithiane was notorious, it is likely that some of these materials results from decomposition of 1-Li. Table I collects the most relevant observations from this reaction.

What is the origin of 13? On the basis of the New-comb/Curran recent analysis of these types of reactions,[27,28] the following considerations seem pertinent:

(1) A reasonable representation of the reaction mechanism can be formulated along the lines of Scheme VI. Here A represents an initial hexenyl/dithianyl radical pair still in the solvent cage and B freely diffusing radicals.

While we were initially inclined to propose that cyclization of the hexenyl radical within the caged radical pair gives a radical pair containing the cyclopentylmethyl and dithianyl radicals (A → C; Scheme VI), kinetic evidence[33,34] indicates that such a process is not possible. Indeed, the rate constant for diffusion-limited escape from the radical cage in a low viscosity solvent like THF is about 2×10^{10} s^{-1} at 25 °C whereas the rate constant for cyclization of the dimethylhexenyl radical is 3.6×10^6 s^{-1}. Therefore, escape from the cage is about 4 or 5 orders of magnitude faster than rearrangement.[33] In other words, $k_{diffsn} \gg k_{cc}$.
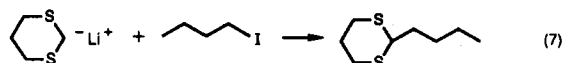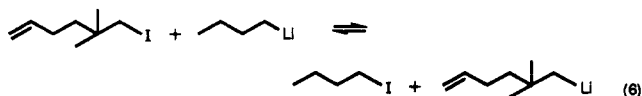
(Scheme VI) and the only way the radical can rearrange is when it is formed as a free species in solution (C → D; Scheme VI).

Formation of the addition product 13 from freely diffusing radicals appears to require a selective cross-coupling of dithianyl and cyclopentylmethyl radicals in competition with the many other fast reactions that R•s might be expected to undergo. In an elegant analysis, Fischer[35] has shown that in a system in which two radicals are generated, one of which (here the dithianyl) is persistent[36] and disappears mainly by cross-reaction while the other (here cyclopentylmethyl radical) can disappear by cross-reaction and a number of other paths, the former will quickly build up in concentration to the point where cross-reaction becomes the dominant fate of both species. Therefore, process D → 13 could explain the formation of the latter. Nevertheless, it is surprising that no significant amounts of self-termination product (dithiane dimer) was identified.

(2) The rearranged product 13 could also originate from a normal S_N2 reaction between rearranged iodide 14 (produced by iodine atom transfer reactions[28]) and 2-lithio-1,3-dithiane. However, the absence of cyclized iodide 14 in the reaction mixture (Table I) could indicate that I-atom transfer ($k_{I\text{-transfer}}$, Scheme VI) reactions are not important here. Furthermore, in our hands, 1-Li and 14 in solvent THF failed to react, possibly due to significant steric requirements in the substrate iodide.

(3) Several arguments can be presented against an $S_{RN}1$ chain as responsible for the formation of 13. $S_{RN}1$ chain reactions are expected to be much slower than I-atom transfer,[28] which seems to be inefficient here (see above). In addition, the localized nature of the 1,3-dithian-2-yl-carbanion[37,38] does not facilitate the formation of radical anions 12•$^-$ and 13•$^-$.

(4) Could decomposition products of 2-lithio-1,3-dithiane have initiated the SET reactions? 1-Li and 5 were also allowed to react for 12 h at ambient temperature to probe this question. The observation that a similar yield of the SET product 13 was found after 2 and 12 h of reaction time at ambient temperature, whereas the loss of heterocycle is about double in the latter case, seems to be a strong evidence against the exposed argument.

(5) In principle, adduct 13 can arise from the reaction of hexenyl carbanion and 2-iodo-1,3-dithiane; the former produced by halogen–metal interchange with *n*-BuLi,[32] followed by cyclization[39] (eqs 8 and 9), and the latter again by halogen–metal exchange with iodide (eq 10).

While reactions 8 and 9 seem kinetically favorable,[32,39] the ΔpK_a for the conjugate acids of 1-Li and 5-Li is so large and positive[40] that reaction 10 seems unlikely on thermodynamic grounds.

(6) That the initial electron transfer could be due to adventitious impurities cannot be ruled out; nevertheless, all solvents and reagents employed were carefully purified by distillation, crystallization, or sublimation before use (see Experimental Section).

(31) The ^{1}H NMR spectrum of one minor product corresponds to 2-*n*-butyl-1,3-dithiane, presumably formed by halogen–metal exchange[32] between *n*-BuLi and iodide 5, following by reaction of *n*-BuI with 1,3-dithianyllithium (eqs 6 and 7).

(32) Cf. Bailey, W. F.; Patricia, J. J. *J. Organomet. Chem.* 1988, *352*, 1–46.
(33) Newcomb, M. Private communication.
(34) Walling, C. *J. Am. Chem. Soc.* 1988, *110*, 6846–6850.

