treated with 8 mmole of triethylamine, and boiling continued for a further 30 min. The reaction products were isolated as described above.

Benzoylation of the other (I) and separation of the mixtures were carried out similarly. The yields and constants of the compounds obtained are shown in Table 1.

1,3-Diazacyclooctane (IIe) was obtained chromatographically as a fraction (30% yield) containing ≥ 85% of the required compound, with R_f 0.7 (Silufol, benzene–ether, 3:1). PMR spectrum (δ, ppm from HMDS, in $CDCl_3$): 1.17 d (6H, Me), 1.57 m (7H, $NCH_2(CH_2)_3CH_2N$ and Me_2CH), 3.34 br (4H, NCH_2), 5.75 br (1H, NCHN), 7.00-7.50, 7.65-8.17 (2H, Ph).

NN'-Dibenzoyl-2-methyl-1,4-diaminobutane. Yield 52%, mp 130°C. PMR spectrum (δ, ppm from HMDS in $CDCl_3$): 0.95 d (3H, Me), 1.4-2.0 m (3H, $CH_2CH(CH_3)CH_2$), 3.1-3.7 m (4H, NCH_2), 7.1-7.9 (12 H, Ph and NH).

CONCLUSIONS

Benzoylation of the bisazomethines $R{-}CH = N(CH_2)_nN = CH{-}R$ (R = i-C_3H_7, Ph; n = 3-6.8) affords NN'-dibenzoyl-2-R-1,3-diazacycloalkanes and open-chain amides. The yields of 2-R-1,3-diazacycloalkanes are at a maximum when n = 2 and 3, decreasing rapidly as n increases.

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REACTIONS OF A HYDROXIMIC ACID CHLORIDE — A 3-IMIDAZOLINE 3-OXIDE DERIVATIVE — WITH NITROGEN-CONTAINING NUCLEOPHILIC REAGENTS AND PREPARATION OF STABLE AMIDOXIME N-OXYL RADICALS

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N-Methyl-3-imidazoline 3-oxides are "protected" nitroxyl radicals, and the reactivity of the nitrone group in these compounds therefore makes it possible to introduce a fragment that contains a nitroxyl center in "latent" form into various molecules; subsequent oxidative dealkylation leads to nitroxyl radicals [1]. The reactions of 3-imidazoline 3-oxides with electrophilic reagents with activation of the nitrone group by means of metallation [2] or protonation [3] of the latter were examined. To expand the synthetic possibilities of N-methyl-3-imidazoline 3-oxides we studied the reactions with nucleophilic reagents of a

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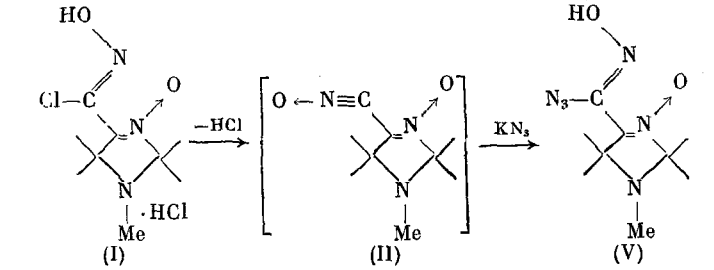
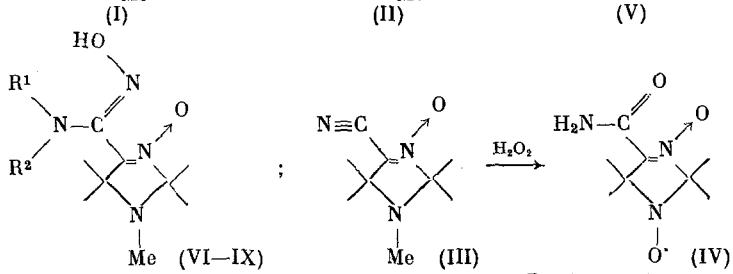
hydroximic acid chloride, viz., 4-chlorooximinomethyl-3-imidazoline 3-oxide, which was obtained by nitrosation of 5-bromoethylimidazoline oxide in an acidic medium [3]. Hydroximic acid chlorides are precursors of nitrile N-oxides, which have a broad spectrum of reactivity [4].

