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.

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METHYLATION OF 1-HYDROXYTETRAZOLES

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

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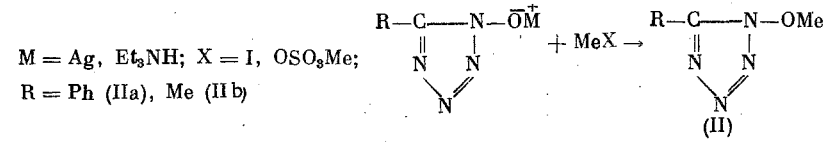
The methylation of 1-hydroxytetrazoles (HT) has been studied in the present work in continuation of investigations of the rules for alkylation of ambident anions with centers of attack on N and O atoms [1].

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-benzoyltetrazole 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 HN_3 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, $(MeO)_2SO_2$, CH_2N_2, and $Me_3O^+BF_4^-$ (TMO) has been studied by us.

It was established that on reacting triethylammonium or Ag salts of (Ia) or (Ib) with MeI or $(MeO)_2SO_2$ the corresponding O-alkylation products (II) were formed:



N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow.

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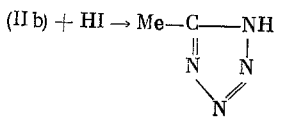
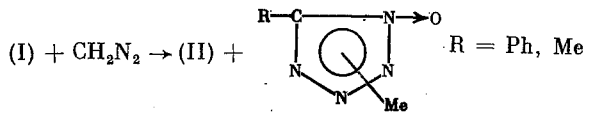
The constitution of the methylation products was confirmed in the case of (IIa) by comparing its spectral characteristics with the authentic compound of [2], and for (IIb) by data of elemental analysis, IR, and PMR spectra, and by reduction with HI to 5-methyltetrazole



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

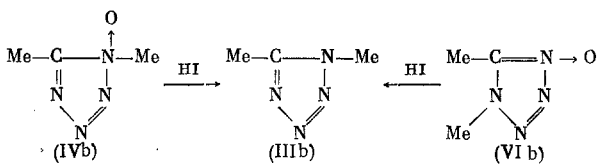


Such a result, if only partial, may be explained by the high reactivity and correspondingly low selectivity of CH_2N_2. In this connection the direction of reaction of NH_4 salts of (Ia) and (Ib) with TMO was checked and it was established that products of N and O methylation were formed in comparable 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.

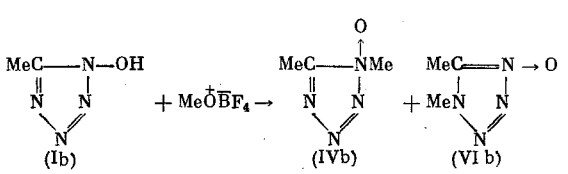
The problem of the structure of N-methylation products proved to be fairly complex and was not fully resolved in the present work.

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.



Comparison of the PMR spectra of (IVb), (VIb), and (IIIb) (Table 1) and also consideration of the influence of the N → 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 there were fragment ions $[M-O]^+$, $[M-N_2]^+$, 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



*See [6] and literature there in.

TABLE 1. PMR Spectra of Tetrazole Derivatives

Compound	Solvent	Chemical shifts, δ, ppm	
		MeC	MeO or MeN
(IIIb)	$CDCl_3$	2,51	3,96
(IIb)	Acetone-d_6	2,55	4,32
(IVb)	$CDCl_3$	2,51	4,03
(VIb)	$CDCl_3$	2,38	4,06
(IIIa)	$CDCl_3$		4,13
(VII)	$CDCl_3$		4,33
	Acetone-d_6		4,23
(IIa)	Acetone-d_6		4,41
(V)	$CDCl_3$		4,19
(IVa) or (VIa)	$CDCl_3$		4,19

