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Reactivities of Diastereoisomeric Carbanions in Dianions Generated from $\beta\text{-Hydroxysulfoxides}$

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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, 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 $(R_{S}^{\star}, 2S^{\star})$ - and $(S_{S}^{\star}, 2S^{\star})$ -l-phenylsulfinyl-2-propanols [(1) and (2)].⁷⁾ Dilithiation (2.2 equiv. $n-C_4H_9Li/THF/-78$ °C/30 min) of <u>1</u> or <u>2</u>, followed by alkylation (1.5 equiv. $n-C_8H_{17}I/THF/-78$ °C-r.t./l h) produced a diastereoisomeric mixture of ($R_5^*, 2s^*$)-3-phenylsulfinyl-2-undecanol (<u>3a</u>) (threo/erythro=66/34⁸) in 71% yield or ($S_5^*, 2s^*$)-3-phenylsulfinyl-2-undecanol (<u>4a</u>) (threo/erythro=96/4) in 67% yield. On the other hand, treatment of the same dianion (<u>5</u> or <u>6</u>) with an aldehyde (1.2 equiv. $n-C_9H_{19}$ CHO/THF/-78 °C-r.t./30 min) generated ($R_5^*, 2s^*$)-3phenylsulfinyl-2,4-tridecanediol (<u>3b</u>) in 63% yield or $(S_5^*, 2s^*)$ -3-phenylsulfinyl-2,4-tridecanediol (<u>4b</u>) in 63% yield, but their threo/erythro ratios (<u>3b</u>; 19/81 and <u>4b</u>; 51/49) were quite different from those of <u>3a</u> and <u>4a</u>. The similar threo/erythro ratio was obtained by quenching reaction of <u>5</u> or <u>6</u> with D₂O (15 equiv./THF/-78 °C/ 30 min) to give ($R_5^*, 2s^*$)-1-deuterio-1-phenylsulfinyl-2-propanol (<u>3c</u>) (threo/erythro =25/75) in 83% yield or ($S_5^*, 2s^*$)-1-deuterio-1-phenylsulfinyl-2-propanol (<u>4c</u>) (threo/erythro=50/50) in 83% yield.



The present results cannot be rationalized simply in terms of steric effect.^{7,9)} In the dianions <u>5</u> and <u>6</u>, 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*-<u>3a</u> with 2 equiv. $n-C_4H_9Li$ (THF/ -78 °C-r.t./2 h) gave a mixture of *threo*- and *erythro*-<u>3a</u> in a ratio of 62/38, while neither monoanion of *erythro*-<u>3a</u> nor trianion of *erythro*-<u>3b</u> underwent the configurational interconversion. At -78 °C the dianions of *threo*- and *erythro*-<u>3a</u> $(Y=n-C_8H_{17} \text{ in } \underline{3})$ did not interconvert, but the interconversion was observed in the dianion of 3-phenylsulfinyl-2-butanol $(Y=CH_3 \text{ in } \underline{3})$. These findings suggest that the configurational interconversion of the diastereoisomeric carbanions in $\underline{5}$ or $\underline{6}$ would take place even at -78 °C, and the ratio of threo- $\underline{5}/erythro-\underline{5}$ formed initially might vary with reaction time. The threo/erythro ratio of $\underline{3a}$ was, in fact, found to vary as shown in Fig. 1. The yield of $\underline{3a}$ 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 $\underline{5}$, followed by immediate quenching with D_2O (15 equiv./-78 °C) produced $\underline{3a}$ and $\underline{3c}$ in threo/erythro=44/56 and 67/33 ratios, respectively.

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





Fig. 1. Time-course of *threo/erythro* ratio and yield of <u>3a</u>. Reaction conditions; <u>1</u> (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_2^0 is small and reactive. On the other hand, during alkylation using bulky and moderately reactive $n-C_8^{H}H_{17}^{I}$ 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.

This work was partially supported by a Grant-in-Aid for Scientific Research No. 62470021 from the Ministry of Education, Science and Culture.

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- 10) Although the carbanion is assumed to be sp³ hybridized, the same arguments are valid by assuming an sp²-hybridized carbanion with asymmetrically coordinated Li⁺ cation.
- 11) The configurations of <u>3a</u>, <u>4a</u>, <u>3c</u>, and <u>4c</u> were determined on the basis of $J_{H\alpha,H\beta}$ values in ¹H NMR spectra of $C_{6}H_{5}S(0)-CH_{\alpha}Y-CH_{\beta}(CH_{3})OH$: threo-<u>3a</u>, <u>4a</u>, <u>3c</u>, <u>4c</u>, erythro-<u>3a</u>, <u>4a</u>, <u>3c</u>, <u>4c</u>; J=6.0, 7.6, 9.8, 9.8, 1.0, __, 0.0, 0.0 Hz, respectively. Those of <u>3b</u> and <u>4b</u>, after being oxidized and converted into acetals (<u>7</u>) $[C_{6}H_{5}SO_{2}-CH_{\alpha}-CH_{\beta}(CH_{3})-O-C(CH_{3})_{2}-O-(n-C_{9}H_{19})CH^{-}]$, ¹²) were determined similarly: <u>7</u> from threo-<u>3b</u> & <u>4b</u>, erythro-<u>3b</u> & <u>4b</u>; J=2.5 & 4.5, 7.5 & 8.0, respectively.
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(Received March 16, 1988)