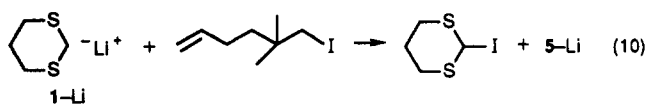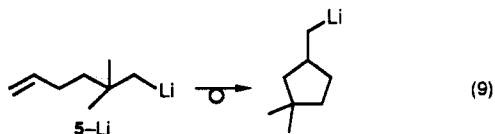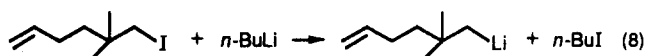(35) Fischer, H. *J. Am. Chem. Soc.* 1986, *108*, 3925–3927.
(36) The kinetic stability of sulfur-substituted radicals is well known: Block, E. *Reactions of Organosulfur Compounds*; Academic Press: New York, 1978; Chapter 5.
(37) Streitwieser, A., Jr.; Williams, J. E., Jr. *J. Am. Chem. Soc.* 1975, *97*, 191–192.
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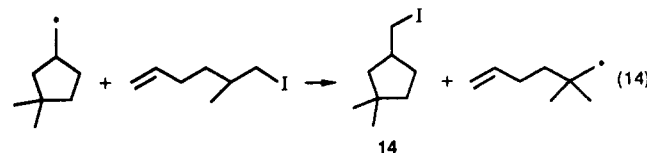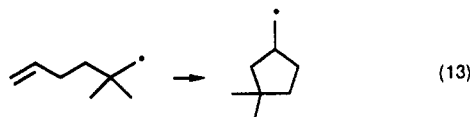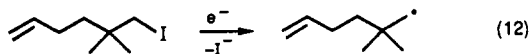
(8)

(9)

5-Li

(10)

1-Li

radical-chain isomerization of suitable substrates.[41,42]

Conclusions

(1) The observation that the reaction of 2-lithio-1,3-dithiane (1-Li) with (R)-2-iodooctane proceeds with complete inversion of configuration suggests that *the S$_N$2 mechanism is the normal pathway* for reaction between dithianyllithium and unhindered alkyl halides.

(2) The low-yield isolation of rearranged product **13** from the reaction of 1-Li with the neopentyl-type probe **5** indicates that *when the S$_N$2 pathway is blocked*, SET mechanisms become operative, although quite reluctantly. This skepticism is especially justified when considering that chain reactions can greatly amplify the extent of radical formation and that the rearranged product **13** could form by a conventional S$_N$2 reaction of the dithianyllithium with cyclized iodide **14**.

(3) The complete racemization of the optically active probe, and the high-yield production of cyclized iodide **14** *under heterogeneous conditions* (1-Li in hexane), shows for the first time that 2-lithio-1,3-dithiane can act as an e$^-$ donor initiator. This result may have useful synthetic applications.

B.2. Reaction in THF–TMEDA. In this experiment 1 equiv of N,N,N',N'-tetramethylethylenediamine (TMEDA) was added in order to solvate the lithium counterion, a fact that could favor either S$_N$2 or SET mechanisms. Starting materials 1 and 5 were again mostly recovered, and deuteration of the 1,3-dithiane exceeded 90%. Significantly, the contributions of **12** and **13** to the crude product increased to 2.5 and 11%, respectively (Table I). These higher yields could be due to the greater reactivity of the solvated carbanion, i.e., a greater tendency to give off an electron.

B.3. Reaction in Hexane. As reported in section A.2., the 1,3-dithianyllithium is not sufficiently soluble in hexane. Nevertheless, iodide 5 was exposed to 1-Li for 90 min at 0 °C and 2 h at ambient temperature before quenching with D$_2$O. Although the starting 1,3-dithiane was recovered (ca. 92% deuteration), most of the iodide 5 was consumed; the cyclized iodide 14 was obtained instead in ca. 86% VPC yield! In addition, a very small amount of a product tentatively assigned as 1,1,3-trimethylcyclopentane was isolated (cf. eq 11).

+ solvent–H → + S· (11)
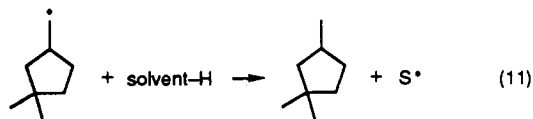
The possibility that a slight excess of n-BuLi was responsible for the formation of cyclized iodide 14 via lithium–halogen exchange and subsequent cyclization of the hexenyl carbanion[39] was deemed unlikely when in a control experiment 1 equiv of n-BuLi in hexane was found to be ca. 10 times less efficient than 1-Li in causing the isomerization of iodide 5.

The results obtained in hexane support those described in section A.2., i.e., that electron transfer from 2-lithio-1,3-dithiane can be an efficient process under heterogeneous conditions. The high yield of cyclized iodide 14 must be due to a chain reaction[27-30] (eqs 12–14) and to the inaccessibility of the 1,3-dithianyl radical in the crystal lattice (this explains the absence of products 12 and 13).

