ACTA CHEMICA SCANDINAVICA 21 (1967) 1007–1016

Deamination of Simple Aliphatic Amines in Aprotic Media

JAN BAKKE

Institutt for organisk kjemi, Norges tekniske høgskole, Trondheim, Norway *

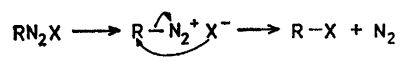
Octylamine and butylamine have been deaminated in ether at −70° with nitrosyl chloride as deaminating agent. The gas evolution at −70° was measured. The main products were octyl chloride and butyl chloride, respectively. From octylamine 5 % of octene and 3 % of octyl ethyl ether were obtained together with 27 % of a substance believed to be 1-chloro-octaldoxime. Deamination of octylamine with N_2O_3 gave less than 5 % octyl alcohol and octyl nitrite, together with octylammonium nitrite and octylammonium nitrate.

The deamination of aliphatic primary amines in protic media like water and acetic acid is one of the more studied types of reactions in organic chemistry.[1] The reaction between these amines and deaminating agents in aprotic solvents is far less studied. Solonina [2] deaminated isobutylamine with nitrosyl chloride in ether already in 1898. Smith, Bear, and Ege [3] reacted butylamine with nitrosyl chloride in ether, and showed the volatile part of the product to consist mainly of butyl chloride. No isobutyl chloride could be detected by infrared spectroscopy. Felkin [4] deaminated D-α-methylbenzylamine in dioxane with nitrosyl chloride and showed the resulting chloride to have partial retention of configuration. Felkin [5] also deaminated several α-hydroxylamines in dioxane. By reacting methylamine and nitrosyl chloride in ether at −70°C, Müller, Haiss and Rundel [6] were able to show the presence of N-nitrosomethylamine in the reaction mixture. Diazomethane was also produced. Roedig and Grohe [7] later tried to obtain 2,2,2-trichlorodiazoethane by reacting 2,2,2-trichloroethylamine under the same conditions but without success. Other examples of aprotic deaminations are the works of Curtin,[8] of Friedman,[9] and works cited by these authors.

By deamination in protic media, extensive rearrangements of the molecular skeleton occur involving hydride and alkyl shifts.[1] These rearrangements make the protic deamination less fit for transformations of the amino group into other reactive groups (*e.g.* hydroxyl or halogen groups). As the work of Smith *et al.*[3] showed, aprotic deamination gives less rearrangements of the molecular skeleton.

* Present address: AB Bofors, Nobelkrut, Bofors, Sweden.

The mechanistic aspects of the aprotic deamination have been discussed by Wilhelm and Curtin,[10] by Felkin,[4] and by others.[11] The high yields of non-isomerized products under these conditions can be explained by a S_Ni reaction:



a path analogous to the reaction between an alcohol and thionylchloride. Another explanation is the formation of an ion-pair during the loss of the nitrogen molecule:

$$R-N_2^+ X^- \longrightarrow \underset{\text{ion-pair}}{\{R^+ X^-\}} + N_2 \longrightarrow RX$$

This mechanism is analogous to the reaction path White and Aufdermarsch[12] have shown to operate in the aprotic deamination of N-sec. alkylamides. It does not seem possible to make a choice between these two paths at present, and both of them and possibly others may be operating simultaneously.

Since earlier workers thus had shown the skeletal rearrangements by deamination in aprotic solvents to be less extensive than in protic ones, it was considered worth while to investigate the reaction of simple aliphatic amines and nitrosyl chloride in such solvents, especially as vapor phase chromatography (VPC) would make it easy to determine the extent of isomerisation. By working at low temperatures, it was hoped to avoid side reactions. Beside nitrosyl chloride, it was also of interest to determine the preparative value of other deaminating agents as N_2O_4 and N_2O_3. White and Feldman[13] have investigated the reaction of N_2O_4 with hexylamine. Only low yields of hexyl alcohol and hexyl nitrate were obtained beside products (hexylammonium nitrate, hexylammonium nitrite, N-nitrohexylamine) with the amine-nitrogen still present.