The action of Et_3N on a suspension of 4-chlorooximinomethyl-1,2,2,5,5-pentamethyl-3-imidazoline 3-oxide (I) in ether at −100°C gives a complex mixture of products, from which one can isolate nitrile III (30% yield), the oxidation of which leads to amide radical IV. Like most N-oxides of nitriles of the aliphatic series, intermediate nitrile oxide II is evidently a highly reactive compound that cannot be isolated in the free state. In such cases one uses the nitrile oxide *in situ*, since replacement of the halogen in hydroximoyl halides occurs through the intermediate formation of a nitrile oxide [5]. The reaction of chloro oxime I with KN_3 in MeOH leads to azido oxime V, in the IR spectrum of which one observes bands at 2140 and 2170 cm^{-1}. Compound V is stable in solid form and in solutions in polar solvents; however, nitrile III is formed upon heating or irradiation in C_6H_6 or when it is allowed to stand in $MeCO_2H$ (see [6]).





$R^1 = R^2 = H$ (VI); $R^1 = H$, $R^2 = Me$ (VII); $R^1 = H$, $R^2 = t$-Bu (VIII); $R^1 = R^2 = Et$ (IX).

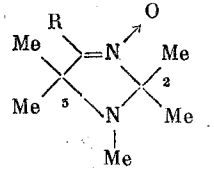
The reaction of I with NH_3 gives amido oxime VI in quantitative yield; VI was previously obtained by the addition of hydroxylamine to nitrile III [7]. Monosubstituted amidoximes VII and VIII are formed smoothly upon treatment of a solution of hydroximoyl chloride I with methylamine or tert-butylamine. Disubstituted amidoxime IX was similarly obtained with diethylamine.

According to the UV spectra of VII-IX (Table 1), the amidoxime group is removed from conjugation with the nitrone group in N-methyl- and N-tert-butylamidoximes VII and VIII in alcohol solutions. Upon passing to heptane or to solid samples in KBr the bands in the UV spectra of these compounds undergo a significant bathochromic shift. These changes can be explained by the formation of intermolecular hydrogen bonds with the solvent, which leads to deviation of the amidoxime group from the plane of the imidazoline ring. Bands at 1560 and 1650 cm^{-1} are observed in the Raman spectrum of VIII; the low-frequency band is the most intense band. This makes it possible to assume that monosubstituted amidoximes VII and VIII exist in the form of planar S-cis conformers in nonpolar solvents and in the solid form [8]. In contrast to the monosubstituted amidoximes, disubstituted amidoxime IX has a nonplanar structure of the N=C—C=N → O fragment, as indicated by the UV spectra of solutions in alcohol and heptane, which have the maximum at 238 nm that is characteristic for unconjugated nitrones.

Nitrile III is formed in quantitative yield when a solution of I is treated with hydrazine hydrate, i.e., the reaction of the hydroximic acid chloride with hydrazine proceeds as reduction of intermediate nitrile oxide II rather than via replacement of the halogen. Hydroxylamine also has reducing properties: I reacts with excess hydroxylamine to give a mixture of amidoxime VI and nitrile III.

In contrast to this, tert-butylhydroxylamine adds smoothly to nitrile oxide II. Treatment of I with a fivefold excess of tert-butylhydroxylamine gives N-hydroxyamidoxime X in high yield; according to the IR and UV spectra, X is similar to amidoxime VIII. However, in the reaction of I with a twofold excess of tert-butylhydroxylamine, in addition to nitrile