(12)

(13)

(14)

14

The high-yield preparation of cyclized iodide 14 also suggests that this method could be of synthetic use for

Experimental Section

General Information. Melting points, determined with a Mel-Temp apparatus, are uncorrected.

Proton NMR spectra were recorded on Varian EM-360 (60 MHz), Varian EM-390 (90 MHz), or JEOL FX-90Q (89.55 MHz) spectrometers. Carbon-13 NMR spectra were recorded on the JEOL FX-90Q (22.49 MHz) instrument operated in pulsed Fourier transform mode and locked on solvent deuterium. Samples were prepared as CDCl$_3$ or CCl$_4$ solutions with ~1% Me$_4$Si as internal reference in 5-mm o.d. tubes.

Flasks, stirring bars, and hypodermic needles used for the generation and reactions of alkyllithiums were dried for at least 4 h at 120 °C and allowed to cool in a desiccator over anhydrous calcium sulfate. Anhydrous ether solvents were obtained by distillation from benzophenone ketyl. Hexane (HPLC grade) was distilled from LiAlH$_4$ under nitrogen and TMEDA from calcium oxide under a nitrogen atmosphere. The n-butyllithium employed was titrated according to the method of Juaristi et al.[43]

The chromatographic analyses were performed on Varian 9176 (thermal conductivity detector) and Varian 2830 (flame ionization detector) VPC chromatographs provided with steel columns ($^1/_8$ in. i.d. and 210-cm length). The injection block and the detector were maintained at 260 °C.

The optical rotations were determined on a Perkin-Elmer 241 polarimeter provided with 1- or 10-cm cells. The sodium D line (589 nm) was used. Before each measurement, the solutions or samples in the cell were allowed to reach the instrument's temperature (28–29 °C).

2-(Chloromethyl)tetrahydropyran. In a 250-mL, round-bottom flask provided with addition funnel, magnetic stirrer, and rubber septa, 50.0 g (0.43 mol, 48.6 mL) of tetrahydropyran-2-methanol and 51.0 g (0.65 mol, 52.2 mL) of dry pyridine were placed under nitrogen. The flask was submerged in an ice–water bath and 62.5 g (0.53 mol, 38.3 mL) of thionyl chloride freshly distilled was added dropwise. The reaction mixture was stirred for 14 h (clear → milky → red → blackish red) and then extracted several times with 40-mL portions of ether until the extracts were colorless (ca. 400 mL ether total). The ether extracts were combined and washed three times with 50-mL portions of water, once with saturated aqueous NaCl solution, and once with saturated aqueous K$_2$CO$_3$. The organic phase was then dried over anhydrous

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Na$_2$SO$_4$, concentrated in a rotary evaporator, and distilled (75–77 °C/29 mmHg; lit.[44] by 56–57 °C/15 mm) to afford 42.3 g (73% yield) of the desired product as a colorless liquid: ^{1}H NMR (90 MHz, CCl$_4$) δ 1.00–2.10 (m, 6 H), 3.37 (m, 4 H), 3.77–4.13 (m, 1 H); ^{13}C NMR (CDCl$_3$, 22.49 MHz) δ 77.13 [C(2)], 68.48 [C(6)], 47.42 [C(7)], 29.09 [C(3)], 25.54 [C(5)], 22.85 [C(4)]; IR, 2939 (s), 2850 (s), 2738 (w), 1098 (s), 1083 (s), 1060 (s), 740 (m) cm^{-1}.

5-Hexen-1-ol. In a 500-mL round-bottom flask with a nitrogen atmosphere, 21.3 g (0.93 mol) of sodium and 60 mL of xylene were placed. The flask was capped with rubber septa and heated carefully until the sodium melted, at which point vigorous stirring was initiated so that the metal was divided in very small spheres. The flask was then allowed to cool to ambient temperature and fitted with condenser, addition funnel, and magnetic stirrer. The xylene was removed with a cannula, the sodium was rinsed twice with dry ether and then suspended in 130 mL of ether. From the addition funnel 42.3 g (0.32 mol) of 2-(chloromethyl)tetrahydropyran in 40 mL of ether was added slowly. When the exothermic reaction began, the flask was submerged in an ice–water bath. When the addition was complete the reaction mixture presented a sky-blue color. Stirring was continued for 16 h and then the residual sodium was decanted and removed by filtration. The filtrate was carefully treated with 100 mL of water (blue → yellow), washed with 100 mL of saturated brine solution, dried over anhydrous Na$_2$SO$_4$, and concentrated. The crude product was distilled (72–73 °C/25 mmHg; lit.[45] by 152–155 °C) to furnish 26.4 g (83.5% yield) of the desired product as a colorless liquid: ^{1}H NMR (90 MHz, CCl$_4$) δ 1.23–1.75 (m, 4 H), 1.85–2.30 (m, 2 H), 3.00 (s, 1 H), 3.40–3.70 (m, 2 H), 4.92 (ddt, 1 H, J_{gem} = 2.3 Hz, J_{cis} = 10.5 Hz), 4.97 (m, 1 H), 5.78 (ddt, 1 H, J_{vic} = 6.3 Hz, J_{cis} = 10.5 Hz, J_{trans} = 18 Hz); IR, 3348 (s), 3076 (m), 2934, 2862 (s), 1641 (m), 1441 (s), 1070, 1048 (s), 994 (s), 910, 637 (m) cm^{-1}.

