syn-anti DICHOTOMY IN ZINC-PROMOTED DEHALOGENATION OF OPEN-CHAIN VICINAL DIHALIDES: THE EFFECT OF THE LEAVING GROUPS*

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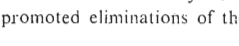
The title effect has been investigated in the homologous series of *erythro*- and *threo*-5,6-dihalodecanes (X = Br, Y = I; X = Cl, Y = I; X = F, Y = I; X = Br, Y = Br; X = Cl, Y = Br; X = F, Y = Br; X = Cl, Y = Cl; X = F, Y = Cl). It has been found that proportion of *syn*-elimination in the overall reaction varies with the variation of the halogen leaving groups in the order I < Br < Cl < F, ranging between the extreme 3–30% in the *erythro*- and 5–60% in the *threo*-series. On basis of the variable transition state theory, the observed pattern of *syn-anti* dichotomy has been correlated with the extent of double bond development in the transition state.

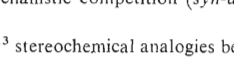
It is now well documented that two stereochemically distinct mechanisms, *syn* and *anti*, participate in the base-promoted eliminations of the type (*A*). The intricate role of base



(*A*)

and leaving group in the mechanistic competition (*syn-anti* dichotomy) has been recently reviewed[1].

In order to probe possible[2,3] stereochemical analogies between the base-promoted eliminations (*A*) and the metal-promoted dehalogenations (*B*), we have now prepared



(*B*)

a series of *erythro*- and *threo*-5,6-dihalodecanes *Ia–Ih* and investigated the influence of the halogen group identity on the *syn-anti* dichotomy in several dehalogenation reactions. In this paper we report the results from the zinc-promoted reaction.

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$C_4H_9.CH(X).CH(Y).C_4H_9$

Ia: X = Br, Y = I
Ib: X = Cl, Y = I
Ic: X = F, Y = I
Id: X = Br, Y = Br
Ie: X = Cl, Y = Br
If: X = F, Y = Br
Ig: X = Cl, Y = Cl
Ih: X = F, Y = Cl

EXPERIMENTAL

cis-5-Decene

A solution of 5-decyne[4] (70 g; 0·51 mol) in ether (100 ml) was added to suspension of P-2 Ni catalyst[5] (32·5 mmol) in ethanol (260 ml) and ethylenediamine (5·2 ml). The mixture was shaken with hydrogen at room temperature and at atmospheric pressure until the consumption ceased (7 h). The isolated product (54 g; 76%) had b.p. 61°C/1 703 Pa and was shown by VPC to contain less than 3% of the *trans*-isomer.

erythro- and *threo*-5-Bromo-6-iododecanes (*erythro*- and *threo*-*Ia*)

erythro-Ia: A solution of *trans*-5-decene[6] (0·5 g; 3·6 mmol), uniform by VPC., in chloroform (5 ml) was treated at 10°C in the course of 10 min with bromoiodide[7] (0·82 g; 4 mmol) diluted with chloroform (5 ml). The solution was allowed to come to room temperature and the product was isolated. *threo-Ia*: Prepared analogously from *cis*-5-decene. Yields, boiling points and elemental analyses are in Table I.

erythro- and *threo*-5-Chloro-6-iododecanes (*erythro*- and *threo*-*Ib*)

erythro-Ib: Anhydrous cupric chloride (4·44 g; 33 mmol) was treated with iodine (4·18 g; 16·5 mmol) in acetonitrile (70 ml). After 15 min stirring *trans*-5-decene (2·1 g; 15 mmol) was added and the mixture was heated at 70°C for 1 h. Inorganic salts were filtered off over a short column of silica and the product was isolated. *threo-Ib*: Prepared analogously from *cis*-5-decene. Yields, boiling points and elemental analyses are in Table I.

