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STEREOCHEMISTRY OF BASE-CATALYZED ELIMINATIONS FROM 2-ALKYL BROMIDES

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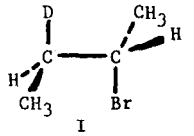
A syn-elimination stereochemistry has been postulated in eliminations from 2-hexyl chloride, bromide, and iodide induced by t-BuOK/DMSO on the basis of the very high trans-/cis-2-hexene ratios observed (1). A stereochemical study of eliminations from 2-alkyl halides exhibiting high trans-/cis-2-alkene ratios (i.e., promoted by t-BuOK/DMSO and n-Bu_4NF/DMF (2)) seemed warranted. We report the results of such an investigation using erythro-3-deutero-2-bromobutane, I.



I

I was prepared by the procedure of Skell and Hall (3) with the modification of keeping the reaction mixture temperature between -95° and -85° during irradiation. The presence of approximately 3% of contaminating threo-isomer was indicated by 6% of trans-2-butene-d in the trans-2-butene formed in reactions of I with KOEt/EtOH (Table 2).

I and undeuterated 2-butyl bromide, II, were subjected to elimination reactions in three different base/solvent systems. The relative olefinic proportions are presented in Table 1. The k_H/k_D values in Table 1 are calculated from the product percentages (4).

The k_H/k_D values show that deuterium was not removed during formation of cis-2-butene, but deuterium loss was involved in formation of trans-2-butene. The isotopic analysis of the olefins (Table 2) supports this conclusion. The data demonstrate quite clearly that both cis- and trans-2-butene are formed by anti-elimination in reactions of I with t-BuOK/DMSO and n-Bu_4NF/DMF.

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TABLE 1

Olefin Proportions and k_H/k_D Values from Elimination of erythro-3-Deutero-2-bromobutane

Reaction Conditions	Reactant	1-Butene %	trans-2-Butene[a] %	trans-2-Butene[a] k_H/k_D	cis-2-Butene %	cis-2-Butene k_H/k_D
EtOK/EtOH (70°)	I	35.8[b]	29.4	3.4	34.8	1.0
	II	20.8	58.6	---	20.6	---
t-BuOK/DMSO (30°)	I	53.3	21.0	4.5	25.7	1.1
	II	29.4	55.0	---	15.5	---
n-Bu_4NF/DMF (50°)	I	33.1	33.1	3.6	33.8	1.1
	II	16.7	64.5	---	18.7	---

[a] Corrected for presence of trans-2-butene-d.
[b] These olefinic proportions agree with those given in reference 3.

TABLE 2

Isotopic Composition[a,b] of Olefins from Elimination of erythro-3-Deuterio-2-bromobutane

	EtOK/EtOH %	t-BuOK/DMSO %	n-Bu_4NF/DMF %
1-butene-d	100	100	100
1-butene	0	0	0
trans-2-butene-d	6	6	6
trans-2-butene	94	94	94
cis-2-butene-d	100	100	100
cis-2-butene	0	0	0

[a] Measured by mass spectrometry at low ionizing voltage.
[b] Uncertainty estimate as ± 1%.

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