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A NOVEL MODE OF BASE-INDUCED DECOMPOSITION OF *N*-ALKOXYPYRIDINIUM SALTS

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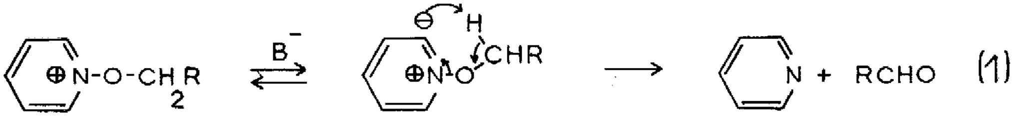
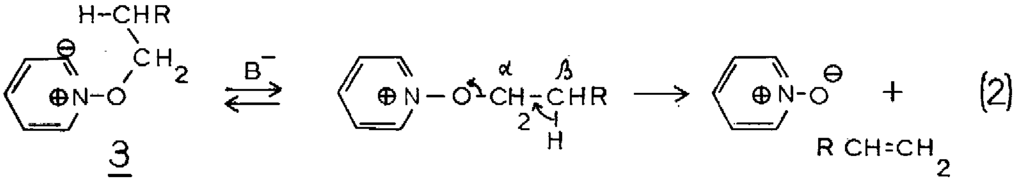
Since the work of Katritzky *et al*[1,2] it has been known that the action of nucleophiles on *N*-alkoxypyridinium salts can lead to four kinds of reactions, of which the most common is a decomposition to a carbonyl derivative and a deoxygenated pyridine carried out under the action of bases.

The mechanism of this reaction, first described as the result of the direct abstraction of the α-proton by the base[3] would seem to be in reality more complex and involving an intermediary ylide which rapidly forms in a basic medium by abstraction of the -2 proton[4] (eq. 1)



We wish to report a novel mode of base-induced decomposition of *N*-alkoxypyridinium salts carrying a β-hydrogen in their alkoxy chain. In these compounds the *N*-oxide moiety can act as a leaving group in an elimination reaction[5] yielding an ethylenic derivative (eq. 2). The mechanism of this new decomposition does not involve an ylide in the abstraction of the β-hydrogen (at least not in our working conditions).



Although this elimination reaction was forseen in the thermolysis of some particular salts[2,6,7] it was not noticed during the study of the base-induced decompositions of *N*-alkoxypyridinium salts carried out so far. This gives a fifth possible reaction for nucleophiles on theses derivatives, that can be distinguished from the substitution at C_α by the fact that the *N*-oxide produced is accompanied here by an olefinic compound and not by an alcohol.

We have studied the decomposition of salts 1 and 2[8] by 2.5 *N* NaOH at 25°C. Owing to the high solubility of pyridine *N*-oxide in water, the resulting heterocyclic products were continuously extracted by $CHCl_3$ over 24 hours and analyzed by quantitative VPC. In fact the reaction was achieved within a few minutes, as shown by the NMR study performed in 2.5 *N* NaOD in D_2O ; the deuterium content reported below was deduced from the spectra recorded after 15 min.

	Decomposition Products		
	N-oxide	Deoxy-heterocycle	Deuteration in -2 and -6
1 : $\mathrm{Pyr\overset{+}{N}\text{-}OCH_2CH_2CO_2H,\ NO_3^-}$	78 %	3 %	95 %
2 : $\mathrm{3,5\text{-}Lut\overset{+}{N}\text{-}OCH_2CH_2CO_2H,\ NO_3^-}$	89 %	4 %	96 %

The results given above show that the decomposition according to eq. 2 is highly predominant, the classical decomposition being here very reduced. The nucleophilic substitution at C_α would normally also produce an *N*-oxide but here it is not observed to any detectable extent as shown in NMR by the ratio acrylate / *N*-oxide = 1, and by the absence of hydracrylate signals.

The high percentage observed for deuteration implies a fast and almost complete base-catalyzed exchange of the -2 and -6 hydrogen atoms in 1 and 2 prior to elimination[9], and shows that abstraction of the β-proton does not result from an intramolecular transfer affecting an ylide such as 3, for if this was the case the deuteration of the produced *N*-oxide would not exceed 50 %.

The competition between the two types of alkaline decomposition shown by eq. 1 and 2, notably in terms of the nature of the base, is presently being studied.

References and Notes

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9. Though *N*-alkoxypyridinium salts exchange very rapidly their -2 and -6 protons in the presence of hydroxide ions, this exchange is considerably slower in the case of the *N*-oxides themselves[10]. We checked that in 2.5 *N* NaOD at 25° C no exchange was revealed after 15 min. for the *N*-oxides which were not substituted at the oxygen atom ; we also checked that the β-hydrogens did not undergo any previous exchange (the acrylate produced was not deuterated).
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