erythro- and *threo*-5-Fluoro-6-iododecanes (*erythro*- and *threo*-*Ic*)

erythro-Ic: Into a 250 ml polyethylene flask containing 70% w/w hydrogen fluoride/pyridine solution[8] (50 ml) and tetramethyl sulfone (20 ml), N-iodosuccinimide[9] (36 mmol) was added. To this mixture, cooled by an ice bath, *trans*-5-decene (4·2 g; 30 mmol) was dropwise added. After 2 h stirring at room temperature the product was isolated. *threo-Ic*: Prepared analogously from *cis*-5-decene. Yields, boiling points and elemental analyses are in Table I.

erythro- and *threo*-5,6-Dibromodecanes (*erythro*- and *threo*-*Id*)

erythro-Id: A solution of *trans*-5-decene (4·2 g; 30 mmol) in tetrachloromethane (20 ml) was treated at 0°C in the course of 10 min with a solution of bromine (5·3 g; 33 mmol) in tetrachloromethane. After 1 h stirring at room temperature, the mixture was worked up. *threo-Id*: Prepared analogously from *cis*-5-decene. Yields, boiling points and elemental analyses are in Table. I.

TABLE I

erythro- and *threo*-5,6-Dihalodecanes *Ia*—*Ih*

Dihalide	Yield %	B.p., °C/Pa	Formula (m.wt.)	Calculated/Found	
				% C	% H
erythro-Ia	83	—[a]	$C_{10}H_{20}BrI$ (347·1)	34·61 35·09	5·81 5·82
threo-Ia	83	—[a]	$C_{10}H_{20}BrI$ (347·1)	34·61 35·08	5·81 5·82
erythro-Ib	76	86/65	$C_{10}H_{20}ClI$ (302·6)	39·69 40·49	6·66 6·55
threo-Ib	77	105/131	$C_{10}H_{20}ClI$ (302·6)	39·69 40·03	6·66 6·55
erythro-Ic	69	74/131	$C_{10}H_{20}FI$ (286·2)	41·97 42·35	7·04 7·56
threo-Ic	72	74/131	$C_{10}H_{20}FI$ (286·2)	41·97 40·85	7·04 7·44
erythro-Id	93	100/131	$C_{10}H_{20}Br_2$ (300·1)	40·03 50·17	6·72 6·84
threo-Id	80	82/40	$C_{10}H_{20}Br_2$ (300·1)	40·03 40·01	6·72 6·60
erythro-Ie	82	91/196	$C_{10}H_{20}BrCl$ (255·6)	46·99 46·96	7·88 7·83
threo-Ie	87	78/65	$C_{10}H_{20}BrCl$ (255·6)	46·99 47·37	7·88 7·81
erythro-If	89[b]	71/131	$C_{10}H_{20}BrF$ (239·2)	50·22 47·63	8·43 7·74
threo-If	86[c]	74/131	$C_{10}H_{20}BrF$ (239·2)	50·22 49·18	8·43 8·20
erythro-Ig	63	64/65	$C_{10}H_{20}Cl_2$ (211·2)	56·88 57·35	9·55 9·49
threo-Ig	68	66/52	$C_{10}H_{20}Cl_2$ (211·2)	56·88 56·44	9·55 9·13
erythro-Ih	74[d]	59/98	$C_{10}H_{20}FCl$ (194·7)	61·68 60·03	10·35 10·14
threo-Ih	72[e]	64/131	$C_{10}H_{20}FCl$ (194·7)	61·68 60·77	10·35 10·70

[a] Not determined. [b] The sample contained about 15% of *erythro-Id*. [c] The sample contained about 15% of *threo-Id*. [d] The sample contained about 10% of *erythro-Ig*. [e] The sample contained about 10% of *threo-Ig*.

erythro- and *threo*-5-Chloro-6-bromodecanes (*erythro*- and *threo*-*Ie*)

erythro-Ie: A solution of *trans*-5-decene (4·2 g; 30 mmol) in chloroform (80 ml) was saturated with anhydrous hydrogen chloride and treated at −5 °C with a solution of N-bromoacetamide[10] (4·5 g; 33 mmol) in chloroform (150 ml). The mixture was allowed to come to room temperature and the product was isolated. *threo-Ie*: Prepared analogously from *cis*-5-decene. Yields, boiling points and elemental analyses are in Table I.

