GEMINAL SYSTEMS.
16.* REACTIONS OF N-CHLORO-N-ALKOXY-N-ALKYLAMINES WITH AMINES

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N-Chloro-N-alkoxy-N-tert-alkylamines act as alkoxyaminating agents relative to alcohols [2] and other nucleophiles [1]. The alkoxyamination of amines by these compounds, similar to the aminoamination of $MeNH_2$ by alkoxydiazenium salts [3], is of interest as a means of producing the N–N bond since the scope of the Raschig reaction is limited as a consequence of the dehydrochlorination of N-chloroamines containing an α proton [4]. In the present work, we studied the reactions of XN(Cl)OMe, where X = R = MeO_2CCMe_2 (Ia) or X = R′ = $MeO_2CCH_2CMe_2$ (Ib), with amines.

The reaction of (Ia) with an excess of NH_3 leads to the formation α-chloroisobutyramide (II), whose structure was proven by back synthesis, and of azoxy compound (III). This result is apparently due to the initial nucleophilic substitution at the nitrogen atom, subsequent decomposition of the intermediate N-alkoxyhydrazine, † and homolytic decomposition of the NH-diazene [7] to yield a tery-alkyl radical, whose reaction with (Ia) and ammonolysis lead to the final products

$$MeO_2CCMe_2N(Cl)OMe \xrightarrow[-HCl]{NH_3} \left[R{-}N(OMe)NH_2 \xrightarrow[-MeOH]{} R{-}N{=}NH \xrightarrow[-N_2;\ -H\cdot]{} \right.$$

(Ia)

$$\left. R\cdot \xrightarrow[-R\dot{N}OMe]{(Ia)} R{-}Cl \right] \xrightarrow[-MeOH]{NH_3} ClCMe_2CONH_2$$

(II)

$$[2R\dot{N}OMe \rightarrow RN(OMe)N(OMe)R \xrightarrow[-MeO^-]{} R\overset{+}{N}(OMe){=}NR] \xrightarrow[-Me_2O]{MeO^-}$$

$$\rightarrow MeO_2CCMe_2N(O){=}NCMe_2CO_2Me$$

(III)

In accord with this scheme, the reactions of (Ia) with primary amines give exclusively asymmetrical diazenes (IV) and (V) in high yield

$$(Ia) \xrightarrow[-HCl;\ -MeOH]{R''NH_2} [R{-}N{=}N{-}R''] \xrightarrow[-MeOH]{R''NH_2} R''NHCOCMe_2N{=}N{-}R''$$

R″ = Me (IV), Et (V).

The reaction of (Ib) with dimethylamine unexpectedly leads to the formation of 2,5,5-trimethylpyrazolidone (VI) in high yield. This product was identified by comparison with the compound described by Johnson and Hatch [8] and further characterized as the tosylate (VII). This result is readily explained as follows. The diazenium salt formed upon the decomposition of alkoxyhydrazine undergoes characteristic decomposition with loss of the α proton [3, 9] and generation of a dipole, which forms an asymmetric aminal by adding Me_2NH. This aminal undergoes disproportionation characteristic for the aminals of highly basic amines to yield bis-dimethylaminomethane (detected in the mass spectrum of the reaction mixture) and an asymmetrically substituted hydrazine. The spontaneous cyclization of this hydrazine is confirmed by the synthesis of (VI) from methylhydrazine and methyl β, β-dimethylacrylate

$$MeO_2CCH_2CMe_2N(Cl)OMe \xrightarrow[-HCl]{Me_2NH} \left[R'N(OMe)NMe_2 \xrightarrow[-MeOH]{H^+} R'{-}N{=}\overset{+}{N}Me_2 \rightarrow \right.$$

(Ib)

$$\xrightarrow[-H^+]{} R'{-}\overset{-}{N}{-}\overset{+}{N}{=}CH_2 \xrightarrow{Me_2NH} R'NH{-}\underset{Me}{N}{-}CH_2NMe_2 \xrightarrow[-(Me_2N)_2CH_2]{Me_2NH}$$

*For Communication 15, see previous article [1].

