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PREFERRED OVERALL SYN-ELIMINATION IN METAL PROMOTED CYCLOALKENE FORMATION FROM VICINAL DIBROMIDES[★]

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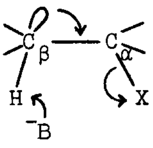
Conclusive evidence in now available (2-4) showing that the generally held view (5) of exclusive anti-elimination in base-promoted processes of the type (1) is no longer tenable and that, in fact, many of these common

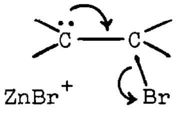
$$R.CH_2.CH(X)R' \ + \ B^- \longrightarrow R.CH = CH.R' \ + \ X^- \qquad (\underline{1})$$

reactions preferentially take place by a syn-elimination route.

It is thought that the transition state in these concerted syn-eliminations is E1cb-like (considerable C-H, and little C-X bond breaking in the transition state) (6-11). Further, it has been argued (12) that, if, in the syn-elimination, the process of C-X bond fission is to receive assistance from the C_β-H electron pair this should occur as shown in Scheme 1a, i.e. with "inversion" at C_β.



1a



1b

The reaction of vicinal dibromides with bivalent metals (2) which

$$R.CH.Br.CH.Br.R' \ + \ M^{II} \longrightarrow R.CH = CH.R' \ + \ MBr_2 \qquad (\underline{2})$$

represents another well known olefin forming elimination process, probably proceeds by way of a short lived carbanionic intermediate (13,14). It has

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[★] This is the eighteenth of a series of papers dealing with the mechanism of elimination reactions, previous paper see ref. (1).

been suggested (14) that such a species, when formed from a Br,Br syn-conformer, might undergo inversion more rapidly than it would rotate into a conformation suitable for anti-elimination. It would thus give the olefin through an overall syn-elimination sequence (Scheme 1b) which bears some resemblance to the concerted syn-elimination mechanism (Scheme 1a) of the base-catalysed eliminations.

TABLE cis-trans Alkene Composition (and Steric Course) in Alkene Formation from vic.-Dibromides

	Zn/MeOH[a]		Mg/THF[a]		Li/THF[a]		KI/MeOH[b]	
Dibromide	cis	trans[c]	cis	trans	cis	trans	cis	trans
	(anti)	(syn)	(anti)	(syn)	(anti)	(syn)	(anti)	(syn)
threo-5,6-Dibromodecane (I)	95	5	71	29	72	28	86	14
trans-1,2-Dibromocyclodecane (II)	13	87	51	49	40	60	82	18
trans-1,2-Dibromo-5,5,8,8-tetramethylcyclodecane (III)	10	90	18	82	11	89	100	0
trans-1,2-Dibromocyclododecane (IV)	12	88	12	88	9	91	80	20
trans-1,2-Dibromo-6,6,9,9-tetramethylcyclododecane (V)	5	95	12	88	4	96	74	26
	(syn)	(anti)	(syn)	(anti)	(syn)	(anti)	(syn)	(anti)
erythro-5,6-Dibromodecane (VI)	4	96	18	82	24	76	9	91
cis-1,2-Dibromocyclododecane (VII)	53	47	79	21	80	20	16	84

[a] 0.15 mmol of the dibromide, a ten-fold excess of the metal and about 1 g of crushed glass in 5 ml of the solvent were shaken for 7 hours in sealed ampoules at room temperature under nitrogen. The yields of the olefin mixtures were better than 90%.

[b] Performed according to Weinstock et al. (22), at 90°. The reaction was interrupted after a period corresponding to about 30% of the reaction, this being the interval in which the process follows second order kinetics. The olefins have been shown to be stable under the reaction conditions.

[c] The analyses of cis-trans composition were by glpc; the 5-decenes and cyclodecenes on 5% $AgNO_3$ in triethylene glycol; the cyclododecenes on Apiezon (50 m capillary^3).

In open-chain and cyclohexyl systems the metal promoted elimination of vicinal dibromides is known to exhibit considerable, though frequently not complete, anti-stereospecificity (15,16).* In our studies of base induced eliminations of the type (1) we found that the tendency towards syn-elimination is particularly pronounced in medium ring substrates (17-19). We therefore thought that preferred syn-elimination might be encountered in the metal promoted eliminations on the medium ring cycloalkyl-1,2-dibromides: this has now indeed been found to be the case. The results are summarized in the Table. The two open-chain dibromides, threo- and erythro-5,6-dibromodecane (I and VI, resp.) show a distinct preference for anti-elimination in the reaction with zinc and with magnesium, in agreement with earlier findings (15) on related substrates, and also in the reaction with lithium. The cyclodecyl and cyclododecyl dibromides (II - V and VII) under analogous conditions almost invariably gave products corresponding to predominant overall syn-elimination. Thus, e.g. the cis-trans cycloalkene mixture formed (in high yield) from trans-1,2-dibromocyclododecane contained 88% trans-cyclododecene; that obtained from the corresponding cis-1,2-dibromo-isomer VII contained 79% of cis-cyclododecene. In twelve out of the fifteen processes examined, syn-elimination accounts for at least ~80% of the cycloolefin-forming reaction; in agreement with considerations of R vs R' interactions it is the threo-isomer in the 5,6-dibromodecane pair and the trans-isomer in the 1,2-dibromocyclododecane pair which have the stronger tendency to react by syn-elimination. Some time ago we examined the reaction of cis-1,2-dibromocyclohexadecane with zinc (20): the outcome corresponded to predominant anti-elimination, in contrast to the now observed behaviour of the corresponding ten- and twelve-membered ring derivatives.

The fact that the enhanced tendency towards syn-eliminations in the ten- and twelve-membered rings exists both for the base-catalyzed and the metal induced eliminations (processes 1 and 2) suggests that it is the "inversion component" which in these substrates takes place with particular ease.

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*This does not apply to substrates in which R = R' = C_6H_5 or CO_2H; here both diastereoisomers afforded the trans-olefin, practically exclusively (13).

Structural features which may be responsible for this have been discussed previously (19).

The reaction of the dibromides with potassium iodide, which was run for comparison, may be seen (Table) to proceed predominantly - though not exclusively - by anti-elimination in all the compounds investigated. The percentage of products which correspond to overall syn-elimination is, on the average, not greater in the ten- or twelve-membered ring compounds than in the open-chain substrates; this suggests that these minor products are formed by substitution followed by anti-elimination, rather than by a genuine one-step syn-elimination mechanism.

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