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ACYLISOCYANATE BIS-ACETALS TO N-(1-ALKOXYALKYLIDEN)CARBAMATE ACETALS ISOMERIZATION. (*)

M.L. Graziano, M.R. Iesce, R. Palombi and R. Scarpati*
Istituto di Chimica Organica dell'Università
Via Mezzocannone 16 - 80134 Napoli (Italy)

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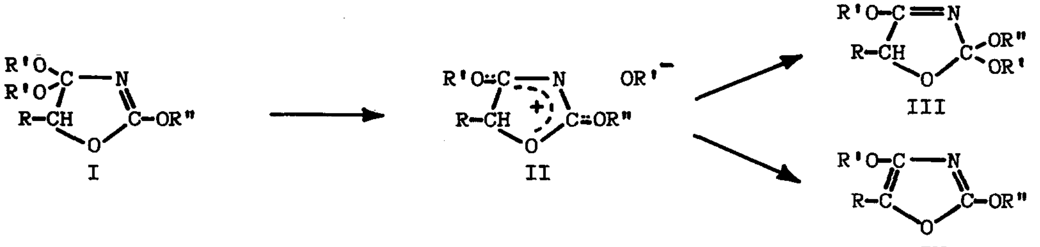
In previous papers[1,2] we reported the synthesis of Δ^2-oxazolines I which can be considered cyclic bis-acetals of acylisocyanates. Acetals of acylisocyanates are relatively little known[3] and nothing is reported on the properties of their bis-acetal derivatives, except their behaviour in acid hydrolysis[1,2].

We wish now to report that compounds I undergo isomerization to Δ^3-oxazolines III which are the first examples of N-alkylidencarbamate acetals.



a, $R=H$ $R'=CH_3$ $R''=CH_3$
b, $R=H$ $R'=CH_3$ $R''=C_2H_5$
c, $R=C_6H_5$ $R'=CH_3$ $R''=C_2H_5$

A 4% solution of compound Ia[1] in CH_3OH was heated at 35°. After 90 days, removal of the solvent afforded IIIa[4] in pure form $\left[\tau\ 5.70\ (s,2H,{>}CH_2),\ 6.09\ (s,3H,{=}\underset{|}{C}{-}OCH_3),\ 6.76\ (s,6H,2{-}OCH_3)\right]$.

In the above conditions also Ib[1] and Ic[2] isomerized to IIIb and IIIc respectively, which slowly converted into trimethoxy- Δ^3-oxazolines[4] by transesterification.

Compounds IIIa and IIIb were also obtained from Ia and Ib in CD_3NO_2,CD_3CN, $C_6D_5NO_2$, C_6D_5CN, C_6D_{12} runs with solvent dependent rates of reaction. When solvents other than CH_3OH were used for Ic, a drastic change of the reaction pathway was observed, and IVc[2b] was obtained quantitatively.

Isomerization of I to III is an anionotropic transformation proceeding by alkoxy transfer[5]. A possible explanation of all the results till now obtained is that compounds I exist in equilibrium with the intimate ion pairs II[6] and that in ion pair IIc the effect of the C_5 phenyl substituent is to withdraw electrons from the C_5 carbon atom of the ion pair cationic part and so to loosen the attached hydrogen and to favour elimination reaction[7]. The reversibility of this reaction would be the simplest explanation of the fact that in CH_3OH isomerization to IIIc takes place.

If this explanation is valid, and if a dissociation of II to free ions promoted by electrophilic attack by solvent molecules on the negative end of the forming ion pair occurs, will be ascertained through additional data which are in progress.

NOTES AND REFERENCES

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