TABLE 1. Spectral Characteristics of the Synthesized Compounds

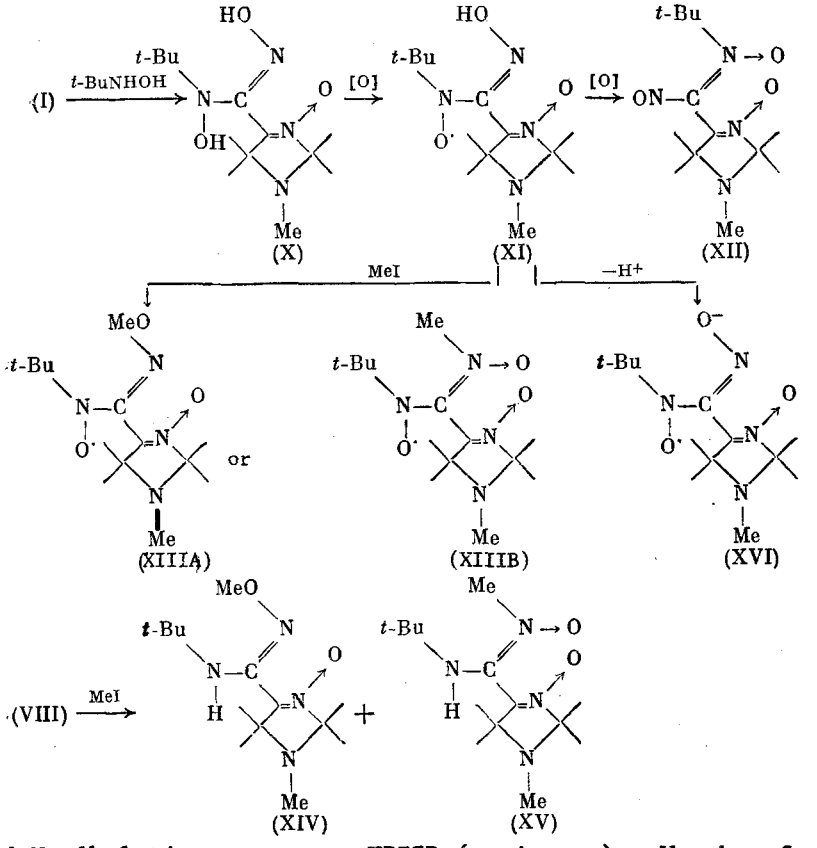


Compound	UV spectrum, λ, nm (log ε)		IR spectrum, ν, cm^{-1} (in KBr)		PMR spectrum, δ, ppm (in $CDCl_3$)			
	EtOH	C_7H_{16}	C=N	other bands	2-Me	5-Me	NMe	R
(V)	287 (3,97)		1570	1590 (C=N), 2140, 2170 ($-N_3$)	1,46	1,39	2,36	
(VII)	230 (4,06) 294 i (3,47)	268 (3,98) 312 i (3,64)	1600		1,46	1,34	2,37	2,90 (3H)[a]
(VIII)	235 (4,00) 269 i (3,91)	286 (4,10)	1610	1640 (C=N)	1,43	1,37	2,34	1,29 (9H)
(IX)	238 (4,05)	239 (3,89)	1600	1610 (C=N)	1,49	1,32	2,36	1,11 t (6H)[b]; 3,10q (4H)
(X)	242 (3,81)	285 (4,03)	1600	1630 (C=N)	1,50	1,50	2,37	1,21 (9H)
(XI)	236 (4,02) 455 (2,30)	289 (4,06) 458 (2,30)	1600	1630 (C=N)				
(XII)	235 (3,93) 331 (4,14)		1580	1360 (N=O)	1,34	0,92	2,27	1,99 (9H)[c]
(XIII)	238 (4,03) 276 (4,00) 456 (2,30)	270 (3,91) 458 (2,30)	1590[c]	2820 ($N-CH_3$, $O-CH_3$) 1630 (C=N)				
(XIV)	264 (3,90)	276 (3,92)	1590	2820 ($N-CH_3$, $O-CH_3$) 1640 (C=N)	1,41	1,31	2,32	3,74 (3H)[d]
(XV)	250 (4,06) 307 i (3,75)	254 (4,00) 317 (3,78)	1580		1,44	1,24	2,36	3,44 (3H)[e]

[a]Broad signal; a doublet with J_{CH-NH} = 5 Hz at −30°C. [b]J_{CH-CH} = 6 Hz. [c]In CCl_4. [d]Carbon-13 NMR spectrum (in $CHCl_3$, δ, ppm): 140.3 (C=N), 143.3 (C=N), 90.5 (C^2), 65.3 (C^5), 24.7 (2-Me), 23.9 (5-Me), 52.7 (CN), 31.0 ($\underline{Me}_3C$), 26.7 (MeN), and 61.0 (MeO). [e]Carbon-13 NMR spectrum (in $CHCl_3$, δ, ppm): 136.6 (C=N), 138.8 (C=N), 90.5 (C^2), 64.5 (C^5), 23.2 (2-Me), 24.5 and 24.3 (5-Me), 56.2 (CN), 30.2 ($\underline{Me}_3C$), 26.9 (MeN), and 45.0 (MeN).