†Only a single N-alkoxyhydrazine has been described [5], and N. B. Tavakalyan and G. V. Shustov in our laboratory were unable to reproduce its synthesis. In earlier work [3], we proposed these species as intermediates. The instability of N-alkoxy-N-alkyl-substituted hydrazines is apparently due to the facile ionic dissociation of the N–O bond and formation of diazenium cations which undergo further transformations. The introduction of electronegative substituents to the N′ atom of N-alkoxyhydrazines decreases the mesomeric positive capacity of these compounds, retards the ionic dissociation of the N–O bond, and thereby provides the stability of such hydrazines (as, for example, in our previous work [6]).

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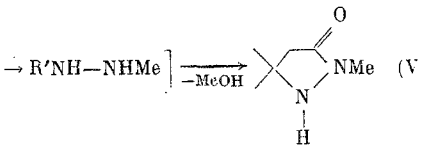
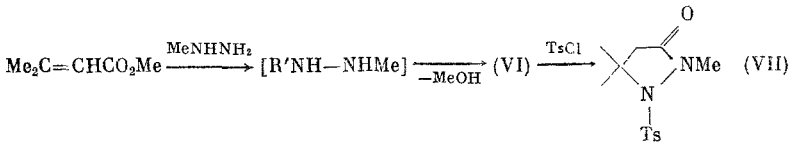
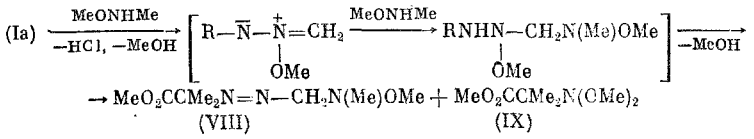


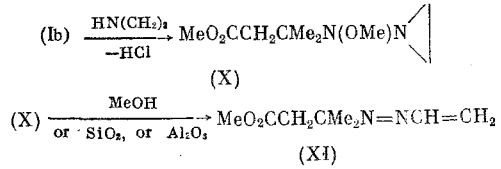


In the reaction of (Ia) with the less basic N-methoxy-N-methylamine obtained by an analogous scheme, the aminal does not disproportionate, but rather yields diazene (VIII) with the elimination of MeOH



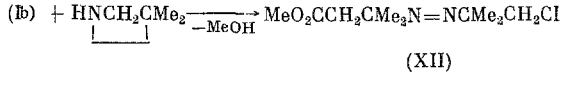
The formation of (IX) is attributed to the reaction of (Ia) with the methanol liberated in the reaction.

The reaction of (Ib) with ethyleneimine yields alkoxyhydrazine (X), the product of the first stage of alkoxyamination. The stability of this product, as discussed above, is a consequence of the reduction in the lability of the methoxy group due to the weak mesomeric positive capacity of the ethyleneimine nitrogen. For this reason, for example, the carbon analog of (X), methoxymethylaziridine, does not act as an aminomethylating agent relative to ethyleneimine, in contrast to N-methoxymethyl derivatives of other secondary amines, while N-ethyleneiminocarbinols do not participate in the Mannich reaction [10]



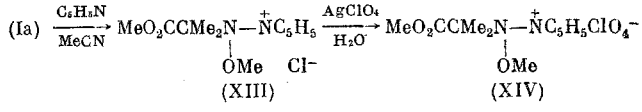
A completely unusual ring opening is found for (X). Upon maintenance in methanol at 20°C and upon chromatography on SiO_2 or Al_2O_3, (X) is entirely converted to the bright yellow vinyldiazene (XI) which is similar in its spectral characteristics to the compounds described by Tsuji and Kosower [7]. The slow electrophilic or nucleophilic ring opening in this case apparently leads initially to a substituted methoxyhydrazine, which by the elimination of MeOH gives a diazene containing a labile α proton. Loss of the α proton and the β substituent accounts for the formation of the vinyl group.

The reaction of (Ib) with 2,2-dimethylethyleneimine under the same conditions as the reaction with ethyleneimine gives only the ring opening product (XII). The structure of (XII) confirms S_N2 ring opening



Apparently, the higher basicity of 2,2-dimethylethyleneimine relative to unsubstituted ethyleneimine provides for rapid protonation and subsequent attack on the more available ring carbon atom by the chloride ion, which is the only sterically unhindered nucleophile in the medium. Then, slow elimination of methanol leads to product (XII). This interpretation permits explanation of the following findings: a) the methanol eliminated does not participate in the reaction and b) the alcoholysis of the diazenium ion  examined by Allred et al. [11] occurs by a different pathway.