Our preliminary investigation of the reaction between N_2O_3 and octylamine showed also this deaminating agent to be of little preparative value under these conditions. Low yields of octyl nitrite and octyl alcohol (less than 5 % yield of each) were obtained, beside octylammonium nitrite and octylammonium nitrate. The last substance was probably due to a contamination of N_2O_3 with N_2O_4.

Nitrosyl chloride was then tried as deaminating agent. The reactions were run in ethyl ether, and as nitrosyl chloride is a rather reactive substance it was always passed into the ether at −70° (reaction temperature). Excess nitrosyl chloride was removed from the reaction mixture before warming to room temperature. In the first orientating experiment, nitrosyl chloride was carried by N_2 gas directly into the amine solution at −70°. A white precipitate occurred, which was stable during the warming of the reaction mixture and later was shown to be octylammonium chloride. This was contrary to the observation of Smith *et al.*[3] of a decomposing precipitate obtained in their low-temperature deamination of butylamine. No gas evolution could be seen after the N_2-stream was stopped, nor during the warming period. Also in this respect our experiment gave a result different from that of Smith *et al.*[3] who

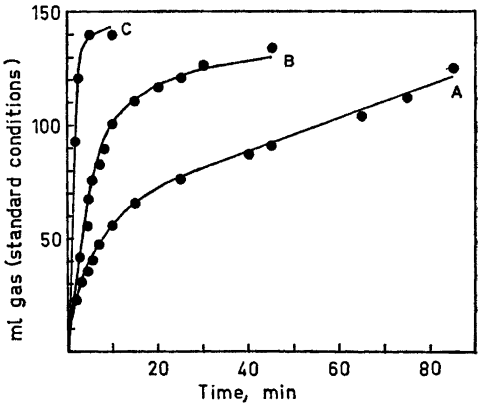
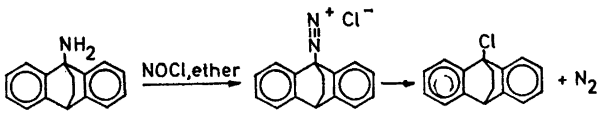


Fig. 1. Gas evolution from deamination reactions as a function of time. Start concentrations: Curve A: 4×10^{-2} moles/l of octylamine and 6.3×10^{-2} moles/l of nitrosyl chloride. Curve B: 6.9×10^{-2} moles/l of butylamine and 7.5×10^{-2} moles/l of nitrosyl chloride. Curve C: 10^{-1} moles/l of octylamine and 8.5×10^{-2} moles/l of N_2O_3. Ether was used as a solvent in all three experiments. Reaction temperature $-70°C$.

obtained gas evolution during 13 h. The reasons for these experimental differences are not known.

To see if any gas evolution could be detected at $-70°$, the simple gas measurement equipment described in the experimental section was used. The gas evolution as a function of time is reproduced in Fig. 1. The gas evolution was rather rapid. If one assumes the reaction between nitrosyl chloride and the amine to be the rate determining step for the gas evolution, an initial second order rate constant of approximately 1 $(\text{mole/l min})^{-1}$ is obtained.

By making the hypothetical assumption that the break-down of the diazonium chloride II is the rate determining step in the deamination of the bridgehead amine I, Wilhelm *et al.*[10] obtained a lower limit for the rate of the nitrogen loss from the diazonium salt II.



I II

They found this lower limit for the first order rate constant to be 10^{-2} sec^{-1}. If the same hypothetical assumption is made in our nitrosyl chloride deamination of octylamine, a lower limit for the break-down of the diazonium salt is found to be approximately 10^{-3} sec^{-1}; that is, of the same order of magnitude as found by Wilhelm *et al.*[10]

As will be seen from Fig. 1, the orientating run with N_2O_3 as deaminating agent gave an even faster gas evolution than the one with nitrosyl chloride. Due to the low preparative value of N_2O_3 as deaminating agent (*vide supra*), this point was not investigated any further.

