Novel Condensation Products of Cyanamides with Hydroxylamine: Amino-oxyformamidines

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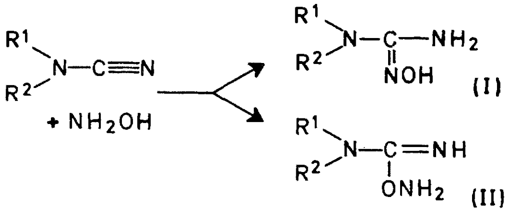
Summary Disubstituted cyanamides reacted with hydroxylamine to give, depending on the reaction conditions, hydroxyguanidines or amino-oxyformamidines.

THE condensation of cyanamide with hydroxylamine hydrochloride was first reported by Praetorius-Seidler,[1] who obtained a mixture of ammonium chloride and hydroxyguanidine hydrochloride identified as the chloroplatinates. The preparation of 1,1-disubstituted hydroxyguanidines was attempted by Braun and Schwarz,[2] who obtained "oximes of urea" by treating disubstituted cyanamides in alcoholic solution with 1 mol of hydroxylamine.

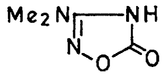
The addition of hydroxylamine base to the $-C{\equiv}N$ bond in disubstituted cyanamides was found in this work to yield, depending on the nature of the solvent and substituents at the nitrogen atom in cyanamide, either disubstituted hydroxyguanidines (I) or *NN*-disubstituted-1-amino-oxyformamidines (II). Compounds (Ia—f) were prepared in satisfactory yields (50—70%) when the addition of hydroxylamine was effected in anhydrous dioxan. (Ie) and (If) were unstable and could be separated only as salts.

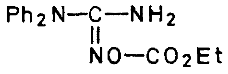


(Ia) : $R^1 = R^2 = Ph$
(Ib), (IIb) : $R^1 = Ph, R^2 = Me$
(Ic), (IIc) : $R^1R^2N{-} =$ piperidino
(Id : $R^1R^2N{-} =$ morpholino
(Ie), (IIe) : $R^1 = R^2 = Me$
(If), (IIf) : $R^1 = R^2 = Bu^n$

A similar addition reaction with hydroxylamine base in anhydrous ethanol gave (Ia) and (Id) in substantially lower yields, whereas the isomeric amino-oxyformamidines (IIb, c, e, and f) were obtained instead of the corresponding hydroxyguanidines; (IIe) was unstable and could be separated only as the benzoate.

Hydroxyguanidines (I) were easily converted into their salts with inorganic and organic acids. With acylating agents (AcCl, BzCl) they gave *O*-acyl- or *ONN*-triacyl derivatives. When ethyl chloroformate was used, the product was an *O*-ethoxycarbonyl derivative (*e.g.* IV) or a cyclic compound, 3-dimethylamino-Δ^2-oxadiazolin-5-one (III).


(III)


$Ph_2N{-}C(=NO{-}CO_2Et){-}NH_2$
(IV)

Amino-oxyformamidines (IIb) and (IIe) isomerised on treatment with HCl or acylating agents to give the corresponding hydrochlorides or *ONN*-triacetyl derivatives of (Ib) and (Ie) respectively. Amino-oxyformamidines (IIc) and (IIf) were more stable and could be converted into hydrochlorides without isomerisation.

Compounds (I) had i.r. absorption bands typical for NH_2 (3500—3400 cm^{-1}) and OH (3610 cm^{-1}), the two amine bands being separated as expected by approximately 100 cm^{-1}. Amino-oxyformamidines (II) showed no OH absorption; typical bands were noted for the imine (=NH, 3340 cm^{-1}) and amino-oxy-group, ONH_2, the latter in the form of two peaks separated by about 120 cm^{-1} (3535 and 3415 cm^{-1}). The n.m.r. spectra confirm the i.r. data.

Further differences between (I) and (II) were observed in the shape of the potentiometric titration curves.

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[1] G. Praetorius-Seidler, *J. prakt. Chem.*, 1880, [2], **21**, 129.
[2] J. Braun and R. Schwarz, *Ber.*, 1903, **36**, 3660.