A somewhat different picture was observed on N-methylation of (Ia) and its NH_4 salt. The methylation product gave a single extended spot on TLC but in the PMR spectrum there was one peak for an N-Me group. After three to four recrystallizations from acetone the same isomer of N-methyl-5-phenyltetrazole N-oxide was isolated which had been obtained previously in [1], and to which the structure 3-methyl-5-phenyltetrazole had been ascribed on the basis of reduction to 2-methyl-5-phenyltetrazole (VII) and of its mass spectrum. However the difference in chemical shifts of the N-Me group of the product of methylation and of (VII) (see Table 1) favors 2-methyl-5-phenyltetrazole 1-oxide (V). The 1-methyl- or 4-methyl-5-phenyltetrazole 1-oxides (IVa) or (VIa) are seemingly obtained with it which follows from the formation of 1-methyl-5-phenyltetrazole (IIIa) together with (VII) on reduction of the methylation product.

It was therefore established that methylation of OT may be effected at the O atom and at least at the three N atoms. The direction of methylation is determined by the nature of the alkylating agent and the compound being alkylated (OT or its salt) and also by the character of the substituent at position 5 of the ring.

EXPERIMENTAL

PMR spectra were recorded on a Perkin-Elmer R-12 spectrometer (60 MHz), IR spectra on a UR-10 spectrometer, mass spectra on a Varian MAT GmbH CH-6 spectrometer with direct insertion of the specimen into the source.

Methylation of Salts of (Ia) and (Ib) with MeI and $(MeO)_2SO_2$. a) MeI (1.35 ml) was added to the Ag salt of (Ib) (0.91 g) in abs. MeCN (20 ml) and the reaction mixture stirred for 7 days at 20°C. The precipitate of AgI was separated and the solvent removed. Compound (IIb) (0.41 g: 82%) was obtained having mp 47-49°C (after TLC on silica gel and two recrystallizations from pentane). Found: C 31.80; H 5.50; N 49.40%. $C_3H_6N_4O$. Calculated: C 31.57; H 5.26; N 49.12%. IR spectrum (ν, cm^{-1}): 735 m, 965 vs, 980 m, 1060 m, 1080 m, 1150 m, 1160 w, 1250 s, 1290 s, 1400 w, 1460 s, 1480 s, 1560 s.

b) Compound (IIa) (0.16 g: 76%) was obtained from the Ag salt of (Ia) (0.33g) and MeI (0.23 ml) in MeCN (10 ml) after 5 days of storage. IR spectrum (ν, cm^{-1}): 705 s, 740 s, 790 s, 975 s, 1110 m, 1260 s, 1295 s, 1450 m, 1490 s.

c) Trimethylamine (0.5 ml) and then MeI (0.69 ml) were added to a suspension of (Ib) (0.37 g) in MeCN (20 ml). The solvent was removed after 3 days and (IIb) (0.3 g: 71%) was extracted from the residue with ether.

Triethylamine (0.34 ml), then $(MeO)_2SO_2$ (0.23 ml) were added to (Ia) (0.4 g) in MeCN (10 ml) and the mixture stored for 10 days. The solvent was removed and (IIa) was extracted from the residue with ethyl acetate.

Methylation of (Ia) and (Ib) with CH_2N_2. a) A solution of CH_2N_2 in ether was added to a solution of (Ib) (0.5 g) in ethyl acetate until the end of decolorization. The mixture was left overnight, the solvent removed, and a mixture of the products of O and N alkylation in the ratio 5:1 was obtained.

b) On methylating (Ia) (0.4 g) with CH_2N_2 a mixture (0.43 g) of the products of O and N alkylation in the ratio 6:1 was obtained.

Methylation of (Ia), (Ib), and Their NH_4 Salts with TMO. a) TMO (0.36 g) was sprinkled onto a suspension of (Ia) (0.4 g) in abs. CH_2Cl_2 (15 ml). The mixture was stirred for 20 h

at 20°C and the solvent removed. A mixture (0.37 g) of the products of N and O alkylation in the ratio 10:1 was obtained. After three recrystallizations from acetone, product (V) was obtained having mp 133-136°C. Found: C 52.08; H 4.95; N 30.94%. $C_8H_8N_4O \cdot 0.5\,H_2O$. Calculated: C 51.89; H 4.86; N 30.27%. IR spectrum (ν, cm^{-1}): 720 s, 780 s, 830 w, 1030 m, 1060 w, 1270 w, 1320 m, 1430 s, 1450 m, 1560 m, 1680 m, 3450 s.

