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# Reactivities of Diastereoisomeric Carbanions in Dianions Generated from β-Hydroxysulfoxides

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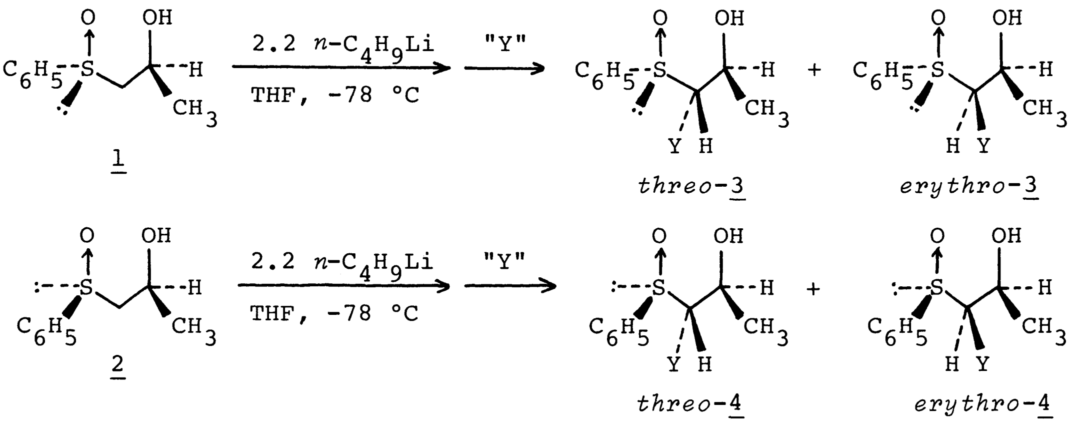
Dianions generated from β-hydroxysulfoxides reacted with $n$-$C_8H_{17}I$, $n$-$C_9H_{19}CHO$, and $D_2O$ to give products in different *threo/erythro* ratios, but those ratios were found to be essentially same in the early stage. The configurational interconversion of the diastereoisomeric carbanions would play an important role.

Alpha-lithiated sulfoxides are useful synthetic intermediates, and the configurations of these carbanions are generally determined by trapping the lithiated species with reactive electrophiles such as $D_2O$, alkyl iodide, and acetone.[1-4] However, the earlier configurational assignment of the deutrated product from benzyl *t*-butyl sulfoxide was found to be in error,[5] and the stereochemistry of the carbanion derived from that sulfoxide has been reevaluated.[6] The stereochemistry of the reaction products from the carbanions is assumed to be affected by the following factors; (1) the stereochemistry of the carbanion formed initially, (2) the configurational interconversion of the carbanions, and (3) the difference in the reactivities of the diastereoisomeric carbanions. In addition, the stereochemistry of electrophilic attack may depend on an electrophile.[1-4,6]

Recently we found that in stereoselective alkylation of the dianions derived from β-hydroxysulfoxides chelation of $Li^+$ cation between an oxyanion and a sulfinyl group played an important role.[7] Now we wish to report interesting results concerning the stereochemical behaviors of the diastereoisomeric carbanions formed secondarily in the dianions of ($R_S^*$,2$S$*)- and ($S_S^*$,2$S$*)-1-phenylsulfinyl-2-propanols [(1) and (2)].[7]

Dilithiation (2.2 equiv. $n$-$C_4H_9Li$/THF/-78 °C/30 min) of 1 or 2, followed by alkylation (1.5 equiv. $n$-$C_8H_{17}I$/THF/-78 °C-r.t./1 h) produced a diastereoisomeric mixture of ($R^*_S$,2$S^*$)-3-phenylsulfinyl-2-undecanol (3a) (*threo/erythro*=66/34[8]) in 71% yield or ($S^*_S$,2$S^*$)-3-phenylsulfinyl-2-undecanol (4a) (*threo/erythro*=96/4) in 67% yield. On the other hand, treatment of the same dianion (5 or 6) with an aldehyde (1.2 equiv. $n$-$C_9H_{19}CHO$/THF/-78 °C-r.t./30 min) generated ($R^*_S$,2$S^*$)-3-phenylsulfinyl-2,4-tridecanediol (3b) in 63% yield or ($S^*_S$,2$S^*$)-3-phenylsulfinyl-2,4-tridecanediol (4b) in 63% yield, but their *threo/erythro* ratios (3b; 19/81 and 4b; 51/49) were quite different from those of 3a and 4a. The similar *threo/erythro* ratio was obtained by quenching reaction of 5 or 6 with $D_2O$ (15 equiv./THF/-78 °C/30 min) to give ($R^*_S$,2$S^*$)-1-deuterio-1-phenylsulfinyl-2-propanol (3c) (*threo/erythro* =25/75) in 83% yield or ($S^*_S$,2$S^*$)-1-deuterio-1-phenylsulfinyl-2-propanol (4c) (*threo/erythro*=50/50) in 83% yield.