III, one observes the formation of red XI, which, according to its IR spectrum, is similar to N-hydroxyamidoxime X. Compound XI is paramagnetic, and a free-radical structure, viz., 4-(N-oxyl-N-tert-butylcarboxamidoximino)-1,2,2,5,5-pentamethyl-3-imidazoline 3-oxide (XI), was therefore assigned to it. The formation of XI in the reaction of the hydroximoyl chloride with tert-butylhydroxylamine can be explained by oxidation of the intermediate sterically hindered hydroxylamine X by nitrile oxide II, which undergoes deoxygenation to nitrile III (see [9]). The XI radical is also formed in the oxidation of N-hydroxyamidoxime X under the influence of air O_2. It should be noted that radicals similar to N-oxylamidoxime XI have been studied by EPR methods [10]; however, they were not isolated preparatively. In this connection, some properties of radicals XI were examined. Thus greenish diamagnetic product XII is formed in the oxidation of XI or its precursor X with PbO_2 or MnO_2. The UV spectrum of XII provides evidence for the presence of a conjugated nitrone grouping. Signals of protons of geminal Me groups in the 2 position of the heteroring, a tert-Bu group (1.99 ppm), and Me groups in the 5 position of the heteroring (0.92 ppm) are observed in the PMR spectrum. The 0.5-ppm shift to weak field of the signal of the tert-Bu group as compared with X and the 0.4-ppm shift to strong field of the signal of the gem-Me groups make it possible to assume the presence of a grouping with a strong anisotropic effect in the XII molecule. On the basis of this, the N-tert-butyl-α-(1,2,2,5,5-pentamethyl-3-imidazolin-4-yl)-α-nitrosonitrone 3-oxide (XII) structure was assigned to XII.

Radical XI reacts with MeI in the presence of a base to give paramagnetic derivative XIII, the IR spectrum of which does not contain a band of an OH group at 3600 cm^{-1}; its UV spectrum provides evidence for the presence of a conjugated nitrone grouping. These data do not make it possible to make an unambiguous choice between O-alkylation structure XIIIA (an



amidoxime ether) and N-alkylation structure XIIIB (a nitrone). We therefore undertook the synthesis of similarly constructed diamagnetic analogs of XIII. The reaction of N-tert-butylamidoxime VIII with MeI under the same conditions leads to a mixture of two isomers (XIV and XV) with the UV spectra of conjugated nitrones. An increase (as compared with starting amidoxime VIII) in the intensity of the band at 2820 cm^{-1} (stretching vibrations of the C–H bond or MeO or MeN groups) is observed in the IR spectrum of XIV. In the ^{13}C NMR spectrum the signal of the Me group introduced by alkylation is found at weaker field (by 16 ppm) as compared with XV. This makes it possible to assume that XIV is the O-alkylation product, viz., amidoxime ether XIV, and that XV is the N-alkylation product, viz., nitrone XV. A comparison of the IR and UV spectra of paramagnetic alkylation product XIII and amidoxime

