NITROXYL RADICALS OF 3-IMIDAZOLINE AND 3-IMIDAZOLINIUM IN THE VILSMEIER REACTION

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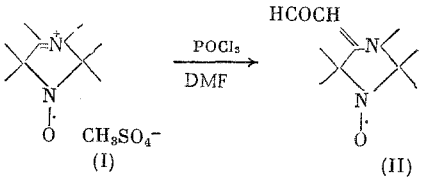
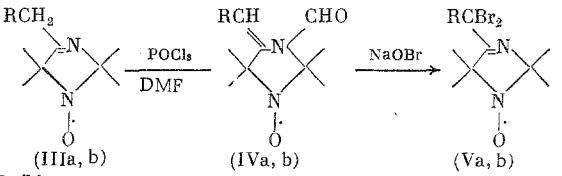
It was shown previously in [1] that the stability of nitroxyl radicals of 3-imidazolinium in acidic media made it possible to carry out reactions under these conditions with retention of the radical center. While continuing the study of the properties of these compounds we effected the Vilsmeier reaction with 3-imidazolinium methylsulfate (I). The enaminoaldehyde 2,2,3,5,5-pentamethyl-4-(2-hydroxyethylidene)imidazolidin-1-oxyl (II) of mp 153-155°C was formed in this way. IR spectrum (KBr, ν, cm^{-1}): 1640 (C=O), 1590 (C=C). UV spectrum in ethanol, λ_{max}, nm (log ε): 298 (4.52).



(I) (II)

The unchanged derivatives of 3-imidazoline (IIIa, b) also underwent formylation without affecting the radical center. However in this case the reaction proceeded in another direction [2] and the products had the structure 2,2,5,5-tetramethyl-4-methylene-3-formylimidazolidin-1-oxyl (IVa) of mp 91-93°C, IR spectrum (KBr, ν, cm^{-1}): 1680 (C=O) and 2,2,5,5-tetramethyl-3-formyl-4-ethylidenimidazolidin-1-oxyl (IVb) of mp 80-81°C, IR spectrum (KBr, ν, cm^{-1}): 1680 (C=O).



(IIIa, b) (IVa, b) (Va, b)

R = H (a), CH_3 (b)

Compounds (IV) readily lost the formyl group on treatment with acids or with electrophilic reagents. Thus treatment with NaOBr led to the dibromo derivative (Va, b) unaccessible by other routes. In this way compounds (IV) opened a new route to the synthesis of functional derivatives of imidazoline nitroxyl radicals.

LITERATURE CITED

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