Hex-5-enoic Acid. In a 1000-mL round-bottom flask provided with thermometer, mechanical stirrer, and addition funnel 600 mL of acetone (previously distilled over KMnO$_4$) and 6 g (53 mmol, 7.2 mL) of 5-hexen-1-ol were placed. The flask was immersed in an ice–water bath, and 40 mL of a 8 N solution of chromic acid[46] was added dropwise with stirring and maintaining the temperature below 5 °C (orange → green). The addition was stopped when the orange color persisted (ca. 30 mL chromic acid solution), and the contents of the flask were transferred to a separatory funnel and diluted with 600 mL of water before the product was extracted with three 150-mL portions of methylene chloride. The combined extracts were washed with two 240-mL portions of water and the desired product was then separated from the organic phase in two 240-mL portions of aqueous potassium bicarbonate (15 g of KHCO$_3$ in 480 mL of water). The aqueous phase was acidified with concentrated HCl and extracted with three 100-mL portions of methylene chloride. The combined extracts were dried over anhydrous sodium sulfate, filtered, concentrated, and distilled at reduced pressure to afford the desired product (bp 69.5–70.5 °C/0.9 mmHg; lit.[47] bp 110 °C (bath temperature)/1.5 mmHg) in 76.6% yield (4.63 g): ^{1}H NMR (90 MHz, CDCl$_3$) δ 1.78 (distorted q, 2 H), 2.13 (dt, 2 H, J_{vic} = 6.5 Hz), 2.40 (t, 2 H, J_{vic} = 7.5 Hz), 4.90–5.25 (m, 2 H), 5.83 (ddt, 1 H, J_{vic} = 6.5 Hz, J_{cis} = 10.4 Hz, J_{trans} = 17.6 Hz), 10.73 (s, 1 H); IR, 3500–2300 (s), 3079, 2972, 2939, 1720 (s), 1642 (m), 1029 (m) cm^{-1}.

Ethyl Hex-5-enoate. The general procedure of Johnstone and Rose[48] was slightly modified. In a 250-mL round-bottom flask provided with magnetic stirrer, 10.3 g (90 mmol) of hex-5-enoic acid, 180 mL of DMSO, and 7.6 g (135 mmol) of powdered KOH were placed. The mixture was stirred at ambient temperature for 5 min and then 29.4 g (270 mmol, 20.2 mL) of ethyl bromide was added via syringe. Stirring was continued for 18 h and then the reaction mixture was diluted with 1000 mL of water. The

product was extracted with three 100-mL portions of CH$_2$Cl$_2$, and the combined organic extracts were washed with three 250-mL portions of water, dried over anhydrous Na$_2$SO$_4$, and concentrated. The desired product was purified by distillation at reduced pressure (40 °C/4 mmHg; lit.[49] bp 73–75 °C/27 mmHg) to afford 10.3 g (81.0% yield) of the pure product: ^{1}H NMR (90 MHz, CDCl$_3$) δ 1.24 (t, 3 H, J_{vic} = 6.7 Hz), 1.55–2.40 (m, 6 H), 4.14 (q, 2 H, J_{vic} = 6.7 Hz), 4.98 (ddt, 1 H, J_{cis} = 10.3 Hz), 5.03 (ddt, 1 H, J_{trans} = 17.0 Hz), 5.81 (ddt, 1 H, J_{vic} = 6.4 Hz, J_{cis} = 10.3 Hz, J_{trans} = 17.0 Hz); ^{13}C NMR (22.49 MHz, CDCl$_3$) δ 14.11 [CH$_3$], 24.00 [—CH$_2$CH$_2$CH$_2$—], 32.97 [=CCH$_2$], 33.51 [—CH$_2$C=O] 60.03 [OCH$_2$—], 115.18 [CH$_2$=], 137.61 [=CH—], 173.39 [C=O]; IR, 3077 (w), 2979, 2939 (m), 1737 (s), 1641 (m), 1180 (s) cm^{-1}.