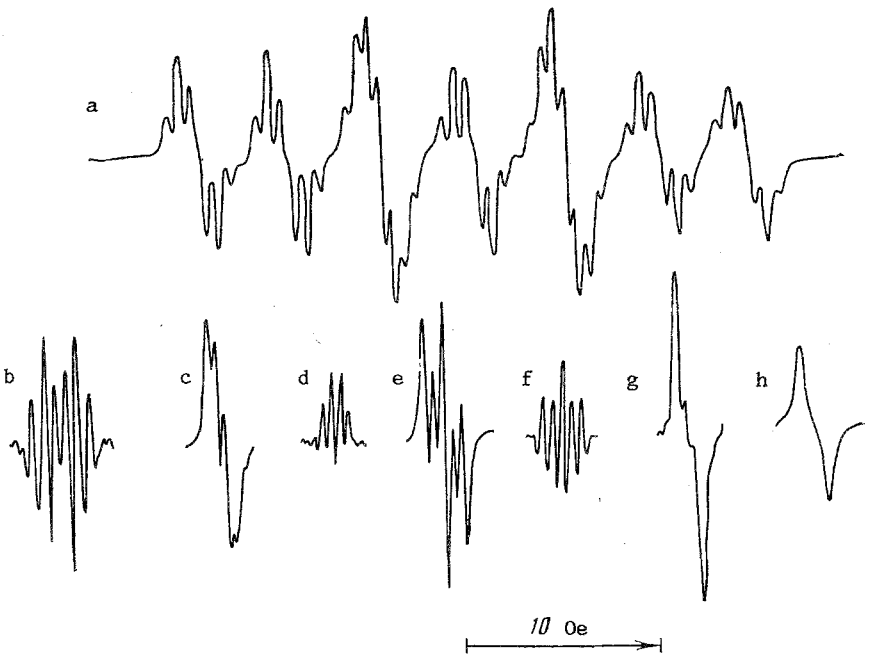


Fig. 1. First derivative of the EPR spectrum of XIII (a). Additional hfs of the second component of the EPR spectra at low field: second derivative of the spectrum of XIII in $CHCl_3$ (b); first (c) and second (d) derivatives of the spectrum of XI in $CHCl_3$; first (e) and second (f) derivatives of the spectrum of XI in iso-PrOH; first derivative of the spectra of XI in iso-PrOD (g) and XIII with a CD_3 group in $CHCl_3$ (h).

ether XIV made it possible to conclude that XIII is also an O-alkylation product, viz., 4-(N-oxyl-N-tert-butylmethoxycarboxamidoximino)-1,2,2,5,5-pentamethyl-3-imidazoline 3-oxide. The formation of only an O-alkylation product in the case of the nitroxyl radical can evidently be explained by the fact that the strongly electron-acceptor nitroxyl fragment decreases the accessibility of the unshared pair of the N atom of the oxime group with respect to the alkylating reagent.

Seven principal components of the hyperfine structure (hfs) with an intensity ratio close to 1:1:2:1:2:1:1 are observed in the EPR spectra of radicals XI and XIII in iso-PrOH and $CHCl_3$ (Fig. 1). This hfs can be explained by hyperfine coupling (HFC) of the unpaired electron with the nuclei of two N atoms. The g factor in all cases is 2.0061 ± 0.0003. The isotropic HFC constants in both solvents in radical XI are a_N^1 = 10 Oe and a_N^2 = 4.6 Oe; a_N^1 = 9.5 Oe and a_N^2 = 4.5 Oe in XIII. The accuracy in the determination of the constants was ±0.1 Oe. In analogy with [9], one may assume that the larger HFC constant characterizes coupling with the N nucleus of the N-oxyl group and that the smaller constant characterizes coupling with the N nucleus of the oxime group. Each of the principal components of the EPR spectra has an additional hfs that does not depend on the solvent in the case of radical XIII but changes in the case of radical XI on passing from $CHCl_3$ to iso-PrOH. In order to ascertain the origin of this hfs we replaced H by D in the HON and MeON groups. This leads to simplification of the additional hfs, although, as before, the weakly manifested triplet splitting, which can be explained by isotropic HFC with the N nucleus of the nitrone fragment, is retained.

An analysis of the additional hfs of the first and second derivatives of the EPR spectra with normal and deuterated fragments makes it possible to estimate the constants of hyperfine coupling with the protons and the third N nucleus. Thus a_N^3 = 0.6 Oe and a_{OH} = 0.5 Oe for radical XI in $CHCl_3$; in iso-PrOH a_N^3 = 0.06 Oe and a_{OH} = 0.9 Oe. For ether oxime XIII in both solvents a_N^3 = 0.5 Oe and a_{CH} = 0.6 Oe. When NaH is added to radical XI in iso-PrOH the solution takes on a dark crimson coloration due to the corresponding anion radical XVI, the EPR spectrum of which has the following parameters: a_N^1 = 11.2 Oe and a_N^2 = 4.5 Oe.