VPC of the reaction products from the nitrosyl chloride deamination of octylamine and butylamine showed this deaminating agent to be the more promising of the ones tried. The main volatile products were found to be the

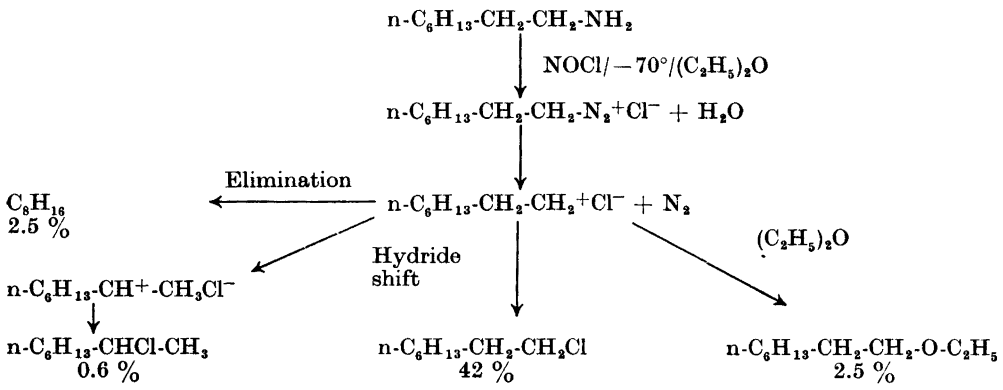


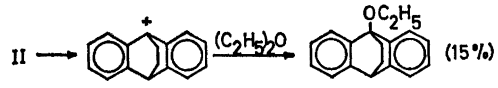
Chart I

primary alkyl chlorides, only slightly contaminated with the corresponding 2-chloro-alkanes (1.5 % of the total chlorides in the case of octylamine and 3 % in the butylamine case). The available VPC equipment would not separate 1- and 2-alkylamines. The two amines used were claimed by the makers (Fluka AG) to be more than 98 % pure. The contamination of the primary chlorides may therefore be partly or completely due to slightly impure starting material.

The other products from the deamination of octylamine identified by VPC were octyl ethyl ether (5 % of VPC area), octyl nitrate (4 % of area), and octene (5 % of area): See Chart I.

The yields in Chart I are based on reacted amine, octylammonium chloride being treated as unreacted amine.

Chart I shows a few interesting points. The formation of octyl ethyl ether corresponds to the ether formation reported by Wilhelm *et al.*:[10]



III

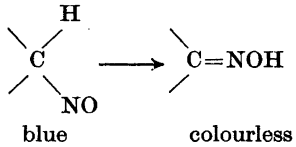
Wilhelm *et al.*[10] assumed the formation of this ether to be mainly due to the high electrophilic power of the non-planar carbonium ion III. The occurrence of octyl ethyl ether in our reaction indicates the ether formation to be partly due to the reaction conditions, that is, the formation of a high-energy, poorly solvated carbonium ion, and not only to the particular geometrical form of this carbonium ion.

The low yield of elimination product (octene, 2.5 %) gives an interesting example of the importance of the reaction conditions. When Friedman *et al.*[9] deaminated butylamine, closely related to octylamine, with alkyl nitrite/HCl in $CHCl_3$, 1-butene was one of their major products (92 %). Unfortunately,

our own VPC equipment did not allow detection of butene in our reaction with butylamine. Octene formed in our deamination of octylamine could have been removed by reaction with nitrosyl chloride present in the reaction mixture. However, a control run with 1-octene (from heptanal and methyl-triphenyl-phosphonium iodide) and nitrosyl chloride in ether at −70° showed this compound to be inert towards NOCl under these conditions.

The presence of small amounts of octyl nitrate in the reaction mixture is obscure, but it may have been formed from N_2O_4 contaminating the nitrosyl chloride.