Reactions (Ia) and (Ib) with pyridine terminate with nucleophilic substitution. Salt (XIII) is hygroscopic and thus it was characterized as the corresponding perchlorate (XIV)



$$(Ib) \xrightarrow[MeCN]{C_5H_5N} MeO_2CCH_2CMe_2N(OMe)-\overset{+}{N}C_5H_5Cl^- \quad (XV)$$

The stability of these N-alkoxyhydrazinium salts is a result of screening of the nitrogen atom electron pair.

Diethylamine and triethylamine act as one-electron reducing reagents in reactions with (Ia) and (Ib) due to steric hindrance to nucleophilic attack and only products of the transformation of the corresponding alkoxyaminyl radicals which were detected by ESR spectroscopy in our previous work [2]

$$(Ia) \xrightarrow[\text{or } Et_3N]{Et_2NH} (II)$$

$$(Ib) \xrightarrow{Et_2NH} MeO_2CCH_2CMe_2N(O)=NCMe_2CH_2CO_2Me \quad (XV)$$

The mechanism for these transformations was examined in our previous work [2]. We should stress that in the presence of a suitable nucleophile, the reducing activity of, for example, Et_3N is completely repressed by nucleophilic substitution. Thus, (Ia) and (Ib) react with primary alcohols in the presence of Et_3N to yield N, N-dialkoxyamines in excellent yield [2].

The structure of all the compounds synthesized was demonstrated by spectroscopic methods (Table 1 and the Experimental section).

The inversion barriers in N-alkoxyhydrazine (X) and N-alkoxyhydrazinium salts (XIV) and (XV) were measured (Table 2). The lower barrier in (X) relative to dialkoxyamines [2] is a factor of the lower electronegativity of the nitrogen atom of ethyleneimine in comparison to the oxygen atom. In (XIV) and (XV), despite the introduction of the more electronegative ammonium nitrogen, the barrier is still lower, apparently as a result of $p-\pi$ conjugation with the pyridinium system. Reversible dissociation of the N–N bond is excluded in this case since salts (XIV) and (XV) are stable in water, methanol, CF_3CH_2OH, DMSO, and pyridine, while the inversion barrier of (XIV) is virtually identical in CD_3CN and CD_3OD (see Table 2).

EXPERIMENTAL

The PMR spectra were taken on Tesla BS-487C and JNM-C-60-HL spectrometers and the ^{13}C NMR spectra were taken on an XL-100 spectrometer. The mass spectra were taken on an MKh-1303 mass spectrometer with direct inlet of the sample into the ion source with ionizing electron energy 30 eV (peaks >10% were mainly given). The IR spectra were taken on the UR-20 spectrometer.

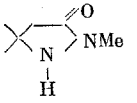
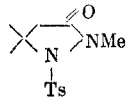
A sample of methyl α-(N-chloro-N-methoxyamino)isobutyrate (Ia) was obtained according to our previous work [2] in ~100% yield. Methyl β-(N-chloro-N-methoxyamino)isovalerate (Ib) was obtained according to our previous work [2] in 64% yield, bp 40-41°C (0.7 mm).

Reaction of (Ia) with NH_3. A solution of 1.39 g (7.7 mmoles) (Ia) in liquid ammonia was maintained in a sealed ampul for 13.5 h at −78°C and then 1 h at 20°C and 16 h at 1°C. The excess ammonia was removed and the residue was subjected to chromatography on a silica gel column with ether eluent to yield 0.11 g (11.7%) dimethyl azoxyisobutyrate (III), mp 50-51°C (from hexane), identified by comparison with an authentic sample [2] using PMR spectroscopy. In addition, a yield of 0.25 g (26.8%) α-chloroisobutyramide (II) was obtained with mp 117-119°C (from CCl_4). Mass spectrum, m/z (rel. int., %): 124 (0.4), M^+ 123 (1.7), 122 (1), M^+ 121 (4.1), 86 (89.6), 79 (20.6), 77 (60.8), 69 (20.6), 58 (14.4), 46 (64.9), 44 (100), 42 (21.6), 41 (42.2). m*: 121 → 86, 61.1 (61.1), 123 → 86, 60.1 (60.1), 86 → 69, 55.4 (55.5), 86 → 46, 24.6 (24.5), 69 → 41, 24.4 (24.5), 77 → 42, 21.8 (22.0), 86 → 42, 20.5 (20.8). Found: C 40.49; H 6.55; N 11.49%. Calculated for C_4H_8NOCl: C 39.52; H 6.63; N 11.52%.