Thus the reactivity of hydroximoyl chloride I makes it possible to use it as a starting compound for the synthesis of various precursors of nitroxyl radicals of 3-imidazoline 3-oxide 1-oxyls, as well as little-studied radicals — derivatives of amidoxime-N-oxyls.

TABLE 2. Characteristics of the Synthesized Compounds

Compound	Yield, %	mp, °C	Found/calc., %			Empirical formula
			C	H	N	
(V)	71	117 (dec)[a]	45,4 45,0	6,9 6,7	34,8 35,0	$C_9H_{16}N_6O_2$
(VII)	88	150–151[a]	52,9 52,6	8,7 8,8	24,8 24,6	$C_{10}H_{20}N_4O_2$
(VIII)	76	170–171[a]	58,2 57,8	9,8 9,6	21,0 20,8	$C_{13}H_{26}N_4O_2$
(IX)	63	101–103[b]	57,4 57,8	9,5 9,6	21,0 20,8	$C_{13}H_{26}N_4O_2$
(X)	62	116(dec.)[a]	54,6 54,5	8,9 9,1	19,9 19,6	$C_{13}H_{26}N_4O_3$
(XI)	50[c]	110(dec.)[a]	54,9 54,7	8,6 8,8	19,6 19,6	$C_{13}H_{25}N_4O_3$
(XII)	90	70–72[a]	55,4 54,9	8,5 8,5	19,5 19,7	$C_{13}H_{24}N_4O_3$
(XIII)	70	Liquid	55,7 56,2	8,7 9,0	19,0 18,7	$C_{14}H_{27}N_4O_3$
(XIV)	20	60–62[b]	59,3 59,2	10,0 9,9	19,7 19,7	$C_{14}H_{28}N_4O_2$
(XV)	75	109–111[a]	59,2 59,2	10,1 9,9	19,7 19,7	$C_{14}H_{28}N_4O_2$

[a]From C_7H_{16}–$MeCO_2Et$ (3:1). [b]From C_6H_{14}. [c]Along with 20% nitrile III.

EXPERIMENTAL

The IR spectra of KBr pellets and solutions of the compounds in CCl_4 were recorded with UR-20 and Perkin-Elmer-180 spectrometers. The Raman spectrum of a solid sample was recorded with a Coderg PH-1 spectrometer. The UV spectra were obtained with a Specord UV-VIS spectrophotometer. The NMR spectra were recorded with Varian A-56-60A (^1H) and Bruker HX-90 (^{13}C) spectrometers. The EPR spectra of $5 \cdot 10^{-4}$ M solutions in absolute solvents were recorded with a Bruker ER-200 spectrometer. The samples were degassed beforehand by evacuation to 10^{-3} torr, and the spectra were recorded at 293 ± 1°K. The spectral characteristics of the products are presented in Table 1, and the yields, constants, and results of elementary analysis are given in Table 2.

Neutralization of I. A 0.1-ml sample of Et_3N was added at −100°C to a suspension of 0.27 g (1 mmole) of I in 20 ml of ether, and the mixture was stirred at this temperature for 1 h. It was then warmed up to 20°C and evaporated, and the residue was chromatographed with a column packed with silica gel by elution with $CHCl_3$ to give nitrile III [7] in 30% yield.

4-Carbamoyl-2,2,5,5-tetramethyl-3-imidazoline 3-Oxide 1-Oxyl (IV). A 2-ml sample of 30% H_2O_2 was added to a suspension of 0.1 g of nitrile III, 0.05 g of $Na_2WO_4 \cdot 2H_2O$, and 0.02 g of Trilon B in 1 ml of H_2O, and the mixture was stirred for 10 h. It was then allowed to stand for 3 days, after which it was extracted with $CHCl_3$. The extract was dried with $MgSO_4$, and the $CHCl_3$ was removed by distillation to give amide IV [10] in 92% yield.

4-Azidoiminomethyl-1,2,2,5,5-pentamethyl-3-imidazoline 3-Oxide (V). A 0.17 g (2.1 mmole) sample of KN_3 was added with stirring to a suspension of 0.27 g (1 mmole) of I in 20 ml of MeOH, and the mixture was stirred for another 15 min. It was then poured into 100 ml of H_2O, an the aqueous mixture was extracted with $CHCl_3$. The extract was dried with $MgSO_4$, and the $CHCl_3$ was removed by distillation. The residue was recrystallized (without prolonged boiling) from heptane–ethyl acetate (3:1).