The products from the deamination of octylamine identified by VPC corresponded to 50 % of the reacted amine. As will be seen from Fig. 1, the gas obtained by the reaction corresponded to 90 % of the reacted amine, thus indicating some further, non-volatile products to have been present in the reaction mixture. Thin layer chromatography (TLC) indeed indicated one such product to be present. This compound (compound A) was isolated by preparative TLC followed by sublimation, and consisted of a colourless oil (yield 27 % of the reacted amine). Compound A had an IR spectrum indicating a hydroxyl group to be present. The reaction mixture from the deamination reaction was blue-coloured. When reaching room temperature, the colour was fading. This colour was thought to be due to a nitroso group, rearranging to a colourless oxime at room temperature:

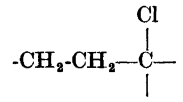


blue colourless

This oxime could then be compound A, thus explaining the hydroxyl band in the IR spectrum. As an oxime should give a ketone or an aldehyde on acid hydrolysis, compound A was refluxed with 10 % aqueous H_2SO_4. However, VPC of the products gave no peaks indicating simple ketones or aldehydes to be present. A crystalline compound (compound B) was isolated from the hydrolysis mixture. Compound B had a very characteristic IR spectrum, with bands at 3150, 1785, and 1670 cm^{-1}, beside several others.

Beilstein test of compound A showed halogen to be present in the molecule. As a control run with 1-octene and nitrosyl chloride had shown these two compounds not to react with each other under the deamination conditions, compound A was less likely to be 2-chloro-octaldoxime.

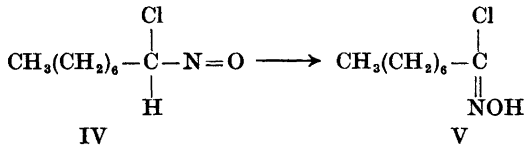
The NMR spectrum of compound A was too weak to give a reliable integral of the peak areas, however, it indicated an O—H to be present, as well as the combination



(triplet at 7.54 τ) and methyl and other methylene groups.

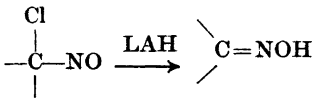
The visible light spectrum of the deamination reaction mixture recorded before the blue colour had disappeared (λ_{max} 645 mμ, shoulder at 605 mμ)

had the same form as that of 1-chloro-1-nitroso-cyclohexane [14] (λ_{max} 655 mμ, shoulder at 610 mμ). These spectroscopic data could then be explained by assuming compound A to be 1-chloro-octaldoxime (V), formed by isomerization of 1-chloro-1-nitroso-octane (IV):



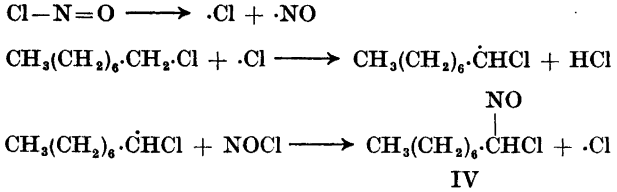
IV V

Further evidence for structure V was obtained by chemical means: Lithium aluminum hydride reduction of compound A gave a compound producing two spots on TLC with R_F-values identical to the R_F-values of the two spots obtained from octaldoxime. This result corresponds in part to the results obtained by Müller, Metzger, and Fries [14] on lithium aluminum hydride reduction of *sec.* 1-chloro-1-nitroso compounds where the corresponding ketoximes were obtained:



Müller *et al.*[14] made their *sec.* 1-chloro-1-nitroso compounds by reacting the corresponding ketoxime with dry chlorine gas in the dark. This procedure with octaldoxime gave a mixture producing two spots on TLC, one close to the front, and one with R_F identical to that of compound A. The mixture had the IR spectrum of compound A together with some other bands. When this mixture was refluxed with 10 % aqueous H_2SO_4, a crystalline compound was obtained with IR spectrum and melting point identical to that of compound B. This last point shows compound A to be identical to a compound formed from octaldoxime and dry chlorine gas in the dark, most probably 1-chloro-octaldoxime V (formed *via* IV).