Back Synthesis of (II). A solution of 2.08 g (20 mmoles) α-hydroxyisobutyric acid and 4.56 (22.5 mmoles) PCl_5 in 10 ml abs. CH_2Cl_2 was heated at reflux for 0.5 h and then maintained for 14.5 h at 20°C. The solvent was removed in vacuum (100 torr) and the residue was distilled. The fraction with bp 43-46°C (83 mm) was dissolved in 10 ml $CHCl_3$ and ammonia was bubbled through the solution obtained. The salt precipitate was removed and the solvent was removed in vacuum. The residue was sublimated at 25°C (2 mm) to yield 0.08 g (3%) (III), which was similar in melting point and PMR and mass spectra to the sample in the previous experiment.

Methylamide of α-(Methylazo)isobutyric Acid (IV). A mixture of 1.40 g (7.7 mmoles) (Ia) and 7.24 g (233 mmoles) $MeNH_2$ were maintained in a sealed ampul at −78°C for 19 h and then for 5 h at −8°C. The $MeNH_2$ was removed, the residue was extracted in ether, and the solvent was removed in vacuum to yield 1.09 g (98.9%)(IV), mp 61-63°C (from hexane). Mass spectrum, m/z (rel. int., %) $[M + 1]^+$ 144 (1), 115 (5), 114 (7), 101 (27.2), 100 (65.3), 87 (20.2), 73 (12.1),

TABLE 1. Spectral Characteristics of Compounds Synthesized

Compound[a]	Chemical formula	PMR spectrum (δ, ppm, J, Hz, in CCl_4 from TMS)					IR spectrum ν(C=O), cm^{-1}
		Me_2C	CH_2	MeO	MeO_2C	other groups	
(II)	$H_2NCOCMe_2Cl$	1,50	–	–	–	6,05 (NH_2)	1650
(IV)	$MeNHCOCMe_2N{=}NMe$[b]	1,14	–	–	–	2,77 (MeNH, J=5,0), 3,75, (MeN=), 6,9 (NH)	1645
(V)	$EtNHCOCMe_2N{=}NEt$[b]	1,14	–	–	–	1,10 & 3,27 (EtNH. J_{HCCH}=6,7, J_{HCNH}=6,0), 1,25 & 3,85 (EtN=, J_{HCCH}=8,0), 6,9 (NH)	1650
(VI)	 [c]	1,14	2,11	–	–	2,87 (MeN) 4,60 (NH)	1670
(VII)		1,41	1,69	–	–	2,46 (MeC_6H_4), 3,18 (MeN), 7,52 (C_6H_4, Δν=23,2, J=8,2)	–
(VIII)	$MeO_2CCMe_2N{=}NCH_2N(Me)OMe$	1,38	4,33	3,48	3,65	2,73 (MeN)	1750
(X)	$MeO_2CCH_2CMe_2N(OMe)N$ [d]	1,15	2,50	3,49	3,55	1,10–1,70 (ring CH_2)	–
(XI)	$MeO_2CCH_2CMe_2N{=}NC(H_C){=}C(H_A)(H_B)$ [e]	1,27	2,50	–	3,51	5,82 (H_A, J_{AC}=7,5, J_{AB}<0,5), 6,01 (H_B, J_{BC}=15), 7,00 (H_C)	– f)
(XII)	$MeO_2CCMe_2N{=}NCMe_2CH_2Cl$	1,18 1,22	2,48	–	3,55	3,60 (CH_2Cl)	–
(XIII)	$MeO_2CCMe_2N(OMe)\overset{+}{N}C_5H_5Cl^-$ (DMF-d_7)	1,42	–	3,76	3,71	8,22–9,57 (C_5H_5N)	–
(XIV)	$MeO_2CCMe_2N(OMe)\overset{+}{N}C_5H_5ClO_4^-$ (DMF-d_7)	1,40	–	3,73	3,67	8,10–9,50 (C_5H_5N)	–
	(DMF-d_7) (CD_3CN)	1,35	–	3,68	3,60	7,88–8,98 (C_5H_5N)	
(XV)	$MeO_2CCH_2CMe_2N(OMe)\overset{+}{N}C_5H_5Cl^-$ (CD_3CN)	1,20	2,63	3,52	3,59	8,30–9,28 (C_5H_5N)	1750
(XVI)	$MeO_2CCH_2CMe_2N(O){=}NCMe_2CH_2CO_2Me$	1,28	2,69	–	3,50	–	–
		1,50	2,73		3,54		