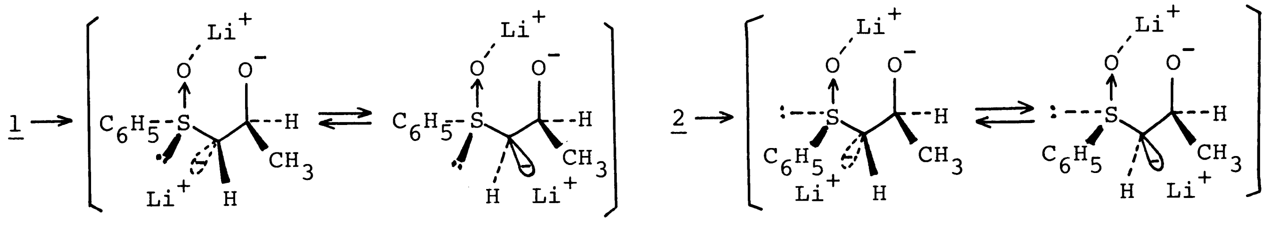


| | | threo/erythro | |
|---|---|---|---|
| a; | Y=$n$-$C_8H_{17}$ | 3a; 66/34 | 4a; 96/4 |
| b; | Y=$n$-$C_9H_{19}CH(OH)$ | 3b; 19/81 | 4b; 51/49 |
| c; | Y=D | 3c; 25/75 | 4c; 50/50 |

The present results cannot be rationalized simply in terms of steric effect.[7,9] In the dianions 5 and 6, chelation of $Li^+$ cation is formed between an oxyanion and a polar sulfinyl group,[7,9] but the other $Li^+$ cation on the secondarily-formed diastereoisomeric carbanion may not be stabilized through coordination. Interestingly, treatment of *erythro*-3a with 2 equiv. $n$-$C_4H_9Li$ (THF/ -78 °C-r.t./2 h) gave a mixture of *threo*- and *erythro*-3a in a ratio of 62/38, while neither monoanion of *erythro*-3a nor trianion of *erythro*-3b underwent the configurational interconversion. At -78 °C the dianions of *threo*- and *erythro*-3a

(Y=$n$-$C_8H_{17}$ in 3) did not interconvert, but the interconversion was observed in the dianion of 3-phenylsulfinyl-2-butanol (Y=$CH_3$ in 3). These findings suggest that the configurational interconversion of the diastereoisomeric carbanions in 5 or 6 would take place even at -78 °C, and the ratio of *threo*-5/*erythro*-5 formed initially might vary with reaction time. The *threo*/*erythro* ratio of 3a was, in fact, found to vary as shown in Fig. 1. The yield of 3a decreased with shortening reaction time, but its *threo*/*erythro* ratio approached those obtained by the reaction with an aldehyde and $D_2O$. Alkylation (1.2 equiv. $n$-$C_8H_{17}I$/THF/-78 °C/15 min) of 5, followed by immediate quenching with $D_2O$ (15 equiv./-78 °C) produced 3a and 3c in *threo*/*erythro*=44/56 and 67/33 ratios, respectively.

