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THE ROLE OF BASE ION-PAIRING IN BIMOLECULAR ELIMINATION: THE EFFECT ON THE SYN-ANTI DICHOTOMY[1]

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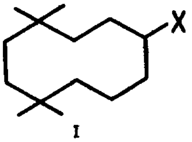
Recently, we have given evidence[3-8] suggesting that the dichotomous syn-anti course of bimolecular elimination can be changed considerably, and in some cases fundamentally[5], by an alternation of the ion-pairing capacity of the base-solvent combination used. This led us to propose[3,4] that both the dissociated and the ion-paired base can take part in the reaction and lead, eventually, to entirely different steric results, the former preferring anti-, but the latter syn-elimination.

The important discovery that macrocyclic polyethers[9] (crown ethers) possess a unique ability to fill the coordination sites of cations and convert contact ion-pairs into separated ions[10] made it possible to test this view and explore the operation of the contact and separated ions of the base participating in the two (syn- and anti-) elimination processes.

We have shown previously that bimolecular elimination of the medium ring derivatives I proceeds in an exceptionally clear-cut manner[8,11,12], the trans-olefins II and III being formed mainly[13] by syn-elimination, whereas the corresponding cis-olefins II and III almost exclusively by anti-elimination.

This, obviously, makes the derivatives I very useful models for mechanistic studies: as a simple consideration shows, an effect of reaction variables on the syn- and anti-mechanistic pathways can be deduced easily from the observed trends in the



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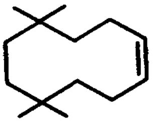
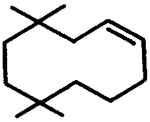


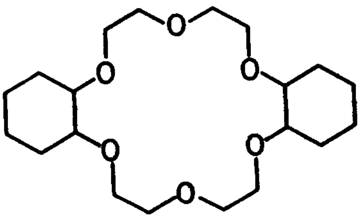
II

(cis- and trans-)



III

(cis- and trans-)



IV

trans- and cis-olefin proportions. Therefore, we have now investigated the effect of dicyclohexyl-18-crown-6-ether (IV)[9,14] on the trans- and cis-olefin composition in reaction of the bromide I (X=Br) and the tosylate I (X=OTs) with potassium tert-butoxide in three very different solvents (benzene, tert-butanol and dimethylformamide). The results are summarised in TABLE 1.

As the data in Table 1 show, the addition of an equimolar amount of the crown ether IV to the base effected a remarkable decrease in the trans- to cis-olefin ratios (trans-II/cis-II as well as trans-III/cis-III) in reactions of the two derivatives I (X=OTS and Br) in all the solvents investigated.

TABLE 1 Effect of the Crown Ether IV on the Olefin Composition in the Reaction of Tosylate I (X=OTs) and Bromide I(X=Br) with Potassium tert-Butoxide in Different Solvents

X[a]	Solvent[b]	II			III		
		%trans	%cis	trans/cis	%trans	%cis	trans/cis
Br	Benzene	83.0	1.5	55.0	14.0	1.5	9.3
	Benzene+IV[c]	9.4	75.8	0.12	0.5	14.3	0.03
Br	t-BuOH	76.0	8.4	9.0	12.2	3.4	3.6
	t-BuOH+IV[c]	8.9	75.3	0.12	1.1	14.7	0.07
Br	DMF	7.0	72.0	0.10	1.0	20.0	0.05
	DMF+IV[c]	3.7	79.4	0.05	0.1	16.8	0.006
OTs	Benzene	88.8	1.4	63.4	8.8	1.0	8.8
	Benzene+IV[c]	12.0	58.4	0.20	0.5	29.1	0.02
OTs	t-BuOH	68.8	7.0	9.8	12.6	11.6	1.1
	t-BuOH+IV[c]	22.2	54.6	0.40	2.8	20.4	0.14
OTs	DMF	40.2	43.0	0.94	2.8	14.0	0.20
	DMF+IV[c]	5.8	68.7	0.08	0.3	25.2	0.01

[a] 50 mg of the reactant was dissolved in 2.5 ml of the alkoxide solution (0.33 M in t-C_4H_9OK) and heated under nitrogen in sealed tubes. [b] The following conditions (°C/hrs) were used in the individual runs: (1): 120/10; (2): 60/2; (3): 100/9; (4): 50/2; (5): 50/0.5; (6): 20/2; (7): 100/8; (8): 50/2; (9): 100/6.5; (10): 100/1; (11): 50/0.5; (12): 30/0.5. The olefins formed have been found to be stable under these conditions. However, isomerisation of the olefins is very substantial at higher temperatures, if the crown ether is present. [c] Equimolar amount of IV was dissolved in the alkoxide solution previous to the reaction.

The most pronounced effect was found in the non-polar solvent benzene. In reaction of I (X=Br as well as OTs) with the "plain" potassium tert-butoxide the trans-olefin formation is the overwhelming process (more than 97%). On the other hand, it is the cis-olefin formation which prevails greatly (more than 87%) in the corresponding reactions, if the base is complexed by IV. Clearly, the contact ion-pairs separating ability of the crown ether IV has to account for the dramatic changes; it is known[10,14] that an equimolar amount of IV suffice to convert the contact ion-pairs into separated ions. Hence, the separated ions of potassium tert-butoxide have to be fully responsible for the course of the reaction with the complexed base and a conclusion can be drawn that they react predominantly though not exclusively by anti-elimination[15]. By contrast, the separated ions took only a meagre, if any, part in the corresponding reaction with the "plain" base, as evidenced by the opposite steric result. Therefore, the contact ions have to be responsible and a conclusion can be drawn that they react with the two derivatives almost exclusively by syn-elimination.

A considerably less striking effect of IV was found in the more polar solvents tert-butanol and dimethylformamide; as inspection of Table 1 shows, the reaction with the "plain" base accounts for this observation. Here, the cis-olefin formation increased substantially on going from benzene (less than 3%) to tert-butanol (12-18%) and became prevalent in dimethylformamide (57-92%). The present results as well as other evidence[16] show unambiguously that the contact ions of the base prevail greatly over the separated ions in the completely non-polar solvent benzene. On the other hand, the separated ions are assumed[16] to become more significant on going to a somewhat more polar solvent tert-butanol and to prevail[4] on going, further still, to the very polar solvent dimethylformamide, accounting thus for the pronounced cis-olefin formation. Hence, the contact-ions separating ability[17] of a solvent appears to be a factor of a decisive importance; by contrdling the proportions of the contact and separated ions in the solution it controls effectively the steric course of the reaction. It may be noted, however, that the crown ether IV exerts a substantial, though less pronounced effect on the trans-olefin formation even in the most polar solvent investigated, indicating that, in absence of IV, the contact-ions separating ability of a common solvent does not suffice[4] to suppress completely the operation of the contact ion-paired base.

Accordingly, the present findings suggest strongly that the contact and the separated ions of the base compete, in greatly varying proportions, in the reactions, the former ions leading almost exclusively to the trans-olefin formation by syn-elimination, but the latter predominantly to the cis-olefin formation by anti-elimination. In this way, these findings bear upon the origin[7,18] of the dichotomous elimination behaviour of the medium-ring derivatives: the syn → trans, anti → cis dichotomy appears to be, in a greater part, a consequence of the dichotomy of the participating base.

REFERENCES AND NOTES

1. This is the twenty fifth of a series of papers dealing with mechanism of elimination reactions; for previous paper see ref. 3.
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