Decomposition of Azidoxime V. A) A 0.1-g sample of V was refluxed in 10 ml of C_6H_6 for 30 min, after which the mixture was evaporated to give nitrile III in quantitative yield.

B) A solution of 0.1 g of V in 10 ml of C_6H_6 was subjected to UV irradiation for 5 min in a quartz ampul, after which the C_6H_6 was removed by distillation to give nitrile III in quantitative yield.

C) A solution of 0.3 g of V in 2 ml of $MeCO_2H$ was allowed to stand for 10 h, after which it was poured into 50 ml of saturated Na_2CO_3 solution. The mixture was extracted with $CHCl_3$,

the extract was dried with $MgSO_4$, and the $CHCl_3$ was removed by distillation to give nitrile III in 85% yield.

Reaction of Hydroximoyl Chloride I with NH_3. A stream of dry NH_3 was bubbled into a solution of 0.27 g (1 mmole) of I in 20 ml of MeOH for 10 min, after which the mixture was evaporated, and the residue was chromatographed with a column packed with silica gel by elution with $CHCl_3$–MeOH (20:1) to give amidoxime VI in 80% yield.

Reaction of Hydroximoyl Chloride I with $MeNH_2$. A solution of 1.12 g (20 mmole) of KOH in 20 ml of MeOH and 0.27 g (1 mmole) of I were added successively to a solution of 1.35 g (20 mmole) of $MeNH_2 \cdot HCl$ in 20 ml of MeOH, after which the mixture was evaporated, and the residue was dissolved in 50 ml of H_2O. The aqueous mixture was extracted with $CHCl_3$, the extract was dried with $MgSO_4$, and the $CHCl_3$ was removed by distillation. 4-(N-Hydroxy-N-tert-butylcarboxamidoximino)-1,2,2,5,5-pentamethyl-3-imidazoline 3-oxide (X) was similarly formed in the reaction of 1 mmole of I with 5 mmole of tert-butylhydroxylamine hydrochloride.

Reaction of Hydroximoyl Chloride I with tert-$BuNH_2$ and Et_2NH. A 0.27-g (1 mmole) sample of I was added with stirring to 5 ml of the amine (or 20 ml of an alcohol solution containing 5 ml of the amine), after which the mixture was evaporated, and the residue was poured into 50 ml of H_2O. The aqueous mixture was extracted with $CHCl_3$, the extract was dried with $MgSO_4$, and the $CHCl_3$ was removed by distillation. The residue was chromatographed with a column packed with silica gel by elution with $CHCl_3$–MeOH (20:1).

Reaction of Hydroximoyl Chloride I with $H_2NNH_2 \cdot H_2O$. A 0.5 ml sample of hydrazine hydrate was added to a solution of 0.27 g (1 mmole) of I in 2 ml of H_2O. After 5 min, 20 ml of H_2O was added, and the mixture was extracted with $CHCl_3$. The extract was dried with $MgSO_4$, and the $CHCl_3$ was removed by distillation to give nitrile III in 85% yield.

Reaction of Hydroximoyl Chloride I with H_2NOH. A solution of 0.4 g (10 mmole) of NaOH in 2 ml of H_2O was added to a solution of 0.27 g (1 mmole) of I and 0.7 g (10 mmole) of $NH_2OH \cdot HCl$ in 20 ml of EtOH, and the mixture was stirred for 0.5 h. It was then evaporated and the residue was dissolved in 50 ml of water. The aqueous solution was extracted with $CHCl_3$, the extract was dried with $MgSO_4$, and the $CHCl_3$ was removed by distillation. The residue was chromatographed with a column packed with silica gel by elution with $CHCl_3$ to give nitrile III (10%) and amidoxime VI (50%).