a) The spectra of (Ia), (Ib), (III), and (IX) are given in our previous work [1].
b) Compare with similar azo and azoxy compounds [7, 12].
c) Compare with Johnson and Hatch [8].
d) ^{13}C NMR spectrum (25.5 MHz, C_6H_6 from TMS, δ, ppm): 24.15 (Me_2C, $\Delta\nu$ = 18.1, ^1J = 124.1), 24.4 (ring CH_2, $\Delta\nu$ = 80.2, ^1J = 170), 42.0 (CCH_2C, ^1J = 127), 50.9 (MeO, ^1J = 146), 64.2 (MeON, ^1J = 142), 66.2 (CN), 171.9 (CO). For the similar compound $MeO_2CH_2CMe_2N$  [13] under the same conditions: 23.2 (Me_2C, ^1J = 126, ^4J = 4.2), 40.5 (CCH_2C, ^1J = 131, ^4J = 3.6), 50.9 (MeO, ^1J = 147), 63.4 (CN, ^2J 5.0), 66.5 (CH_2O, ^1J = 151.2, ^3J <2), 171.5 (CO). Data on the ^{13}C NMR spectra of aziridines are given in our previous work [14].
e) See the work of Tsuji and Kosower [7].
f) UV spectrum (in n-hexane), λ_{max}, nm (log ε): $\pi \rightarrow \pi^*$ 224 (3.67), $n \rightarrow \pi^*$ 400 (1.48), see the work of Tsuji and Kosower [7].

TABLE 2. Activation Parameters for Nitrogen Inversion in Alkoxyhydrazines

Compound	Solvent	Δν a), Hz	T_c, °C	k, sec^{-1}	$\Delta G^{\neq}$, kcal/mole
(X)	Toluene-d_8	3,5	42 b	7,77	17,2
(XIV)	CD_3CN	11,5	2	25,53	14,3
	CD_3OD	10,5	6	23,31	14,5
(XV)	CD_3CN	8,0	18	17,76	15,3
		5,5 c	27	74,42	15,0

a) Observed for the Me_2C group.
b) Begins to decompose at 50°C and decomposes rapidly at 100°C.
c) Observed for the CH_2 group, J_{AB} = 13.5 Hz.

72 (100), 70 (12.3), 58 (81), 56 (12.2), 44 (10), 43 (54.1), 42 (37.3), 41 (69.4), 30 (24.3), 28 (31.4), 27 (11), 15 (22.4). m*: 101 → 72, 51.3 (51.1), 100 → 69, 47.6 (47.8), 69 → 141, 24.4 (24.4), 144 → 143, 12.8 (12.6). Found: C 50.20; H 9.18; N 29.27%. Calculated for $C_6H_{13}N_3O$: C 50.33; H 9.15; N 29.35%.

Ethylamide of α-(Ethylazo)isobutyric Acid (V). Under conditions of the above synthesis, a yield of 1.26 g (92.9%) (V) with bp 65-66°C (1 mm) was obtained from 1.44 g (7.9 mmoles) (Ia) and 13.8 g (307 mmoles) $EtNH_2$. Mass spectrum, m/z (rel. int., %): $[M + 1]^+$ 172 (0.9), 128 (1.2), 115 (38), 114 (40.1), 100 (21), 99 (13), 87 (21), 86 (100), 72 (25), 70 (15), 69 (27.2), 68 (10.1), 58 (40.9), 44 (55.3), 43 (20.2), 42 (13.3), 41 (29.2). Found: C 55.93; H 9.87; N 24.67%. Calculated for $C_8H_{17}N_3O$: C 56.11; H 10.01; N 24.54%.

