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STEREOCHEMISTRY OF ELIMINATIONS FROM 2-BUTYL SYSTEM IN ACETIC ACID

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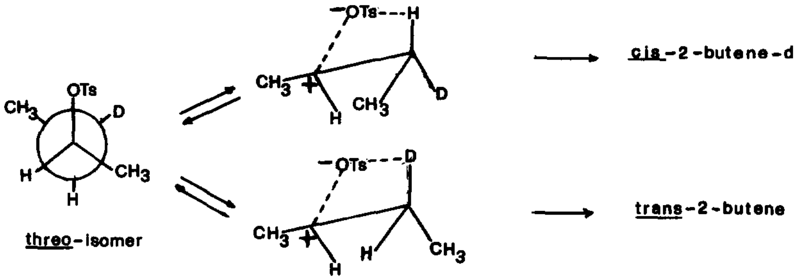
An E1 mechanism *via* ion-pairs has been postulated[1] in the eliminations from *erythro*- and *threo*-3-deutero-2-butyl tosylate in acetic acid in order to account for observed prevalence of *syn*-stereochemistry:



Since the product step of this mechanism involves the leaving-group anion, the nature of the latter would be expected to affect the stereospecificity of the elimination.

This expectation appears not to be fullfilled by the experiments. The data in Table 1 indeed show that the proportion of *syn*-elimination from 2-butyl system in acetic acid is remarkably independent of the nature of the leaving-group for such different leaving-groups as chloride, bromide and tosylate.

Another widely quoted criterion for the E1 ion-pair mechanism is the change of product distribution (elimination *versus* substitution) on changing the leaving-group[2]. Also this criterion fails for 2-butyl system. As shown in Table 2 the elimination fraction is essentially unaffected by leaving-group.

Our results appear to rule out the intervention of either free ions or ion-pairs in the acetolysis of 2-butyl system in agreement with general behaviour of secondary substrates[3]. An E2 involving paenecarbonium[4] transition state appears to be a more likely mechanism for these substrates.

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TABLE 1

Percent[a] olefin formed by *syn*-elimination from *threo*-3-deutero-2-butyl-X in glacial acetic acid

X	*cis*-2-butene %	*trans*-2-butene %	2-butene %
Cl	86	52	69
Br	86	50	68
OTs[b]	82	65	73

a) Measured by mass spectrometry at low ionizing voltage. It must be noticed that percents of *cis*-2-butene and *trans*-2-butene from *syn*-elimination reported (X = Cl, Br) represent *minimum* values, because no allowance has been made for the stereomutation at the α-carbon of the 2-butyl halides which occurs during elimination. However, the data are self-consistent because olefin analyses were carried out at times selected in such a way as to have the same extent of stereomutation at the α-carbon in both cases. That was measured by means of the racemization, in the reaction conditions, of optical active 2-butyl halides.
b) From the data by Skell and Hall, ref. 1

TABLE 2

Fraction of elimination on solvolysis products[a] of 2-butyl-X[b] in glacial acetic acid[c] at 141°

X	elimination/solvolysis
Cl	0.42
Br	0.46
I	0.42
OTs	0.44

a) 1- and 2-butenes, 2-butyl acetate
b) 0.1 M RX
c) 0.1 M NaOAc

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