Ethyl 2,2-Dimethylhex-5-enoate. The general procedure of Petragnani and Yonashiro[50] was followed. In a 250-mL flask provided with rubber septa and under nitrogen, 80 mL of THF and 8.61 g (85 mmol, 11.92 mL) of freshly distilled diisopropylamine were placed. The flask was immersed in an ice–water bath and then 32.7 mL of 2.6 M n-BuLi (85 mmol) was added to form the LDA, which was stirred at 0 °C for 30 min. The flask was then cooled to –78 °C (dry ice–acetone bath) and 11.5 g (81 mmol) of ethyl hex-5-enoate was added via cannula. Stirring was continued for 30 min at –78 °C before the addition of 13.8 g (97.2 mmol, 6.1 mL) of methyl iodide in 14 mL of dry hexamethylphosphoramide (HMPA). Following 30 min of further stirring the reaction mixture was transferred via cannula to a flask containing 85 mmol of LDA and treated with a second portion of CH$_3$I–HMPA. The reaction mixture was stirred at –78 °C for 30 min and then for 2 h at ambient temperature, before it was treated with 125 mL of a saturated aqueous ammonium chloride solution and diluted with 700 mL of water. The product was extracted with three 150-mL portions of ether, and the combined extracts were washed with 500 mL of water and 400 mL of saturated brine solution, dried over anhydrous Na$_2$SO$_4$, and concentrated. The dimethylated product was purified by reduced-pressure distillation (38.5–39.5 °C/0.1 mmHg; lit.[51] bp 75 °C/4 mmHg) to afford 9.54 g (69.1% yield) of the desired product as a colorless liquid: ^{1}H NMR (90 MHz, CCl$_4$) δ 1.14 (s, 6 H), 1.23 (t, 3 H, J_{vic} = 7.2 Hz), 1.43–1.73 (m, 2 H), 1.80–2.17 (m, 2 H), 4.11 (q, 2 H, J_{vic} = 7.2 Hz), 4.80–5.13 (m, 2 H), 5.90 (ddt, 1 H, J_{vic} = 6.3 Hz, J_{cis} = 10.5 Hz, J_{trans} = 17.7 Hz).

2,2-Dimethyl-5-hexen-1-ol. In a three-necked, 500-mL round-bottom flask provided with magnetic stirrer, condenser, and addition funnel, 2.24 g (56 mmol) of LiAlH$_4$ was placed under nitrogen. The flask was cooled to 0 °C, 20 mL of dry ether was added, and then 9.5 g (56 mmol) of ethyl 2,2-dimethyl-5-hexenoate in 50 mL of ether was added very slowly (2 h). The cooling bath was then removed and the stirring was continued for 12 h at ambient temperature. The flask was then again immersed in an ice–water bath, 30 mL of water was added in small portions, and then 30 mL of concentrated HCl in 150 mL of water was also added. The resulting homogeneous solution was transferred to a separatory funnel, the organic phase was removed, the aqueous phase was extracted with two 50-mL portions of ether, and the combined organic extracts were washed with two 100-mL portions of saturated aqueous NaHCO$_3$, dried over anhydrous Na$_2$SO$_4$, and concentrated. The crude product was distilled at reduced pressure (34–36 °C/0.07 mmHg; lit.[30] bp 68–69 °C/8 mmHg) to afford 6.32 g (88.0% yield) of a colorless liquid, identified as the desired alcohol: ^{1}H NMR (90 MHz, CDCl$_3$) δ 0.89 (s, 6 H), 1.20–1.47 (m, 2 H), 1.73–2.23 (m, 3 H, includes the OH), 3.31 (s, 2 H), 4.83–5.17 (m, 2 H), 5.87 (ddt, 1 H, J_{vic} = 6.3 Hz, J_{cis} = 10.7 Hz, J_{trans} = 16.7 Hz).

5,5-Dimethyl-6-iodo-1-hexene (5). 2,2-Dimethyl-5-hexen-1-ol (6.6 g, 51 mmol) was treated with 14.43 g (55 mmol) of triphenylphosphine and 12.94 g (51 mmol) of iodine according to the procedure of Ashby et al.[30] to furnish the crude product, which was distilled (30 °C/0.05 mmHg; lit.[30] bp 46 °C/1.5 mmHg) and further purified on a silica gel column (eluent hexane) to afford 8.0 g (66% yield) of **5** as a colorless liquid: ^{1}H NMR (90 MHz, CDCl$_3$) δ 1.03 (s, 6 H), 1.30–1.53 (m, 2 H), 1.87–2.20 (m, 2 H), 3.14

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(s, 2 H), 4.95 (m, 1 H, J_{gem} = 2.2 Hz, J_{cis} = 9.9 Hz), 5.03 (m, 1 H, J_{gem} = 2.2 Hz, J_{trans} = 17.2 Hz), 5.83 (ddt, 1 H, J_{vic} = 6 Hz, J_{cis} = 9.9 Hz, J_{trans} = 17.2 Hz); ^{13}C NMR (22.49 MHz, CDCl$_3$) δ 24.00 [CH$_2$I], 26.64 [C(CH$_3$)$_2$], 28.68 [=CCH$_2$—], 33.36 [—CH$_2$C(CH$_3$)$_2$—], 40.08 [—CH$_2$CH$_2$C(CH$_3$)$_2$—], 114.36 [CH$_2$=], 138.63 [=CH—]; IR, 3076 (m), 2965, 2867 (s), 1830 (w), 1640 cm^{-1}.

