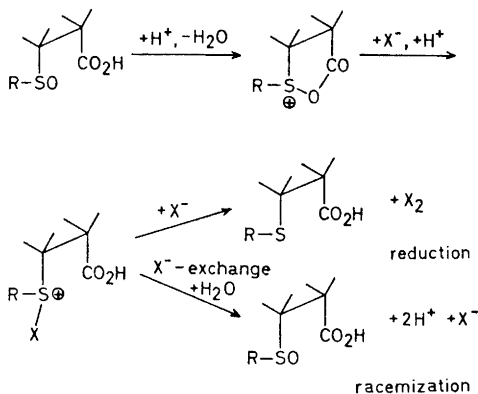


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### Anchimerically Assisted Sulfoxide Reactions IV.

#### Neighbouring Group Participation in the Reduction of *syn*- and *anti-cis*-2-Benzylsulfinylcyclopentane-1-carboxylic Acid by Hydriodic Acid

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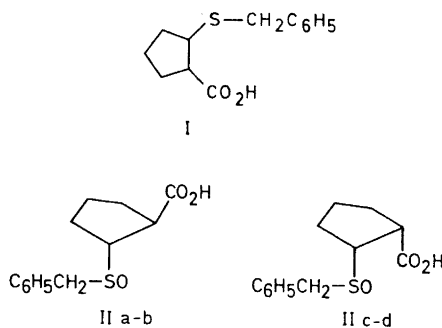
In earlier communications we have described the effect of anchimeric assistance in reduction<sup>1</sup> and racemization<sup>2</sup> of certain carboxylic substituted sulfoxides by hydriodic acid and hydrochloric or hydrobromic acid, respectively. The mechanism of the reaction was believed to involve a nucleophilic attack of the sulfinyl-oxygen upon the protonated carboxyl group with elimination of water to yield a cyclic acyloxysulfonium ion intermediate followed by fast halide ion attack upon the sulfur atom, leading to ring-opening.

In order to gain more information about structure-reactivity relationships<sup>1,3</sup> with respect to these reactions, we undertook a study on the reduction of all four (racemic) isomers of 2-benzylsulfinylcyclopentane-1-carboxylic acid.

The corresponding sulfide-acids (I) were prepared by the addition, in the presence of piperidine and Triton B,<sup>4,5</sup> of benzyl mercaptan to cyclopentene-1-carboxylic acid in benzene solution at 80°, resulting

in an approximately 3:1 mixture of two isomers with m.p. 54° (Ia) and 101° (Ib), respectively. The yield of crude I in this reaction was 70%. The favoured isomer Ia was assumed to be the *trans*-isomer, since Truce<sup>6,7</sup> has shown the nucleophilic addition of thiols to the cyclopentene ring system to be predominantly *cis*.

Oxidation of Ia with peracetic acid gave two sulfoxide isomers (IIa, m.p. 135° and IIb, m.p. 116.5°) which were separated by repeated recrystallization. Similarly, oxidation of Ib resulted in the isomers IIc, m.p. 156°, and IId, m.p. 164.5°.



When compounds IIa–d were studied kinetically under the same reduction conditions (0.5 M HClO<sub>4</sub>, 0.2 M NaI, 50% ethanol, 25.0°), it was found that IIc and IId were readily reduced, whereas IIa and IIb remained quite unchanged. As only reduction of the *cis*-isomers can be anchimerically accelerated in this case,

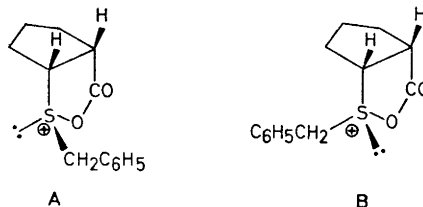
the results are in agreement with the assignment of Ia as the *trans*-isomer. The reaction was followed spectrophotometrically by measuring the optical density at 525  $\mu$  as a function of time (formation of triiodide ion). Under the conditions given above, the two *cis*-isomers, IIc and IId, exhibited significantly different reaction rates, the ratio of the rates being approximately 25:1. The reaction showed good pseudo first-order kinetics. The most reactive isomer (IIc) was, however, more conveniently studied at lower perchloric acid concentrations giving second-order kinetics.<sup>1</sup> The rate constants obtained are given below. An initial concentration of sulfoxide =  $5.0 \times 10^{-3}$  M was used throughout.

	Pseudo first-order rate constant in 0.5 M HClO <sub>4</sub>	Second-order rate constant in 0.025 M HClO <sub>4</sub>
IIc	> 0.6 min <sup>-1</sup>	1.02 l mole <sup>-1</sup> min <sup>-1</sup>
IId	0.0267 min <sup>-1</sup>	0.039 l mole <sup>-1</sup> min <sup>-1</sup>

A change in iodide ion concentration from 0.2 M to 0.4 M showed the reaction to be almost zero-order with respect to iodide ions, in agreement with earlier results.<sup>8,9</sup> The observed rate-difference between IIc and IId in this reaction should therefore be the result of a more favoured geometry in the transition state corresponding to IIc during the formation of the cyclic intermediate. It is reasonable to assume that in such an intermediate the substituents located around the C-S bond are forced to an eclipsed conformation, and accordingly the formation of A, arbitrarily \* designated *anti*-configuration, should be kinetically favoured over B because of less nonbonded interactions.

On the basis of our observations we propose that IIc has the *anti-cis*-con-

\* This definition is consistent with the nomenclature used for corresponding bicyclic compounds.<sup>10</sup>



figuration (*i.e.* corresponds to A) and that IId is the *syn-cis*-isomer. A similar configurational assignment to the two *trans*-isomers, IIa and IIb, has not been possible.

All compounds showed satisfactory elemental (C, H, S) analyses.

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