4-(N-Oxyl-N-tert-butylcarboxamidoximino)-1,2,2,5,5-pentamethyl-3-imidazoline 3-Oxide (XI). A) A solution of 1.1 g (20 mmole) of KOH in 50 ml of MeOH and 2.7 g (10 mmole) of I were added in a stream of argon to a solution of 2.5 g (20 mmole) of tert-BuNHOH in 20 ml of MeOH. After 3 h, the reaction mixture was evaporated, the residue was dissolved in 50 ml of H_2O, and the aqueous solution was extracted with $CHCl_3$. The extract was dried with $MgSO_4$, the $CHCl_3$ was removed by distillation, and the residue was washed with hexane and recrystallized from hexane–ethyl acetate (5:1). The hexane filtrate and mother liquor were evaporated. This procedure gave nitrile III in 20% yield.

B) A solution of 0.1 g of X in 10 ml of MeOH was stirred vigorously in air for 10 h, after which it was evaporated. Radical XI was recrystallized from hexane–ethyl acetate (5:1).

Nitroso Nitrone (XII). A 1-g sample of MnO_2 or PbO_2 was added to a solution of 0.1 g of N-hydroxyamidoxime X or radical XI in 5 ml of $CHCl_3$, after which the mixture was stirred for 2 h and filtered. The filtrate was evaporated, and the residue was chromatographed with a column packed with silica gel by elution with $CHCl_3$.

Alkylation of Nitroxyl Radical XI. A 0.22-g (4 mmole) sample of MeONa was added to a solution of 0.29 g (10 mmole) of XI in 10 ml of MeOH (the solution took on a dark-crimson coloration), after which 0.45 ml (4 mmole) of MeI was added, and the mixture was stirred for 6 h and evaporated. The residue was chromatographed with a column packed with silica gel by elution with $CHCl_3$. The synthesis of the deuterated (in the MeO group) compound was carried out similarly with CD_3I. The alkylation of amidoxime VIII was carried out under the same conditions. The chromatographic characteristics [Silufol UV-254, $CHCl_3$–MeOH (10:1)] of the alkylation products were as follows: R_f 0.6 for ether amidoxime XIV and R_f 0.3 for nitrone XV.

CONCLUSIONS

1. A hydroximic acid chloride, viz., 4-chloroximino-3-imidazoline 3-oxide, reacts with nitrogen-containing nucleophilic reagents to give amidoxime derivatives. The reaction with

tert-butylhydroxylamine leads to an N-hydroxyamidoxime, the oxidation of which made it possible to preparatively isolate an amidoxime N-oxyl radical, viz., 4-(N-oxyl-N-tert-butylcarboxamidoximino)-1,2,2,5,5-pentamethyl-3-imidazoline 3-oxide.

2. Oxidation of the radical gives a nitroso nitrone, and alkylation gives only an O-alkylation product (an ether amidoxime N-oxyl), whereas the similarly constructed amidoxime reacts to give both an O-alkylation product (an ether amidoxime) and an N-alkylation product (a nitrone).

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FUNCTIONAL SULFUR-CONTAINING COMPOUNDS. COMMUNICATION 7. REACTIONS OF 2,3-EPOXYPROPYL ALKYL SULFIDES, SULFOXIDES, AND SULFONES WITH ALKOXIDES AND AMINES

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In a previous paper [1] we described the nucleophilic addition of mercaptans to 2,3-epoxy(epithio)propyl alkyl sulfides, sulfoxides, and sulfones and showed that the specificity of opening of the epoxide ring depends on the structure of the mercaptan and the oxidation state of the sulfur atom in the substituent.

In the present research we studied the nucleophilic addition of alcohols and amines with various structures to 2,3-epoxypropyl alkyl sulfides, sulfoxides, and sulfones. The reactions of epoxy sulfides with alkoxides [2] and with aliphatic, acyclic, and aromatic amines [3-6] have been described in the literature. It is assumed that only products of normal opening of the epoxide ring are obtained in these cases.

We have investigated the addition of alkoxides to epoxy sulfides I at 60-65°C in the corresponding alcohol. The maximum yields (90-93%) of the products of addition of primary and secondary alcohols are achieved at an epoxide:alkoxide molar ratio of 1:1.5, and the yields of products of addition of tert-butyl alcohol do not exceed 5%. Despite the assertion of Rietz and co-workers [2], the reaction of epoxides I with alkoxides does not proceed selectively and leads to mixtures of regioisomers II and III:

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