(S)-(+)-2-Octanol. Following the procedure of Ingersoll, 10.5 g (37.7 mmol) of (S)-2-octyl monophthalate was hydrolyzed with aqueous NaOH.[15] The crude product was distilled in a Kugelrohr apparatus to afford 4.44 g (90.4% yield) of (S)-2-octanol of high optical purity: [α]$_D$ = +10.0° (c = 5, ethanol); [α]$^{28}_D$ = +9.25° (neat); 94% optical purity based on lit.[15] [α]$^{17}_D$ = +9.8° (c = 5, 95% aqueous ethanol); lit.[18] [α]$^{20}_D$ = +9.9° (neat).

(S)-(+)-2-Octyl p-Toluenesulfonate. The common procedure[52] was followed. In a dry 50-mL round-bottom flask provided with magnetic stirrer, 2 g (15.4 mmol) of (S)-(+)-2-octanol and 25 mL of dry pyridine were placed. The flask was immersed in an ice–water bath and 3.67 g (19.3 mmol) of p-toluenesulfonyl chloride was added dropwise with stirring. The reaction mixture was left standing for 24 h at 0 °C and was then poured over 200 g of ice and water, with vigorous stirring. The product was extracted with methylene chloride and the extract was washed with cold aqueous HCl and then with cold H$_2$O. The usual workup procedure afforded 3.6 g (82.2% yield) of the desired tosylate; a colorless, viscous oil: [α]$^{28}_D$ = +11.33° (c = 3.71, hexane); lit.[53] [α]$_D$ = +8.0° (neat); ^{1}H NMR (90 MHz, CDCl$_3$) δ 0.85 (m, 3 H), 1.00–1.80 (m, 13 H), 2.47 (s, 3 H), 4.43–4.77 (m, 1 H), 7.63 (~dd, 4 H, J = 9 Hz); IR, 3066, 3032 (w), 2931, 2858 (s), 1599 (m), 1367 (s), 1178, 1188 (s), 898, 916 (s), 816 (s), 669 (s), 577, 556 (s) cm^{-1}.

(R)-(-)-2-Iodooctane [(R)-6]. The general method of Place et al.[16] was applied. In a 100-mL round-bottom flask provided with magnetic stirrer, condenser, and rubber septa, 1.23 g (50.6 mmol) of magnesium, 45 mL of dry ether, and 6.45 g (25.4 mmol) of iodine were placed under nitrogen. Following 1 h of stirring, the color due to iodine disappeared and the exothermic reaction ceased. Stirring was continued for an additional hour, and then the reaction mixture was left standing until the solid material present sedimented. The liquid phase was transferred via cannula to another flask provided with condenser, magnetic stirrer, and rubber septa. The flask was cooled to 0 °C and treated with 3.6 g (12.7 mmol) of (S)-(+)-2-octyl p-toluensulfonate in 20 mL of anhydrous ether. The reaction mixture was removed from the cooling bath and stirred for 10 min at ambient temperature; TLC (AcOEt/hexane, 5:95) showed total conversion at this time. The reaction flask was immersed again in the ice–water bath and 50 mL of cold water and added. The product was extracted with CH$_2$Cl$_2$, washed with aqueous sodium thiosulfate, dried, and concentrated. The crude product was purified by silica gel column chromatography (hexane) to afford 2.39 g (78.4% yield) of the desired iodide as a colorless liquid, which turns yellow after prolonged exposure to light: [α]$^{28}_D$ = -48.1° (c = 5, ethanol); [α]$^{28}_D$ = -43.9° (neat); 90% optical purity based on lit.[18] [α]$_D$ = +48.6° (neat);[54] ^{1}H NMR (90 MHz, CDCl$_3$) δ 0.90 (m, 3 H), 1.33–2.20 (m, 13 H), 4.05–4.43 (m, 1 H); IR, 2958, 2927, 2856 (s), 1459 (m), 1377 (m), 1205, 1167, 1135 (m), 724 (m) cm^{-1}.