b) TMO (1.83 g) was sprinkled into a suspension of the NH_4 salt of (Ib) (1.6 g) in CH_2Cl_2 (40 ml). The mixture was stirred for 5 days, the solid separated and the filtrate evaporated. From the residue (1.5 g oil) compounds (IIb) (0.8 g: 57%) and (VIb) (0.38 g:27%) mp 49-55°C (from ether) were isolated by TLC on silica gel (eluant was methanol–ether, 2:1). Found: C 32.18; H 5.31; N 49.32. $C_3H_6N_4O$. Calculated: C 31.57; H 5.26; N 49.12%. IR spectrum (ν, cm^{-1}): 690 vs, 860 m, 1000 m, 1015 m, 1270 s, 1290 s, 1360 m, 1387 s, 1425 vs, 1460 s, 1540 s, 1565 s. Compound (IVb) (0.2 g: 14%) of mp 100-102°C (from C_6H_6) was isolated in the same way. Found: C 31.56; H 5.44; N 48.97%. $C_3H_6N_4O$. Calculated: C 31.57; H 5.26; N 49.12%. IR spectrum (ν, cm^{-1}): 730 m, 810 w, 1060 m, 1080 m, 1170 s, 1295 s, 1355 vs, 1395 s, 1515 s, 1580 m, 1590 m.

c) TMO (0.2 g) was sprinkled onto a suspension of the NH_4 salt of (Ia) (0.25 g) in CH_2Cl_2 (12 ml) and the mixture stirred for 8 h at 20°C. The solid was separated off, the solvent removed, and from the residue were isolated (IIa) (0.08 g: 34%) and a mixture (0.1 g: 42%) of (V) with (IVa) or (VIa) by TLC on silica gel (eluant was benzene–ether 1:2).

Reduction of (IIb) with a Mixture of 57% HI and Red Phosphorus. A mixture of (IIb) (0.3 g), 57% HI (6 ml), and red phosphorus (1.2 g) was boiled for 2.5 h. the solid filtered off, the filtrate diluted with water (8 ml), made alkaline to pH 3-4 with dry Na_2CO_3, and decolorized with sodium thiosulfate. Methyltetrazole (0.22 g) of mp 144-147°C (from ethyl acetate) was recovered by extraction with ethyl acetate.

Reduction of (IVb) with a Mixture of 57% HI and Red Phosphorus. A mixture of (IVb) (0.21 g), 57% HI (4.2 ml), and red phosphorus (0.84 g) was boiled for 2 h and after treatment as described above 1,5-dimethyltetrazole (0.14 g: 77%) was obtained. PMR spectrum ($CDCl_3$, δ, ppm): 2.51 s (MeC), 3.96 s (MeN).

Reduction of (VIb) with a Mixture of 57% HI and Red Phosphorus. A mixture of (VIb) (0.3 g), 57% HI (6 ml), and red phosphorus (1.2 g) was boiled for 2 h and after treatment as described above a crystalline product (0.05 g) was obtained from which 1,5-dimethyltetrazole (0.03 g: 12%) was recovered with chloroform. PMR spectrum ($CDCl_3$, δ, ppm): 2.51 s (MeC), 3.96 s (MeN).

Reduction of the Products of N-Methylation of (Ia) with a Mixture of 57% HI and Red Phosphorus. A mixture (0.28 g) of N-methylation products of (Ia), red phosphorus (0.73 g), and 57% HI (3.65 ml) was boiled for 2 h, the red phosphorus was filtered off, the filtrate diluted with water (4 ml), made alkaline with Na_2CO_3, decolorized with sodium thiosulfate, extracted with ethyl acetate, and the extract dried over $MgSO_4$. The solvent was distilled off, a crystalline product (0.17 g: 68% was obtained which, according to data of PMR and mass spectra, was a mixture of 1-methyl-5-phenyltetrazole and 2-methyl-5-phenyltetrazole and 2-methyl-5-phenyltetrazole in a ratio of 1:2.

