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Competition in the Sodium Iodide Catalysed Isomerisation of Some Aziridines

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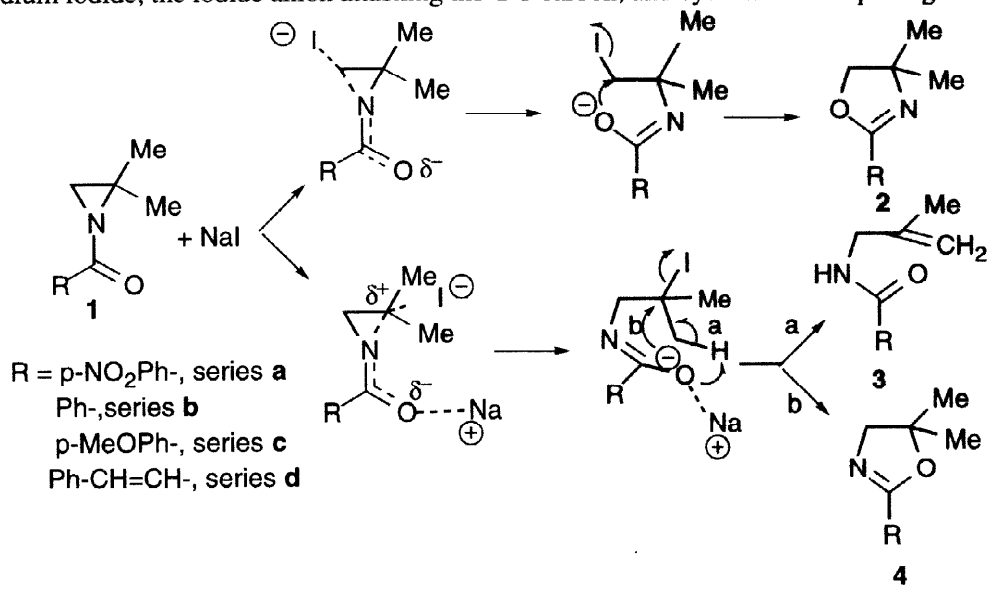
Abstract : N-Acyl-2,2-dimethylaziridines have been shown to be isomerised by sodium iodide into three isomers. The yield of these isomers appears to depend on the electronic effect of the acyl group.

Heine has shown that N-p-nitrobenzoyl-2,2-dimethylaziridine **1a** is isomerised into oxaline **2a** by the action of sodium iodide, the iodide anion attacking the C-3 carbon, and cyclisation completing the reaction.[1]



Scheme

We have now studied the effect of the replacement of the p-nitrobenzoyl group in **1a** by the benzoyl (**1b**), the p-methoxybenzoyl (**1c**), and the cinnamoyl groups (**1d**), and we obtained, under a variety of conditions, mixtures of the three isomers **2b-d**, **3b-d** and **4b-d** (**Scheme**). The unexpected major products **3** and **4** were derived by ring opening on the C-2 side. For the aziridines **1b-d** used in the present investigation, it may be argued that the acyl group increased the conjugation between the aromatic and the carbonyl groups, thus favouring the coordination bonding between the oxygen atom and the sodium cation ; this would loosen the C-2—N bond, facilitating an efficient iodide anion attack of the tertiary carbon. The iodoamidate formed would give, on the one hand the allylic amide **3**, by abstraction of the hydrogen atom of a methyl group, and on the other hand, the oxazoline **4** by cyclisation on the C-2 carbon (Table). We also treated compounds **2b**, **3b**, and **4b** with sodium iodide and recovered only the starting material. Each product results therefore from a direct isomerization of the asiridine **1** by the iodide anion.

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Table : Isomerisation of N-Acyl-2,2-dimethylaziridines 1 by NaI

Aziridines	Method	Yield of isomers (%)		
		2	**3**	**4**
1b : R=Ph	A	40	40	20
	B	15	60	25
	C	23	54	23
1c : R=pMeOPh-	A*	33	40	27
	B	32	36	32
	C	24	43	33
1d : R=Ph-CH=CH-	A	29	29	42
	B*	60	20	20
	C*	40	32	28

A : 2 mmol of aziridines **1** and 7.1 equ. NaI (with lower concentrations, some **1b** is recovered), 56 °C, 19 h (shorter times give incomplete reactions) , acetone (with other solvents, the reaction is not complete in the same conditions : recovered **1b** in MeCN 83 %, in DMSO 61 %, in THF : 38 %, in acetone : 0 %).
B : 2 mmol of aziridiens **1** and 7.1 equ. NaI, 56 °C, 19h, butanone.
C : 2 mmol of aziridines **1** and 1.1 equ. NaI, 80 °C, 3.30 h, butanone.
* 30 % of starting material recovered. The identification of products **2**, **3** and **4** was achieved by HNMR comparison with authentic samples prepared by published procedures.[2]

A radical mechanism[3] appears excluded to explain the cleavage of the C-2—N bond as we did not obtain any pyrrolidone (radical cyclisation of **1d** by sodium naphthalenide) and the iodide anion was reduced at a potential 0.5 V lower than the reduction potential of aziridine **1d** (-2.2 V).

The cleavage of the C-2—N bond by the iodide anion was also reported when isomerising N-benzoyl-2-carbethoxyisopropyl aziridine and N-benzoyl-2-ethyl aziridine.[4] Stamm has also invoked coordination bonding to explain the ethanolysis of the aziridines **1** in the presence of sodium perchlorate.[5]

From these results, we can conclude that the electronic effect was dominant.

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