Considering the coordinative ability of $Li^+$ cation with a carbonyl group, *threo*- and *erythro*-3b (or 4b) must be formed from *threo*- and *erythro*-5 (or 6), respectively. The stereochemistry of 3c (or 4c) is assumed to reflect the



*threo*-5 *erythro*-5 *threo*-6 *erythro*-6

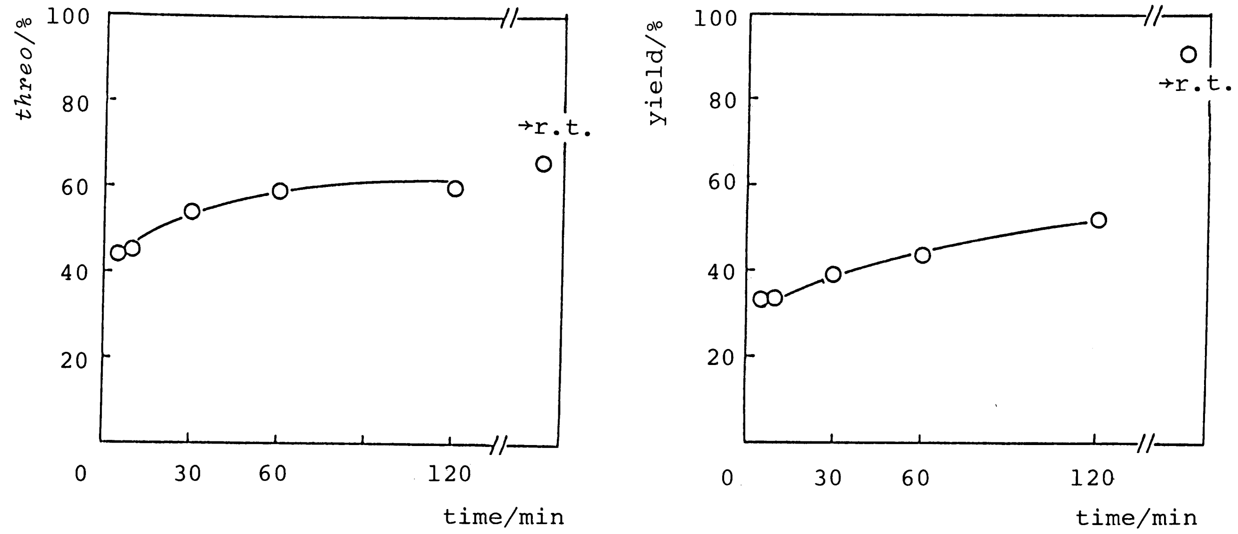


Fig. 1. Time-course of *threo*/*erythro* ratio and yield of 3a. Reaction conditions; 1 (THF/-78 °C) + $n$-$C_4H_9Li$ (2.2 equiv./-78 °C/15 min) + $n$-$C_8H_{17}I$ (1.2 equiv./-78 °C).

initial *threo/erythro* ratio of 5 (or 6) because $D_2O$ is small and reactive. On the other hand, during alkylation using bulky and moderately reactive *n*-$C_8H_{17}I$ the configurational interconversion of the carbanion might take place, and hence the thermodynamic-controlled alkylation product was predominatly obtained, especially from 2.

The present results regarding to the reactivities of diastereoisomeric carbanions may provide significant information to carbanion chemistry.

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8) The ratio was determined by HPLC and/or $^1H$ NMR. The terms *threo* and *erythro* are used as a matter of convenience.
9) T. Sato, T. Itoh, and T. Fujisawa, Tetrahedron Lett., 28, 5677 (1987).
10) Although the carbanion is assumed to be $sp^3$ hybridized, the same arguments are valid by assuming an $sp^2$-hybridized carbanion with asymmetrically coordinated $Li^+$ cation.
11) The configurations of 3a, 4a, 3c, and 4c were determined on the basis of $J_{H\alpha,H\beta}$ values in $^1H$ NMR spectra of $C_6H_5S(O)-CH_\alpha Y-CH_\beta(CH_3)OH$: *threo*-3a, 4a, 3c, 4c, *erythro*-3a, 4a, 3c, 4c; $J$=6.0, 7.6, 9.8, 9.8, 1.0, —, 0.0, 0.0 Hz, respectively. Those of 3b and 4b, after being oxidized and converted into acetals (7) $[C_6H_5SO_2-CH_\alpha-CH_\beta(CH_3)-O-C(CH_3)_2-O-(n\text{-}C_9H_{19})CH]$,[12] were determined similarly: 7 from *threo*-3b & 4b, *erythro*-3b & 4b; $J$=2.5 & 4.5, 7.5 & 8.0, respectively.
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