The authors are grateful to N. F. Karpenko for taking and interpreting the mass spectra.

CONCLUSIONS

1. Methylation of 1-hydroxy-5-methyl(5-phenyl)tetrazoles or their salts with methyl iodide, dimethyl sulfate, or diazomethane was effected mainly or exclusively at the O atom.

2. Under the action of trimethyloxonium tetrafluoroborate, 1-hydroxytetrazoles were methylated mainly at the N atom. Salts of 1-hydroxytetrazoles form comparable amounts of products of N and O methylation with oxonium salts.

3. On N-methylation of 1-hydroxytetrazoles the three N atoms may be subject to electrophilic attack to a lesser extent.

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MODIFICATION OF THE CHEMICAL PROPERTIES OF SULFUR-, SELENIUM-, AND IODINE-CONTAINING ALIPHATIC COMPOUNDS UNDER THE EFFECT OF NITRO GROUPS

A. A. Fainzil'berg, S. A. Shevelev, V. I. Erashko, and V. V. Semenov

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Introduction of nitro groups in aliphatic compounds is known to have a strong effect on the chemical properties of different classes of substances, and this effect is potentiated by an increase in the number of NO_2 groups and when they are close to a functional group or heteroatom. For this reason, it is possible to predict the greatest effect of NO_2 groups in cases where the NO_2 group and functional group or heteroatom is found on the same C atom. In reality, α,α-dinitroketones are hydrolytically split at the CO-C_{NO_2} bond [1, 2]; bis(trinitromethyl)mercury is ionized in water to a significant degree [3]. This strong effect of NO_2 groups is apparently due to both their extremely powerful electron-acceptor effect and thus to the high thermodynamic stability of S-nitrocarbanions, which facilitate splitting of the S-polynitroalkyl residue in heterolytic reactions. However, until our studies, there were almost no systematic studies of the effects of introduction of several NO_2 groups in the α position to a heteroatom or functional group, with the exception of the chemistry of bis(trinitromethyl)mercury (see, e.g., [4]).

Our studies of the modification of the chemical properties of aliphatic compounds under the effect of NO_2 groups on a C atom bound with a heteroatom, S or Se, in different degrees of oxidation and with an I atom are generalized in the present article.

New types of compounds containing an $O_2N-\underset{|}{\overset{|}{C}}-E'$ (E' = S, Se, I) fragment were synthesized, and their chemical transformations, which primarily affect the C_{NO_2}-E' bond, were investigated, since the effect of the NO_2 groups should be manifested to the greatest degree in these processes.

S-Polynitroalkyl Sulfides and Polynitroalkyl Selenides. The reaction of polynitroalkane salts with the corresponding sulfene and selenene halides [5-7] is a convenient and common method of synthesis of α-polynitroalkyl sulfides (I) and α-polynitroalkyl selenides (II)

$$RSHal + R'C(NO_2)_2^-M^+ \xrightarrow[-MHal]{} \underset{(I)}{RSC(NO_2)_2R'}$$

$$R = Me,\ Ph,\ p\text{-}MeOC_6H_4,\ p\text{-}NO_2C_6H_4,\ 2,4\text{-}(NO_2)_2C_6H_3;$$

$$R' = NO_2,\ Me,\ H;\ M^{\oplus} = K^{\oplus},\ Ag^{\oplus},\ (CH_2)_5NH_2;\ Hal = Cl,\ Br.$$

$$RSeHal + R'C(NO_2)_2^{\ominus}M^{\oplus} \xrightarrow[-MHal]{} \underset{(II)}{RSeC(NO_2)_2R'}$$

$$R = Ph;\ R' = NO_2,\ Me;\ M^{\oplus} = K^{\oplus},\ Ag^{\oplus};\ Hal = Cl,\ Br.$$

In all cases, the reactions occur almost uniquely at the C atom of the ambidentate polynitrocarbanions, and the corresponding O derivatives or products of their transformations are absent in the reactive mixture (compare [8]).

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow.
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