2,5,5-Trimethylpyrazolidin-3-one (VI). A mixture of 1.37 g (7 mmoles) and 4.47 g (99.3 mmoles) Me_2NH was maintained in a sealed ampul for 5 h at −78°C and then 15 h at 20°C. The excess Me_2NH was removed, the residue was extracted with ether, the ether was removed in vacuum, and the residue was distilled to yield 0.61 g (68%) (VI), bp 52-54°C (1 mm) (bp 51°C (0.1 mm) [8]). Mass spectrum, m/z (rel. int., %): 129 (10), M^+ 128 (73.2), 114 (98), 113 (100), 87 (3.7), 86 (15.9), 85 (32.9), 83 (41.5), 71 (11), 57 (24), 56 (64.7), 55 (25.6), 46 (19.5), 45 (23.2), 44 (22), 43 (19.5), 42 (39), 41 (32.9), 30 (58.6), 29 (22), 28 (39). Found: C 56.00; H 9.65; N 22.20%. Calculated for $C_6H_{12}N_2O$: C 56.23; H 9.44; N 21.86%.

Back Synthesis of (VI). A mixture of 2.28 g (20 mmoles) methyl β, β-dimethylacrylate and 2.64 g (66 mmoles) methylhydrazine was maintained for 90 h at 20°C. Distillation yielded 1.33 g (52%) (VI), bp 100-104°C (1 mm); the PMR and mass spectra were similar to those given above.

1-Tosyl-2,5,5-trimethylpyrazolidin-3-one (VII). A solution of 0.26 g (2 mmoles) (VI) and 0.42 g (2.2 mmoles) TsCl in 5 ml abs. pyridine was maintained for 1 h at 0°C and for 20 h at 20°C and then diluted with 50 ml ice water and extracted with ether. The ethereal extracts were dried over magnesium sulfate and evaporated in vacuum to yield 0.28 g (49.6%) (VII), mp 99-100°C (from hexane). Found: C 55.27; H 6.37; N 9.40%. Calculated for $C_{13}H_{18}N_2O_3$: C 55.30; H 6.43; N 9.92%.

Reaction of (Ia) with MeONHMe. A mixture of 1.4 g (7.7 mmoles) (Ia) and 1.83 g (30 mmoles) MeONHMe was maintained for 1.5 h at −78°C and then 25 h at 1°C and 1 h at 20°C. The excess amine was removed in vacuum, the residue was extracted in CCl_4, the solvent was removed in vacuum, and the residue was distilled to yield 0.65 g (41.5%) methyl α-(N-methoxy-N-methylaminomethylazo)isobutyrate (VIII), bp 47-48°C (1 mm). Mass spectrum m/z (rel. int., %): 143 (1), 102 (3.8), 101 (2.8), 100 (1.9), 88 (4.7), 87 (2.8), 76 (4.7), 75 (4.7), 74 (100), 73 (8.5), 56 (9.5), 43 (36), 42 (14.2), 28 (17), 15 (20.4), m*: 74 → 41, 23.8 (23.8), 74 → 43, 25.0 (25.0). Found: C 47.21; H 8.33; N 21.02%. Calculated for $C_8H_{17}N_3O_3$: C 47.28%; H 8.43; N 20.67%.

In addition, a yield of 0.51 g of a mixture of (VIII) and methyl α-(N,N-dimethoxyamino)isobutyrate (IX) (PMR analysis) with bp 30-47°C (1 mm) was obtained. Chromatography on a silica gel column with ether eluent yielded 0.09 g (6.59%) (IX) identified by comparison with an authentic sample [2] using PMR and mass spectroscopy.

Methyl β-(N-1-Ethyleneimino-N-methoxyamino)isovalerate (X). A solution of 1.37 g (7 mmoles) (Ib) in 6 ml ether was added dropwise to a solution of 1.67 g (39 mmoles) ethyleneimine in 5 ml abs. ether at −78°C. The mixture was warmed over 15.5 h to 20°C, the precipitate was separated, the solvent was removed from the filtrate in vacuum, and the residue was distilled to yield 0.96 g (69.8%) (X), bp 81-82°C (1 mm). Mass spectrum, m/z (rel. int., %): M^+ 202 (0.7), 187 (0.4), 171 (1.7), 115 (15.5), 83 (19.8), 73 (100), 59 (32.7), 56 (11.2), 55 (31.8), 41 (10.3), 31 (18.9), 28 (26.7), m*: 115 → 83, 59.9 (60.0), 115 → 73, 46.3 (46.4), 83 → 55, 36.4 (36.5). Found: C 53.30; H 8.61; N 14.00%. Calculated for $C_9H_{18}N_2O_3$: C 53.45; H 8.97; N 13.85%.

