

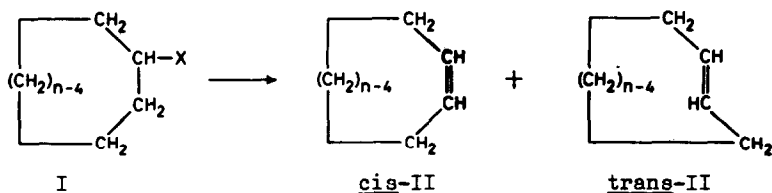
CYCLOALKENE FORMATION FROM 'ONIUM COMPOUNDS AND AMINE OXIDES.  
VARIATION OF RATE WITH RING SIZE AS CRITERION OF ELIMINATION  
MECHANISM<sup>+</sup>

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It has been pointed out that study of the variation of rate with ring size of a given reaction in a homologous series of compounds can serve as a useful mechanistic tool : by relating the reactivity sequence of the process under study to that of a reaction of known mechanism one can obtain evidence on its reaction course (2,3).

One very important reaction type for which data on the dependence of rate on ring size are conspicuously absent are elimination reactions on cycloalkyl-X derivatives (I) leading to cis- and trans-cycloalkenes (II). Moreover, since many



<sup>+</sup>This is the second of a series of papers on the mechanism of elimination reactions; for previous paper see ref. (1).

aspects of the mechanism of elimination reactions still remain to be clarified (4), these seemed to be an excellent object on which to test the above contention. In this note we report results of studies on the rates of reactions of homologous series of cycloalkyldimethylamine oxides (I, X =  $\text{NMe}_2\text{O}$ ) in tert.butanol and of the reaction of cycloalkyl-trimethylammonium chlorides (I, X =  $\text{NMe}_3^+$ ) with potassium tert.butoxide in tert.butanol.

The mechanism of the amine oxide elimination reaction can hardly be in doubt : it is a concerted intramolecular syn-elimination<sup>+</sup> reaction (5) (Scheme 1) and will, in the present context, serve as a "reference reaction" of known mechanism. The mechanism of 'onium salt eliminations presents a more complex problem; however, it is believed (4) that whatever the mechanistic details, the reaction, in general, proceeds by an anti-elimination mechanism (Scheme 1).



Scheme 1

For the rate measurements of the amine oxide elimination we developed a polarographic technique which simultaneously determines the concentrations of the amine oxide and the N,N-dimethylhydroxylamine, one of the reaction products.

<sup>+</sup>We use the terms syn- and anti-elimination as being more descriptive and unambiguous than the more frequently used terms cis- and trans-elimination.

The rates of the Hofmann elimination were determined by a modification of the method of Banthorpe et al. (6). In both cases, overall elimination rates were determined and partitioned into cis- and trans-cyclo-olefin components on the basis of independent determinations of the cis-trans olefin composition by gas chromatography.<sup>†</sup>

Fig. 1A shows the dependence of rate on ring size for the amine oxide elimination. The "rate curves" exhibit very pronounced maxima in the medium ring region, for the eight-membered ring in the cis-series, for the ten-membered ring in the trans-series. Analogous rate maxima have been observed previously for other reactions (3), and satisfactory interpretations have been suggested. The rates here extend over an unusually large range : the rate of cyclohexene formation is lower by a factor greater than five powers of ten than that of trans-cyclodecene. Since, in the present context, the amine oxide elimination is being used only as a "reference process" of known mechanism, an interpretation of the rate dependence will not be attempted here.

Fig. 1B shows the dependence of rate on ring size for the 'onium salt eliminations. There is a very marked difference in the course of the cis and the trans "curves" for this reaction. Provided we accept the tenet that processes possessing mechanisms similar with respect to their salient steric features will exhibit "rate curves" of similar type, we are forced to conclude that, in the 'onium

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<sup>†</sup>Both these reactions have already found preparative use (7) in the medium ring compounds, pyrolytic procedures being used. The cis- to trans-olefin ratios now determined were close to those previously found for pyrolytic reactions.

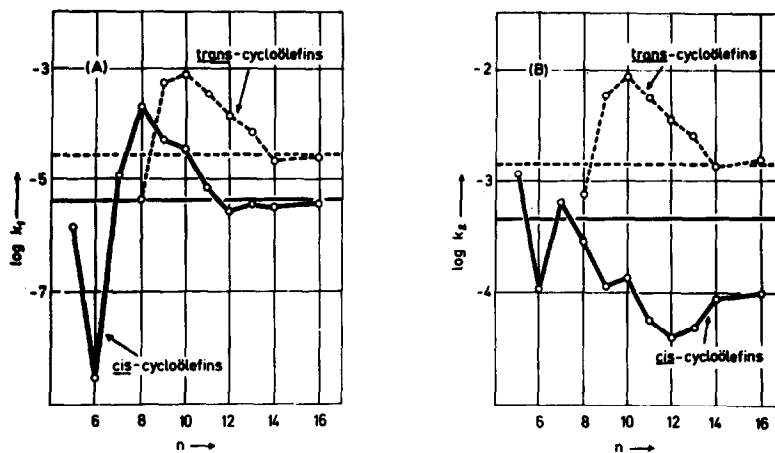


Fig. 1

Effect of Ring Size on Rates of *cis*- and *trans*-Cycloalkene Formation

A : From cycloalkyldimethylamine oxides in tert.butanol at 70.6°C.