Reaction between 2-Lithio-1,3-dithiane (1-Li) and (R)-(-)-2-Iodooctane [(R)-6] in THF. The procedure of Seebach et al.[13] was followed. In a dry Microcaps vial provided with a magnetic stirrer and under nitrogen, 2-lithio-1,3-dithiane was generated[12a] with 0.53 g (4.4 mmol) of 1,3-dithiane, 9 mL of dry THF, and 1.86 mL of 2.36 M n-BuLi (4.4 mmol). To this, 1.0 g (4.2 mmol) of (R)-(-)-2-iodooctane was added, and the reaction mixture was stirred for 72 h at -20 °C and 24 h at ambient temperature. ^{1}H NMR and TLC analysis of aliquots withdrawn each 24 h via syringe indicated that the iodide had been consumed by the first 24 h of reaction. The adduct 2-[(S)-2-octyl]-1,3-dithiane ((S)-7) was isolated in the usual fashion and purified by silica gel column chromatography. The optical rotation was
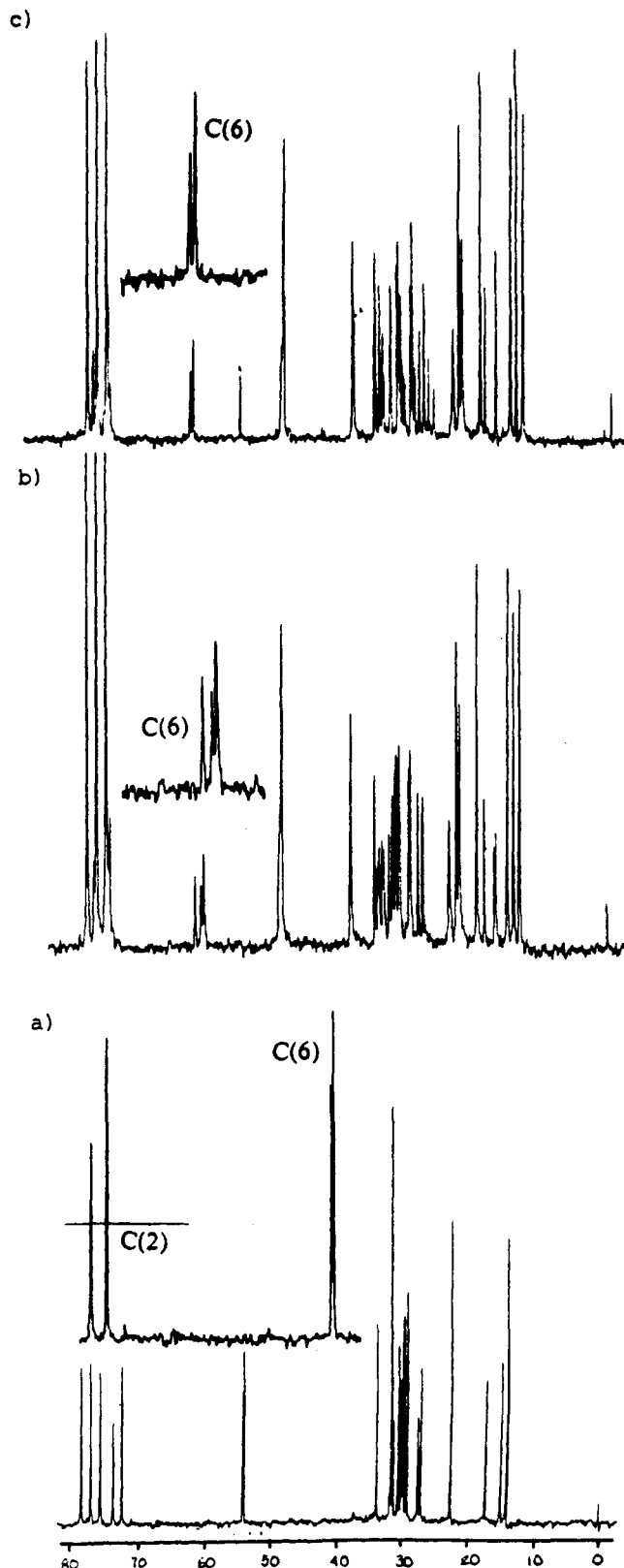

Figure 1. (a) ^{13}C NMR spectrum of racemic sulfoxides 8–11 in the absence of shift reagent. (b) Racemic sulfoxides 8–11 (crude) in the presence of ca. 0.4 equiv of Eu(hfc)$_3$. (c) Optically active sulfoxides (see text) in the presence of Eu(hfc)$_3$. "×" indicates unoxidized dithiane.

constant for all aliquots [α]$^{28}_D$ = -9.6° (c = 3, ethanol) (lit.[13,20] [α]$_D$ = +8.3° (c = 3, ether) for the enantiomer). The combined isolated product amounted to 0.44 g (45% yield): ^{1}H NMR (90 MHz, CDCl$_3$) δ 0.80–1.00 (m, 3 H), 1.07 (d, 3 H, J = 6.8 Hz), 1.15–2.25 (m, 13 H), 2.75–3.00 (m, 4 H), 4.13 (d, 1 H, J = 4.2 Hz); ^{13}C NMR (22.49 MHz, CDCl$_3$) δ 14.11, 17.04, 22.67, 26.49, 27.30,

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(54) Since the optical purity of the precursor (S)-(+)-2-octanol was 94%, racemization in this reaction was only 4% at the most. By comparison, San Filippo's lithium iodide method[53] proceeds with ca. 70% racemization.