Methyl β-(Vinylazo)isovalerate (XI). A solution of 0.15 g (0.74 mmole) (X) in 1.3 ml abs. methanol was maintained for 2 days at 20°C and the solvent was removed in vacuum to yield 0.11 g (87.4%) (XI). Mass spectrum, m/z (rel. int., %):

$[M + 1]^+$ 171 (0.8), M^+ 170 (1.4), 142 (1.7), 115 (18.7), 83 (13.3), 73 (100), 59 (31.2), 56 (9.4), 55 (29.6), 43 (13.3), 41 (20.3), 29 (14), 28 (20.3), 27 (23.4), m*: 115 → 73, 46.3 (46.4), 83 → 55, 36.4 (36.5). Found: N 16.42%. Calculated for $C_8H_{14}N_2O_2$: N 16.48%.

A yield of 0.19 g (38%) (XI) was obtained by passing 0.59 g (2.9 mmoles) (X) through a silica gel column with 1:1 ether–hexane eluent. The same result was obtained by chromatography on Al_2O_3 (act. II-III).

Methyl β-(2-Chloro-1,1-dimethylethylazo)isovalerate (XII). A solution of 1.25 g (6.4 mmoles) (Ib) in 10 ml abs. ether was added dropwise to 1.43 g (20.1 mmoles) 2,2-dimethylethyleneimine in 10 ml abs. ether at −78°C. The mixture was warmed over 15 h to 0°C and maintained for 1 day at 20°C. The precipitate was removed, the solvent was removed from the filtrate in vacuum, and the residue was distilled to yield 1.25 g (83.5%) (XII), bp 72°C (1 mm). Mass spectrum, m/z (rel. int., %): $[M + 1]^+$ 237 (0.035), 235 (0.07), 206 (0.07), 205 (0.4), 204 (0.14) 203 (0.9), 115 (18.9), 83 (14.2), 73 (100), 59 (23), 56 (16.5), 55 (46), 43 (10), 41 (20.1), 29 (10.6); m*: 115 → 73, 46.3 (46.4), 83 → 55, 36.4 (36.5). Found: C 50.90; H 8.07; N 12.33%. Calculated for $C_{10}H_{19}N_2O_2Cl$: 51.17; H 8.16; N 11.93%.

Reaction of (Ia) with Pyridine. A solution of 0.22 g (3 mmoles) pyridine in 1 ml abs. acetonitrile was added to 0.31 g (1.7 mmole) (Ia) at −78°C and maintained for 15 h at −8°C. Then, the solvent was removed in vacuum to yield 0.3 g (67.8%) chloride salt of methyl α-(N-1-pyridinium-N-methoxyamino)isobutyrate (XIII), which was characterized as the perchlorate (XIV) obtained as follows. A solution of 0.35 g (1.7 mmole) $AgClO_4$ in 10 ml H_2O was added to 0.3 g (XIII) in 1 ml H_2O. The AgCl precipitate was removed, the filtrate was partially evaporated in vacuum, the residue was separated, and dried in vacuum to yield 0.32 g (85%) (XIV), mp 123-124°C (from methanol). Found: C 40.54; H 5.09; N 8.63%. Calculated for $C_{11}H_{17}N_2O_7Cl$: C 40.69; H 5.28; N 8.63%.

Reaction of (Ib) with Pyridine. Similar to the above procedure, 9 ml of an oil was obtained from 0.195 g (1 mmole) (Ib) and 0.15 g (2.03 mmoles) pyridine in 2 ml abs. acetonitrile after precipitation with ether. The oil was washed with 2 ml ether and placed in a vacuum for 1 h at 1 mm to yield 0.2 g (74%) (XV). The product was characterized by PMR and IR spectroscopy (see Tables 1 and 2).

Reaction of (Ia) with Et_3N. A solution of 0.31 g (3.2 mmoles) Et_3N in 4 ml abs. ether was added to a solution of 0.54 g (2.9 mmoles) (Ia) in 5 ml abs. ether at −78°C. The temperature was raised over 8 h to −20°C and then the mixture was maintained for 10 h at −8°C and for 3 h at 20°C. The precipitate was removed, the solvent was removed from the filtrate in vacuum, and the residue was sublimated at 75°C (1 torr) to yield 0.24 g (65.8%) dimethyl azoxyisobutyrate (III), mp 50-51°C (from hexane), identified by comparison with an authentic sample [2] relative to melting point and PMR spectrum.