erythro- and *threo*-5-Fluoro-6-bromodecanes (*erythro*- and *threo*-*If*)

Prepared analogously as it was described above for *erythro*- and *threo*-5-fluoro-5-iododecanes *Ic*, using N-bromoacetamide[10] as the brominating agent. Yields, boiling points and elemental analyses are in Table I.

erythro- and *threo*-5,6-Dichlorodecanes (*erythro*- and *threo*-*Ig*)

erythro-Ig: A solution of *trans*-5-decene (4·2 g; 30 mmol) in ether (30 ml) was saturated with chlorine at 0°C (2 h) and the product was isolated. *threo-Ig*: Prepared analogously from *cis*-5-decene. Yields, boiling points and elemental analyses are in Table I.

erythro- and *threo*-5-Fluoro-6-chlorodecanes (*erythro*- and *threo*-*Ih*)

Prepared analogously as it was described above for *erythro*- and *threo*-5-fluoro-6-iododecanes *Ic*, using N-chlorosuccinimide[11] as the chlorinating agent. Yields, boiling points and elemental analyses are in Table I.

Methods

The purity of the dihalides Ia–Ih: In addition to elemental analysis, the purity was checked by vapour phase chromatography and by polarography. Within limits of the experimental detection (±2%), all the dihalides were found to be configurationally uniform. The fluoro chlorides *erythro*- and *threo*-*Ih* were found to contain about 10% of the corresponding dichloride (*erythro*- and *threo*-*Ig*, respectively). The fluoro bromides *erythro*- and *threo*-*If* contained about 15% of the corresponding dibromide (*erythro*- and *threo*-*Id*, respectively).

Elimination runs: The dihalodecane (about 0·2 mmol) and internal standard (n-nonane) were dissolved in methanol (5 ml) and treated, under stirring, with zinc powder (Baker Analyzed Reagent; 60–200 mesh; 650 mg). The metal surface was activated by addition of 1,2-dibromoethane (100 mg). In order to check the progress of the elimination (Table II), aliquots were withdrawn at appropriate time intervals, poured into 25 ml volumetric flasks containing water (23 ml) and pentane (1 ml), the contents were shaken and samples of the pentane layer were directly injected into a gas chromatograph.

Vapour phase chromatography: *trans*- and *cis*-5-Decenes were analyzed on a 50 m capillary coated with dibutyl tetrachlorophthalate under the conditions described previously[12], *erythro*- and *threo*-5,6-Dihalodecanes were analyzed on a Apiezon capillary (50 m) or on the Carbowax/Chromosorb column at 80–120°C. The configurational isomers were cleanly separated under these conditions, the *erythro*-derivatives possessing always shorter retention times than the corresponding *threo*-isomers.

Polarography: The purity of the 5,6-dihalodecanes was checked by polarography under conditions which will be described elsewhere[13].

RESULTS AND DISCUSSION

Stereochemistry of dehalogenation reactions can be evaluated simply on basis of a configurational correlation between reactants and products (Scheme 1). The

TABLE II

Zinc-promoted dehalogenation of dihalides *Ia*—*Ih*: Temperature and time required for 90% conversion

Dihalide	Temperature, °C	Time, h
Ia	20	<0·1
Ib	20	0·3
Ic	20	10
Id	20	0·3
Ie	20	3
If	20	10
Ig	50	>500
Ih	100	>500

TABLE III

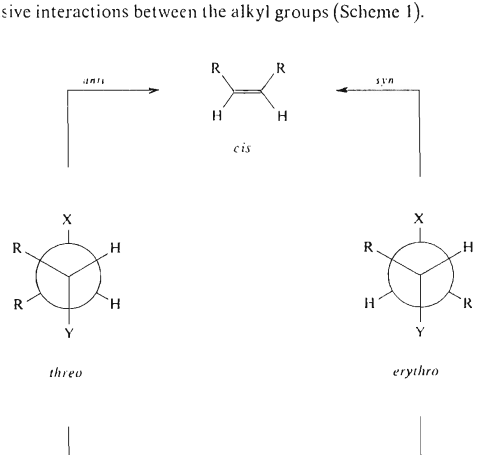
cis-trans 5-Decene composition (and steric course) in the zinc-promoted dehalogenation of *erythro*- and *threo*-5,6-dihalodecanes *Ia*—*Ih*