B : From cycloalkyltrimethylammonium chlorides (0.03 M) and potassium tert. butoxide (0.11 M) in tert. butanol at 55°C.

n : Number of carbon atoms in ring.

The full and the dotted horizontal lines ( ——— and - - - - ) stand for the rates of formation, respectively, of *cis*- and *trans*-4-nonene from 5-nonyldimethylamine oxide (Fig. 1A) and from 5-nonyltrimethylammonium chloride (Fig. 1B), under the same conditions as used in the case of the corresponding alicyclic compounds.

salt eliminations, two sterically different mechanisms are operative; the one, presumably, leading to the trans-olefins, and the other to the cis-olefins.

The rate curve for the trans-olefins exhibits the characteristic maximum for the ten-membered ring, with a fairly rapid falling off towards the rate of the open-chain compound. Superficially, this is the type of rate-on-ring-size dependence found previously for  $E_1$  (solvolytic) reactions (8); however, a logarithmic plot of the rates of this reaction against the rates of trans-cycloalkene formation shows that the resemblance is not at all close. On the other hand a very marked resemblance exists between the curves representing the rates of trans-olefin formation by the two processes now examined and this is borne out by the fact that the logarithmic plot of these two processes (Fig. 2A) gives an excellent fit. trans-Olefin formation by these two processes hence probably proceeds by a sterically similar mechanism; provided we reject the possibility that the amine oxide reaction could take place by an anti-elimination, it would follow that trans-olefin formation from the 'onium salts under the present reaction conditions proceeds by a syn-elimination mechanism, at any rate in the medium ring region.

The rate curve for cis-olefin formation from the 'onium compounds corresponds closely to the known dependence of rate on ring size for the  $S_N2$  reaction of cycloalkyl

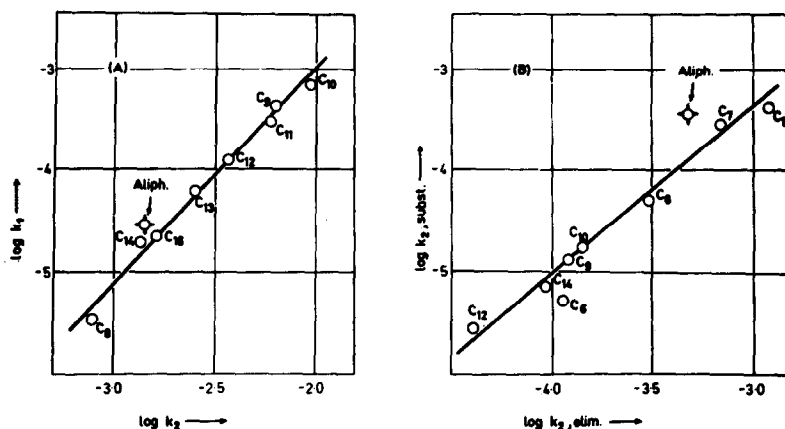


Fig. 2

## Free Energy Relationships

- A : Between rate constants of formation of trans-cycloalkenes from cycloalkyltrimethylammonium chlorides with potassium tert. butoxide in tert. butanol ( $\log k_2$ ) and rate constants of trans-cycloalkene formation from cycloalkyldimethylamine oxides in tert. butanol ( $\log k_1$ ).
- B : Between rate constants of the formation cis-cycloalkene formation from cycloalkyltrimethylammonium chlorides with tert. butoxide in tert. butanol ( $\log k_2, \text{elim.}$ ) and rate constants of the reaction of cycloalkyl bromides with potassium iodide in acetone at 60°C (9) ( $\log k_2, \text{subst.}$ ).

bromides with potassium iodide in acetone (9), as again shown by the satisfactory logarithmic plot (Fig. 2B). As was first pointed out by Hughes (10), a bimolecular anti-elimination can be visualised as involving a concerted rear-side nucleophilic displacement at the  $\alpha$ -carbon by the  $C(\beta)$ -H electrons. On this view it appears possible to conclude that the observed dependence of rate on ring size for the cis-isomer (Fig. 1B) indicates that the cis-cycloalkenes are formed by the customary anti-elimination mechanism.

Further support for these conclusions is presented in the accompanying note in which results of studies on deuterium labeled cyclodecane derivatives are reported.

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