29.36, 30.88, 31.18, 31.83, 34.08, 38.60, and 55.67.

Reaction between 2-Lithio-1,3-dithiane (1-Li) and (R)-(-)-2-Iodooctane [(R)-6] in Hexane. In a dry 25-mL, round-bottom flask provided with a magnetic stirrer and rubber septa was generated under nitrogen 2-lithio-1,3-dithiane[12a] from 0.42 g (3.53 mmol) of 1,3-dithiane and 1.67 mL of 2.11 M *n*-BuLi (3.53 mmol) in 8 mL hexane. The flask was immersed in an ice–water bath and 0.85 g (3.53 mmol) of (R)-(-)-2-iodooctane was added. The heterogeneous reaction mixture was stirred for 60 min at 0 °C and for 90 min at ambient temperature, before it was quenched with H_2O and extracted with CH_2Cl_2. The usual workup procedure afforded only starting materials, which were separated by silica gel column chromatography (eluent, hexane). The recovered iodide did not show any optical activity.

Oxidation of 2-[(S)-2-Octyl]-1,3-dithiane. The general procedure of Carey et al.[21b] was followed. In a 25-mL, round-bottom flask provided with a magnetic stirrer, 0.17 g (0.72 mmol) of 2-[(S)-2-octyl]-1,3-dithiane ((S)-7) in 7 mL of a (9:1) methanol–*p*-dioxane mixture was placed. This solution was cooled to -8 °C and treated dropwise with 0.162 g (0.76 mmol) of $NaIO_4$ in 1.5 mL of water. Stirring was continued for 1 h at -5 °C and 12 h at 6 °C and then the reaction mixture was diluted with water and the product (sulfoxides 8–11) extracted with chloroform. The usual workup procedure afforded 0.17 g (95% yield) of the expected sulfoxides, which were analyzed as the crude product (Figure 1).

Reaction between 2-Lithio-1,3-dithiane (1-Li) and 5,5-Dimethyl-6-iodo-1-hexene (5) in THF. In a dry, round-bottom flask provided with rubber septa and under nitrogen, 5,5-dimethyl-6-iodo-1-hexene was placed in THF (2.7 mL per mmol of halide). The flask was immersed in a dry ice–CCl_4 bath before the addition of 1 equiv of 2-lithio-1,3-dithiane.[12a] The reaction mixture was stirred for 90 min at -20 °C and 2 h at ambient temperature before it was quenched with ca. 0.5 mL of D_2O. The reaction mixture was diluted with three volumes of water and extracted with CH_2Cl_2. The usual workup procedure afforded the crude product, which was purified by silica gel column chromatography; the polarity of the eluent was gradually increased from hexane to AcOEt–hexane (20:80).

2-(2,2-Dimethyl-5-hexenyl)-1,3-dithiane (12): ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.97 (s, 6 H), 1.24–2.30 (m, 8 H), 2.50–3.10 (m, 4 H), 4.04 (t, 1 H, J = 5.5 Hz), 4.80–5.10 (m, 2 H), 5.61–6.10 (m, 1 H).

2-[(3,3-Dimethylcyclopentyl)methyl]-1,3-dithiane (13): ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.97 (s, 3 H), 1.01 (s, 3 H), 1.00–2.40 (m, 11 H), 2.78–2.92 (m, 4 H), 4.02 (t, 1 H, J = 7.2 Hz); ^{13}C NMR (22.49 MHz, $CDCl_3$) δ 26.13, 29.43, 30.34, 30.51, 31.90, 36.23, 38.92, 40.48, 42.52, 46.72, 47.93; HRMS *m/z* (M[+]) 230.1169 (calcd for $C_{12}H_{22}S_2$, 230.1163).

Reaction between 2-Lithio-1,3-dithiane (1-Li) and 5,5-Dimethyl-6-iodo-1-hexene (5) in Hexane. The procedure described for the reactions in THF was followed, with 5.4 mL of hexane per mmol of 1,3-dithiane; the iodide was added to the dithianyllithium.

1-(Iodomethyl)-3,3-dimethylcyclopentane (14): ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.93 (s, 3 H), 1.02 (s, 3 H), 0.80–2.60 (m, 7 H), 3.15 (d, 2 H, J = 7 Hz); ^{13}C NMR (22.49 MHz, $CDCl_3$) δ 14.66 [CH_2I], 29.19 [CH_3], 30.07 [CH_3], 32.63 [$CHCH_2CH_2$], 39.62 [$(CH_3)_2C(CH_2)_2$], 40.63 [CCH_2CH_2], 42.06 [$(CH_2)_3CH$], 48.66 [CCH_2CH]; HRMS *m/z* (M[+]) 238.0219 (calcd for $C_8H_{15}I$, 238.0221).

Supplementary Material Available: ^{1}H and ^{13}C NMR spectra for 12, 13, and 14 (5 pages). Ordering information is given on any current masthead page.