

RELATIVE STABILITY OF ACYCLIC  $\alpha$ -SULPHINYL CARBANIONS

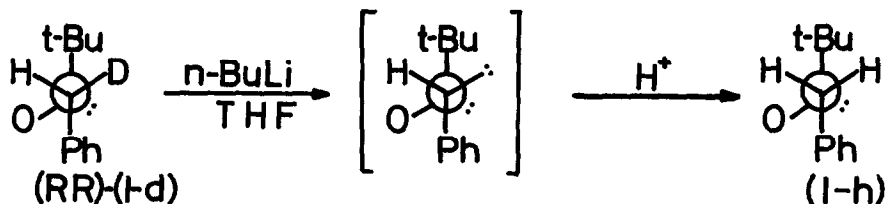
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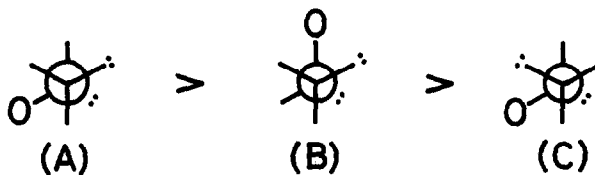
Since Wolfe's finding on a remarkable stereoselectivity in base-catalysed exchange of benzyl methyl sulphoxide<sup>1</sup>, a number of reports have been devoted to this interesting topic in view of establishing the order of stability of the  $\alpha$ -sulphinyl carbanions<sup>2-7</sup>. We here report an observation pertinent to this problem obtained from reprotonation experiments on mono-deuteriated benzyl t-butyl sulphoxides.

Tetrahydrofuran solutions of (RR/SS)-<sup>6b,8</sup> and (RS/SR)- $\alpha$ -deuteriobenzyl t-butyl sulphoxides (I-d) were treated under nitrogen with 1 equiv. of n-butyllithium at  $-70^\circ$ , followed by quenching with excess of water. Usual work-up and spectral analyses (n.m.r. and m.s.<sup>3c</sup>) of the resulting materials revealed that (RR/SS)-diastereomer gave non-deuteriated sulphoxide (I-h) as the almost exclusive product<sup>9</sup> whereas (RS/SR)-(I-d)<sup>10</sup> remained unchanged.



Above facts clearly indicate that the pro-(R) hydrogen (and deuterium) in (R)-sulphoxide is more acidic than the pro-(S) hydrogen (more than enough to overcome the isotope effect:  $k_h/k_d$  ca.  $7^{3c}$ ) and that the carbanion having the carbon-lone pair trans to the S-O and gauche to the sulphur-lone pair (A) is more stable than that having the carbon-lone pair gauche to the S-O and trans to the sulphur-lone pair (C). We assume here that the conformer having the t-butyl group trans to the phenyl group preponderates throughout the reaction process and that the protonation occurs with retention of the configuration.<sup>3c,6b</sup>

This, when put together with earlier observations regarding benzyl methyl sulphoxide<sup>3c</sup> (the carbanion of the type B has been shown to be more stable than the carbanion C), establishes the order of stability of acyclic sulphinyl carbanions as following.



It is interesting that this order well agrees with Katritzky's result on 4-phenylthian 1-oxides<sup>4</sup> and the result on thiolan 1-oxide derivatives by Marquet et al.<sup>7</sup> This conclusion, however, is partially incompatible with Wolfe's computational result<sup>2b</sup> which requires the carbanion B to be more stable than A. Our earlier conclusion (C > A)<sup>3a</sup> should be revised since this was made on the basis of the assignment of the diastereotopic protons of benzyl p-substituted phenyl sulphoxides<sup>11</sup> which now seems to be erroneous.

#### REFERENCES AND FOOTNOTES

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8. Isotopic and isomeric purities are not less than 98 %.
9. This is compatible with Durst's independent finding that non-deuteriated (SR)-phenethyl t-butyl sulphoxide was isolated as the sole product when the lithio derivative of (RR)-(I-d) was treated with excess of methyl iodide in THF; T.Durst, personal communication.
10. Prepared by partial protonation of  $\alpha,\alpha$ -dideuterio-(I).
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