CONCLUSIONS

1. Complexes of diaminoglyoxime with amines have been obtained and investigated for the first time.

2. It was shown on the basis of analysis of vibrational spectra that the product of interaction of diaminoglyoxime and ethylenediamine was a complex with hydrogen bonds in the formation of which the amino groups of diaminoglyoxime and ethylenediamine and the hydroxyl groups of diaminoglyoxime take part.

LITERATURE CITED


METHYLATION OF 1-HYDROXYTETRAZOLE

O. A. Luk'yanov and N. I. Shlykova

The methylation of 1-hydroxytetrazoles (HT) has been studied in the present work in continuation of investigations of the rules for alkylation of ambident anions with centers of attack on N and O atoms [1].

Information on the alkylation of HT is limited to the following examples. On treatment of 1-hydroxy-5-phenyltetrazole (Ia) with MeI or EtI in the presence of NaOH 1-alkoxytetrazoles are obtained in high yield together with a small quantity (1-4%) of N-alkylation products [2]. Products of O-alkylation only were obtained by the alkylation of 1-hydroxy-5-benzhydryltetrazole with MeI in [3] and also 1-hydroxy-5-benzhydryltetrazole with allyl bromide or bromoacetic acid methyl ester [4] in yields of 15-37%. Mention should also be made of methylation with diazomethane of adducts of HN₃ with sodium fulminate which were used as isomeric forms of 1-hydroxytetrazole in [5].

The methylation of (Ia) and of 1-hydroxy-5-methyltetrazole (Ib) and/or their salts under the action of MeI, (MeO)₂SO₂, CH₂N₂, and Me₃O⁺BF₄⁻ (TMO) has been studied by us.

It was established that on reacting triethylammonium or Ag salts of (Ia) or (Ib) with MeI or (MeO)₂SO₂ the corresponding O-alkylation products (II) were formed:

\[
\begin{align*}
R & \quad \text{MeX} \\
\text{M} & \quad \text{MeI} \\
\text{MeI} & \quad \text{MeO} \\
\text{Ia} & \quad \text{Ib}
\end{align*}
\]

The constitution of the methylation products was confirmed in the case of (IIa) by comparing its spectral characteristics with the authentic compound of [2], and for (IIb) by data of elemental analysis, IR, and PMR spectra, and by reduction with HI to 5-methyltetrazole

\[
(\text{IIb}) + \text{HI} \rightarrow \text{Me-C-NH}
\]

In the above-mentioned reactions N-methylation took place to an insignificant degree in addition to the O-methylation. It was more marked on using diazomethane where the ratio of products of O and N methylation was approximately 5:1

\[
(\text{I}) + \text{CH}_2\text{N}_2 \rightarrow (\text{II}) + \text{R} = \text{Ph, Me}
\]

Such a result, if only partial, may be explained by the high reactivity and correspondingly low selectivity of CH\_2\_N\_2. In this connection the direction of reaction of NH\_4 salts of (Ia) and (Ib) with TMO was checked and it was established that products of N and O methylation were formed in comparable amounts. When methylating OT itself almost exclusively N-methylation was observed.

Thus the ratio of N and O alkylation products of OT depended appreciably on the nature of the reactants and their matching, it is possible to achieve fairly selective progress of the reaction at the N or O atoms.

The problem of the structure of N-methylation products proved to be fairly complex and was not fully resolved in the present work.

On methylating (Ib) and its NH\_4 salt by the action of TMO two isomeric N-methylation products were formed. Reduction of these with HI gave the same 1,5-dimethyltetrazole (IIIb). This fact indicates that the products of methylating (Ib) were the N-oxides of 1,5-dimethyltetrazole.

\[
\begin{align*}
\text{Me-C-N-Me} & \xrightarrow{\text{HI}} \text{Me-C-N-Me} \\
\text{(IVb)} & \rightarrow \text{Me-C-N-Me} \rightarrow \text{O} \\
\text{(IIIb)} & \rightarrow \text{Me-C-N-Me} \rightarrow \text{O} \\
\text{(VIb)} &
\end{align*}
\]

Comparison of the PMR spectra of (IVb), (VIb), and (IIIb) (Table 1) and also consideration of the influence of the N \rightarrow O group on the chemical shifts of the Me group signals* made it possible to ascribe the structure of 1,5-dimethyltetrazole 1-N-oxide (IVb) to the isomer with the low field shift of the C-Me group signal and 4,5-dimethyltetrazole 1-N-oxide (VIb) to the other isomer. Such assignments were confirmed by the mass spectra of the compounds. Thus they were fragment ions [M-0]^+, [N-N\_2]^+, and [M-NH\_2]^+ (intensity 15-35% of main peak) together with the molecular ion in the mass spectrum of (IVb) but ions [M-N\_2O]^+ and [M-HN\_2O]^+ (12-25%) in the mass spectrum of (VIb).

The ratio of isomers was 2:1 while on methylation of the NH\_4 salt of (Ib) product (VIb) predominated and on methylation of (Ib) itself (IVb) predominated. It should be recorded that reduction of the reaction mixture obtained on interacting the NH\_4 salt of (Ib) with TMO led to the formation of (IIIb) only. This evidently indicates that methylation at positions 2 or 3 of (Ib) did not occur. Thus (Ib) or its salt gave with TMO a mixture of products of N-methylation at a N atom adjacent to the C atom

\[
\begin{align*}
\text{Me-N-OH} + \text{MeOBF}_4 & \rightarrow \\
\text{(Ib)} & \rightarrow \text{Me-C-NMe} \\
\text{Me-C-NMe} & \rightarrow \text{O} \\
\text{(IVb)} & \rightarrow \text{Me-N} \\
\text{(VIb)} &
\end{align*}
\]

*See [6] and literature there in.