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SOLVENT CONTROL OF PRODUCTS FROM COMPETING DEBROMINATION AND DEHYDROBROMINATION

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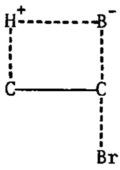
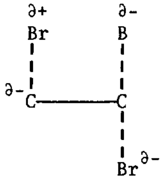
We have noted that *dehydro*bromination of cyclohexyl bromide proceeds through a much "looser" transition state I, (B = SC_6H_5) than does *de*bromination of *trans*-1,2-dibromocyclohexane II (B = SC_6H_5) in the reactions of these bromides with thiophenoxide ion.[1]

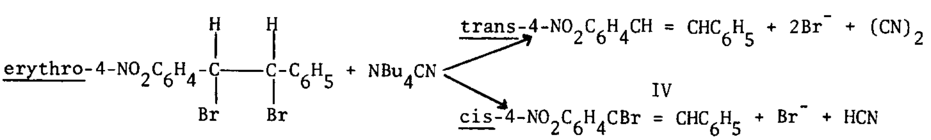


I E2C-like(loose)



II E2Br-like(tight)

A "loose" anionic transition state, I, has negative charge localised on base, B, and leaving group, Br, and so is a relatively strong hydrogen bond acceptor. A "tight" anionic transition state, II, has its charge more dispersed and although it is quite polarizable, it is not a powerful hydrogen bond acceptor.[1,2] Thus we expected that for the same reactants, an E2C-like dehydrobromination would be slowed less than a competing E2Br debromination, by transfer from dipolar aprotic to protic solvent. Our expectation is realised in the Table of the products from reactions 1a and 1b of NBu_4CN with *erythro*-1,2-dibromo-1-(4-nitrophenyl)-2-phenylethane in dimethylformamide-ethanol mixtures.



$$\textit{erythro}\text{-}4\text{-}NO_2C_6H_4\text{-}\underset{Br}{\overset{H}{C}}\text{—}\underset{Br}{\overset{H}{C}}\text{-}C_6H_5 + NBu_4CN$$

III
trans-4-$NO_2C_6H_4CH = CHC_6H_5 + 2Br^- + (CN)_2$ 1a

IV
cis-4-$NO_2C_6H_4CBr = CHC_6H_5 + Br^- + HCN$ 1b

In DMF as solvent, the almost exclusive (>99%) reaction product is that of *anti* debromination, i.e. 4-nitro-*trans*-stilbene III, but as the proportion of ethanol in the solvent is increased the proportion of *anti* dehydrobromination product, i.e. α-bromo-4-nitro-*cis*-stilbene IV, increases, until in pure ethanol, dehydrobromination accounts for 90% of the reaction products. The explanation is that the competing reactions of the one pair of reactants are both slowed by increasing the ethanol content of the solvent, but the E2C-like dehydrobromination is slowed least, because it proceeds through a looser transition state anion, I, (B = CN) which has a relatively stronger hydrogen bonding interaction with ethanol than does the transition state anion II (B = CN).[1]

The observation noted in the Table should be general.[2] When debromination and dehydrobromination by an anionic base compete with each other in a particular solvent, then the proportion of debromination product will be increased by transfer to a less protic solvent (i.e. a less powerful hydrogen bond donor), whereas the proportion of dehydrobromination product will be increased by transfer to a more protic solvent.

TABLE

Debromination (1a) and Dehydrobromination (1b) of erythro-1,2-dibromo-1-(4-nitrophenyl)-2-phenylethane

Solvent v/v		Products[a]		Conditions[b]	
%DMF	%EtOH	%-Br_2 III	%-HBr IV	T°C	Time (hours)
100	0	>99	<1	25	24[c]
100	0	>99	<1	70	0.01
75	25	81	19	40	0.5
50	50	58	42	40	12
25	75	22	78	60	2
0	100	10	90	70	24
0	100	<2.5[d]	<10[d]	70[d]	24[d]

a) Products were analysed by their u.v. absorption and identified by mass spectrometry, using reference samples of II and III. b) The erythro-1,2-dibromo-1-(4-nitrophenyl)-2-phenylethane was $4 - 6 \times 10^{-3}$M and NBu_4CN was $1 - 1.5 \times 10^{-2}$M. c) Reaction was complete in <10 minutes but the spectrum remained unchanged over this period. d) For an ethanolysis in the absence of NBu_4CN, but containing 3×10^{-3}M 2,6-lutidine.

REFERENCES

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2. A.J. Parker, Chem. Reviews., 69, 1 (1969).