Dihalide	X	Y	*erythro*		*threo*	
			% *cis* (*syn*)	% *trans* (*anti*)	% *cis* (*anti*)	% *trans* (*syn*)
Ia	Br	I	3	97	96	4
Ib	Cl	I	5	95	86	14
Ic	F	I	32	68	42	58
Id	Br	Br	6	94	97	3
Ie	Cl	Br	6	94	85	15
If	F	Br	32[a]	68[a]	42[a]	58[a]
Ig	Cl	Cl	10	90	66	34
Ih	F	Cl	32[a]	68[a]	42[a]	58[a]

[a] Corrected on the impurities present in the reactant; *cf.* Experimental.

quantitative results we obtained in the zinc-promoted dehalogenation of the *erythro*- and *threo*-5,6-dihalodecanes *Ia–Ih* in methanol are summarized in Table III.

Inspection of Table III shows that the elimination stereochemistry depends both on the configuration as well on the identity of the halogen leaving groups. Concerning the configuration, the percentage of *syn*-elimination is always higher in the reaction from the *threo*- than from the *erythro*-dihalide. Such a difference can be easily explained in terms of a customary conformational analysis of the elimination based on the repulsive interactions between the alkyl groups (Scheme 1).



SCHEME 1

As it concerns the halogen group identity, the stereochemical course is influenced mainly by the more negative halogen which is designed as X in Table III. A pronounced effect of the X group variation is apparent from the obtained data for the iodides *Ia–Ic* (Y = I), as well as for the bromides *Id–If* (Y = Br) and for the chlorides *Ig–Ih* (Y = Cl) indicating that the proportion of *syn*-elimination increases, for any given Y, in the order X = Br < X = Cl < X = F. The effect of the other, more positive, halogen group Y is much weaker, as evidenced, *e.g.*, by the nearly identical

results obtained with the fluorides *Ic*, *If* and *Ih* (X = F; Y = I, Br and Cl, respectively).

In accordance with the available (indirect) evidence[3,14–16], the zinc-promoted dehalogenation can be regarded as a two-electron transfer from the metal surface on one halogen atom, which is coupled with a nucleofugal departure of the other halogen. For the „mixed" dihalides *Ia–Ic*, *Ie*, *If* and *Ih* it can be assumed that the electron transfer occurs on the more positive halogen atom Y, whereas the nucleofugal departure involves the more negative halogen X. From the data in Table III it may be inferred that it is the latter process which controls the stereochemical course.

A plausible rationale can be provided for these findings in terms of the theory of variable reactantlike–productlike transition state[3]. According to the theory, the extent of double bond development in transition state of the dehalogenation reaction depends on the strength of the carbon–halogen bonds. The weaker are these bonds, the greater double bond development is attained in the transition state. For unequal C—X and C—Y bonds, the extent of double bond development is controlled by the stronger of the two.

Since the strength of carbon–halogen bond is known to increase with increasing electronegativity of the halogen atom (I < Br < Cl < F), it follows that the double bond development in the dihalide series *Ia–Ih* is influenced mainly by the more negative halogen group (X). The increasing preference for *syn* elimination in the order X = Br < X = Cl < X = F thus may be correlated with the diminishing double bond development in the dehalogenation reaction.

There are some indications in literature[17,18] suggesting that such a correlation holds more generally in olefin-forming elimination reactions. Previously[19], we have found a quite analogous effect of halogen group identity on elimination stereochemistry in the base-promoted dehydrohalogenation from a series of 5-decyl halides (X = Br, Cl, F). Another case concerning electrochemical dehalogenation will be shortly reported[13].

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