Perturbation of Rearrangement Courses by Cyclohepta-amylose

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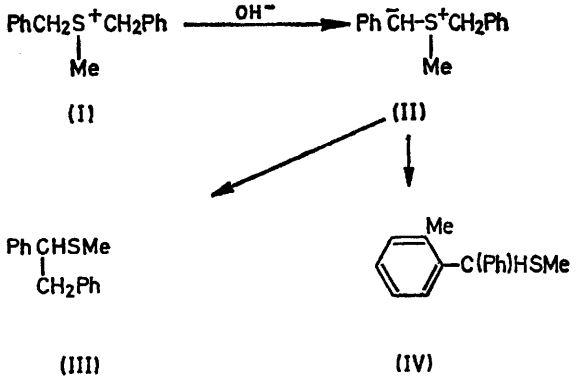
Summary Dibenzylmethylsulphonium fluoroborate (I), when treated with aqueous sodium hydroxide in the presence of cyclohepta-amylose, prefers the Sommelet over the Stevens rearrangement by the formation of an inclusion complex, while rate measurements reveal that cyclohepta-amylose retards slightly the rearrangement reactions.

CYCLOAMYLOSE-CATALYSED reactions have recently attracted much attention as a model for enzyme reactions. However, investigations on the cycloamylose reactions have been mainly focused on rate enhancement[1] while relatively few reports have appeared dealing with the stereospecificity.[2] We now report our novel finding that cyclohepta-amylose alters the rearrangement *via* sulphonium ylides.

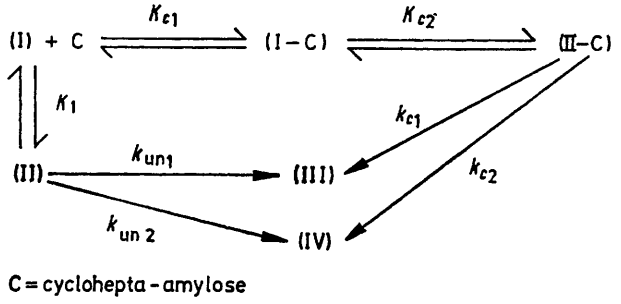
It has been reported that dibenzylmethylsulphonium fluoroborate (I), when treated with aqueous sodium hydroxide, generates the corresponding ylide (II), which then gives the Stevens rearrangement product (III) as the major and the Sommelet rearrangement product (IV) as the minor one (Scheme 1).[3]



SCHEME 1

In the present study, we found that the addition of an equimolar amount of cyclohepta-amylose to an aqueous solution of (I) favours the Sommelet over the Stevens rearrangement [(IV)/(III) = 1·5]. In order to ascertain the mechanism of this cyclohepta-amylose-catalysed reaction, the dependence of the relative product fraction [(IV)/(III)] on cyclohepta-amylose concentration and on the addition of methanol or ethyleneglycol instead of cyclohepta-amylose was examined. A correlation between the (IV)/(III) fraction and cyclohepta-amylose concentration reveals that the fraction [(IV)/(III)] increases in the presence of cyclohepta-amylose, but exhibits the saturation phenomenon with increasing cyclohepta-amylose concentration. However, the ratio does not vary with the addition of methanol or ethyleneglycol [(IV)/(III) = 0·36]. This implies that the preference of the Sommelet over the Stevens rearrangement in the presence of cyclohepta-amylose is derived from the formation of the inclusion complex of (I) with cyclohepta-amylose and not, as previously suggested, from a change in the solvent.[3]

The probable pathway is shown in Scheme 2.



SCHEME 2

Scheme 2 leads to an approximate relative ratio expression in equation (1), which predicts the saturation phenomenon of the relative ratio with an increase in the cyclohepta-amylose concentration.

$$\frac{[IV]}{[III]} = \frac{K_1 \cdot k_{un2} + K_{c1} \cdot K_{c2} \cdot k_{c2} \cdot [C]}{K_1 \cdot k_{un1} + K_{c1} \cdot K_{c2} \cdot k_{c1} \cdot [C]} \quad (1)$$

The pseudo-first-order rate constants for appearance of the rearrangement products (III, IV) in the presence and absence of cyclohepta-amylose are summarized in the Table.

TABLE. Pseudo-first-order rate constants for the formation of the rearrangement products (III, IV).

Solvent	$10^6 k^a_{obsd}/s^{-1}$
Water	4·0
Cyclohepta-amylose $1·60 \times 10^{-2}$ M	2·0
Cyclohepta-amylose $7·12 \times 10^{-3}$ M	2·4

[a] At 20·0°, [I] = $7·19 \times 10^{-3}$ M, [NaOH] = $2·27 \times 10^{-1}$ M.

The results in the Table indicate that cyclohepta-amylose retards the rearrangements slightly.

Two mechanisms are possible for the preference of the Sommelet over the Stevens rearrangement by complexation with cyclohepta-amylose; (1) a steric effect produced by formation of the inclusion complex; (2) an environmental change occurring on complex formation, *i.e.*, the micro-solvent effect of cyclohepta-amylose.

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[1] For example; H. J. Brass and M. L. Bender, *J. Amer. Chem. Soc.*, 1973, **95**, 5391; T. S. Straub and M. L. Bender, *ibid.*, 1972, **94**, 8875; T. S. Straub and M. L. Bender, *ibid.*, 1972, **94**, 8881.
[2] R. Breslow and P. Campbell, *J. Amer. Chem. Soc.*, 1969, **91**, 3085.
[3] Y. Hayashi and R. Oda, 22nd National Meeting of the Japanese Chemical Society, Tokyo, Japan, 1969.