Cycloalkene Formation from Cycloalkyl Bromides: Variation of Rate with Ring Size as Criterion of Mechanism

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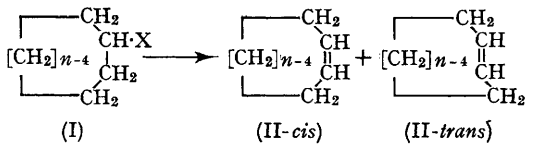
RECENTLY, we have shown[1] that in the reaction of cycloalkyltrimethylammonium chlorides (I; X = NMe_3, n = 5—14, 16) with Bu^tOK–Bu^tOH the *cis*-cycloalkenes (II-*cis*) arise, largely or exclusively, by an *anti*-elimination mechanism, and the *trans*-cycloalkenes (II-*trans*) by a *syn*-elimination mechanism.



(I) (II-*cis*) (II-*trans*)

We now report rates of *cis*- and *trans*-cycloalkene formation from cycloalkyl bromides (I; X = Br, n = 5—14, 16) with Bu^tOK–Bu^tOH and with EtOK–EtOH; rates of *cis*- and *trans*-non-4-ene formation from 5-nonyl bromide are included for comparison.

The pronounced difference in the dependence of rate on ring size for the formation of *cis*-cycloalkenes (II-*cis*) on the one hand and of *trans*-cycloalkenes (II-*trans*) on the other in the Bu^tOK–Bu^tOH reaction (Figure 1A) indicates, following arguments outlined previously,[1] that the isomeric cycloalkenes (II-*cis* and II-*trans*) are formed by stereochemically completely different mechanisms. By contrast, in the EtOK–EtOH reaction, the rate profiles for *cis*- and *trans*-cycloalkene formation (Figure 1B) are no longer distinctly different and the isomers hence appear to be formed by analogous mechanisms.

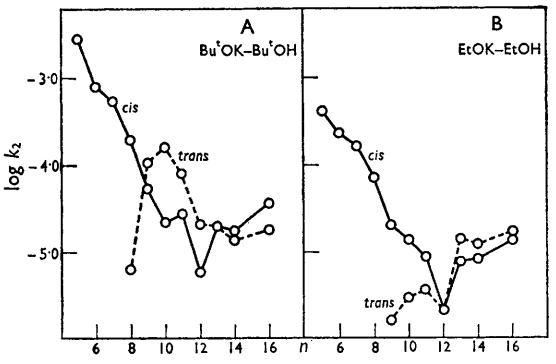
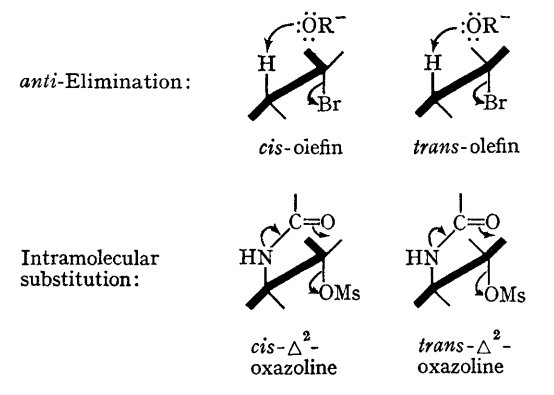


FIGURE 1. *Effect of ring size on rate of* cis- *and* trans-*cycloalkene formation from cycloalkyl bromides* (I; X = Br, n = 5—14, 16). A: *With* Bu^{t}OK–Bu^{t}OH *at* 82·5°. B: *With* EtOK–EtOH *at* 58·5°. *Horizontal lines*: *Rates of* cis- *and* trans-*non-4-ene formation from 5-nonyl bromide.*

The rate against ring-size profile for *cis*-cycloalkene formation under the two sets of conditions is very similar and is characteristic[1] for an *anti*-elimination course of the reactions: a free-energy plot (Figure 2A) of the rates of *cis*-cycloalkene formation and the rates of *cis*-Δ^2-oxazoline formation from the *trans*-2-benzamidocyclohexyl methanesulphonates (Scheme 1) shows that there is some analogy in the rate behaviour in these two processes;* the geometric analogy between them is evident from the scheme.



Scheme 1

The rate profile for *trans*-cycloalkene formation in the Bu^{t}OK–Bu^{t}OH reaction is characteristic[1,4]

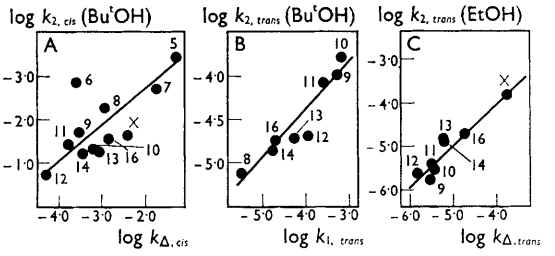
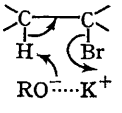


FIGURE 2. *Free-energy relationships.* A: *Between log* $k_{2,cis}$, *the rate constant of formation of* cis-*cycloalkenes from cycloalkyl bromides with* Bu^{t}OK–Bu^{t}OH *and log* $k_{\Delta,cis}$, *the rate constant of* cis-Δ^2-*oxazoline formation from* trans-2-*benzamidocycloalkyl methanesulphonates* (*ref.* 2). B: *Between log* $k_{2,trans}$ *the rate constant of formation of* trans-*cycloalkenes from cycloalkyl bromides with* Bu^{t}OK–Bu^{t}OH *and log* $k_{1,trans}$, *the rate constant of* trans-*cycloalkene formation from cycloalkyldimethylamine oxides in* Bu^{t}OH (*ref.* 1). C: *Between log* $k_{2,trans}$, *the rate constants of* trans-*cycloalkene formation from cycloalkyl bromides with* EtOK–EtOH *and log* $k_{\Delta,trans}$, *the rate constants of* trans-Δ^2-*oxazoline formation from the* cis-2-*benzamidocycloalkyl methanesulphonates* (*ref.* 2). *The points marked* X *refer to rates of "corresponding" non-cyclic compounds.*

for *syn*-elimination reactions: a logarithmic plot (Figure 2B) of the rates of *trans*-cycloalkene formation from the bromides in this reaction and from the cycloalkyldimethylamine oxides (I; X = NMe_2O) in Bu^{t}OH—a *bona fide syn*-elimination[5]—brings out this point. By contrast, the rates of *trans*-cycloalkene formation in the EtOK–EtOH reaction may be approximately correlated (Figure 2C) with rates of the reaction of *trans*-Δ^2-oxazoline formation from the *cis*-2-benzamidocycloalkyl methanesulphonates[2] (Scheme 1). It hence appears that, in the EtOK–EtOH reaction, the *trans*-cycloalkenes (like the *cis*-cycloalkenes) are—largely or perhaps exclusively—formed by an *anti*-elimination path.



Scheme 2

The difference in the behaviour of the cycloalkyl bromides in the two base–solvent systems may be rationalised by assuming that the effective species in the *syn*-elimination is not the alcoholate anion as in *anti*-elimination but the RO$^-$ · · · K$^+$ ion

*A much better fit is obtained when the rates of *cis*-cycloalkene formation are correlated against the rates of the S_N2 reaction of cycloalkyl bromides with potassium iodide (ref. 3). The six-membered compound is distinctly "off" in all these correlations; a rationalisation of this will be given in the full Paper.

pair (Scheme 2). Since conditions for ion pair formation are more favourable in t-butyl alcohol than in ethanol, a *syn*-mechanism should be more favoured in the former solvent.

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