Reaction of (Ia) with Et_2NH. A sample of 20 ml Et_2NH was added to 1.45 g (8 mmoles) (Ia) at −78°C and the mixture was maintained for 16 h. Then, the mixture was warmed to 20°C. The excess amine was removed in vacuum, the residue was extracted in ether, and the extract was evaporated in vacuum to yield 0.95 g (96.5%) (III), mp 51-52°C (from hexane) which had a similar PMR spectrum to that of the sample obtained in the previous experiment.

Reaction of (Ib) with Et_2NH. Under the conditions of the above preparation, a yield of 1.05 g (95.8%) dimethyl azoxyisovalerate (XVI) was obtained from 1.56 g (8 mmoles) (Ib) and 20 ml Et_2NH. Distillation gave 0.69 g (63%) (XVI), bp 89-93°C (1 mm), identified by comparison with an authentic sample [2] relative to boiling point data and the PMR and mass spectra.

CONCLUSIONS

The reactions of N-chloro-N-alkoxy-N-tert-alkylamines with amines are characterized by nucleophilic substitution at the nitrogen atom with formation of the corresponding N-alkoxyhydrazines which are stable in the case of ethyleneimine and pyridine; give diazenes as in the case of $MeNH_2$, $EtNH_2$, and $Me_2\underbrace{CCH_2}NH$; or yield products of further transformations as in the case of NH_3, Me_2NH, and MeO(Me)NH. Nucleophilic substitution is repressed in the reaction with Et_2NH and Et_3N by one-electron reduction with the formation of azoxy compounds.

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NITRATION OF ACYLATED SUBSTITUTED METHYLENEDIAMINES

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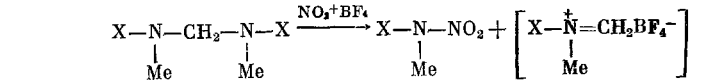
Previously, we showed that during nitration of linear alkylimides by nitronium tetrafluoroborate, the acetyl and methanesulfonyl groups can be replaced by a nitro group [1].

In the present paper, we studied the reaction of nitronium tetrafluoroborate with N′, N-diacylated and N,N′-disulfonylated dialkyl-substituted methylenediamines and also monosulfonylated tri- or N,N-dialkyl-substituted methylenediamines. The literature data on nitration of this type of compound are fragmentary [2-4] and do not make it possible to make any generalizations.

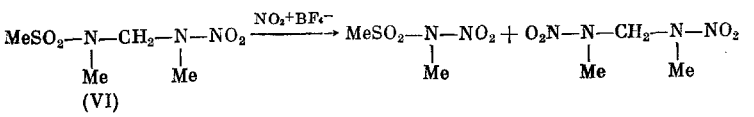
We found that the direction of the reactions of these compounds depended significantly on the nature of the acid groups. In addition, one or both acetyl groups were replaced by a nitro group. The ratio of the products depended significantly on the ratio of the starting reagents (Table 1). In going from acetyl to methanesulfonyl and carbomethoxy derivatives, we observed cleavage of the methylenediamine fragment with formation of the corresponding N-alkyl-N-nitroamides



X = $MeSO_2$, MeOCO.

In this case, the role of the leaving group was performed not by acid groups, but by methyleneamidonium cations.

Nitration of p-toluenesulfonyl derivatives of methylenediamine proceeded in both possible directions. This fact apparently indicates that during nitration the p-toluenesulfonyl group tended more to act as a leaving group than the methanesulfonyl group. It is logical to assume that the direction of the reaction could be changed, at least partially, by a decrease in the thermodynamic stability of the resulting methyleneamidonium cations. Indeed, during nitration of (VI) the expected N,N′-dimethyl-N,N′-dinitromethylenediamine was formed:



(VI)

However, this same methylenedinitroamine was obtained in high yield in the reaction of nitronium tetrafluoroborate with (VII), and the desired N-methyl-N′-isopropyl-N,N′-dinitromethylenediamine was not formed at all. This could be explained with the following scheme:

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