The way of formation of IV is not clear. One could think of a radical mechanism:



However, at higher temperatures (80°) and with $SOCl_2$ as chlorine radical source, hydrogen abstraction is known to occur at carbon atoms 2 and 3, and not at 1.[16]

In summary, nitrosyl chloride deamination of simple, primary aliphatic amines in ether solution at −70° gives a fair yield (approximately 40 %) of the corresponding primary chlorides, and offers a rather convenient method for transformation of these amines into the corresponding chlorides. On the other hand, N_2O_3 and N_2O_4 seem to be less fit for this deamination process.

EXPERIMENTAL

The IR spectra were recorded on a Perkin-Elmer infrared spectrophotometer, Model 21, equipped with NaCl optics. The UV and visible light spectra were recorded on a Beckman DB spectrophotometer. NMR spectra were recorded on a AEI RS2 Spectrometer (60 Mc/sec) using tetramethylsilane as internal standard. TLC chromatograms were run on silica gel chromatostrips and the spots made visible by iodine vapour. VPC chromatograms were recorded on an Aerograph "Hi Fy, Model 600" gas chromatograph, equipped with hydrogen flame ionisation detector. Reaction products were identified by comparing retention times with those of authentic samples on two different columns, a 10′ 20 % SE 30 column and a 5′ 10 % XF-1150 (cyano-silicon) column (Aerograph). Melting points are uncorrected.

N_2O_3 and NOCl were prepared by the methods described by Brauer.[15] NOCl was refluxed for 2 h in a stream of dried N_2 gas and distilled twice from P_2O_5 through P_2O_5 filled tubes before use.

Ether used in the reactions was distilled from lithium aluminum hydride directly into the reaction vessel.

The deamination reactions were performed in the apparatus shown in Fig. 2. The amine was dissolved in ether in the three-neck flask A, equipped with a teflon coated magnetic bar and an "Ascarite" filled drying tube D. The nitrosyl chloride was collected in a pipette sealed to a cold-trap (H). Before reaction, the desired volume of nitrosyl chloride was stripped from H with dry N_2 gas, through a 50 cm tube filled with P_2O_5 on glass wool (G), and *via* a gas inlet tube equipped with a three-way stop-cock (F) into ether kept in the dropping funnel B (equipped with a cooling mantle). The pressures in A and B were equilibrated *via* the rubber tube C. When the nitrosyl chloride had been collected in B, the three-way stop-cock was closed and the ether solution dropped into A. The gas evolved in the deamination reaction was collected in the graduated measuring glass E. E was initially filled with water and turned upside-down in water.

Deamination of octylamine with N_2O_3. Octylamine (2.6 g, 20.2 mmoles) (Fluka, puriss.) in dry ether (100 ml) was cooled to −70° in the apparatus shown in Fig. 2. N_2O_3 (0.9 ml, 17 mmoles) collected in dry ether (100 ml) cooled to −70°, was added during 30 sec to the amine solution. During 12 min, 139 ml of gas (standard conditions, 6.2 mmoles) was collected as shown in Fig. 1. A precipitate appeared during the N_2O_3 addition and the following period. After 12 min, the cooling bath was removed, the reaction vessel evacuated at 2 mm Hg and 20 ml of colourless ether distilled off. When the reaction mixture reached 20°, the ether solution was decanted from the white precipitate. The ether solution was kept at −20° for one week, during which time the first precipitate

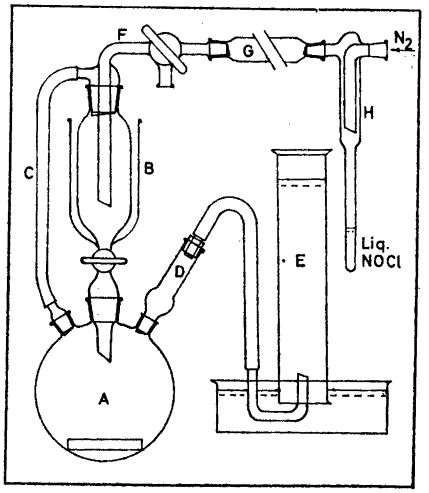


Fig. 2. For explanations, see text.

was left at 20°. When the ether evaporated from this precipitate, it turned into a jelly-like paste (precipitate A) (0.2 g). IR spectrum (10 % $CHCl_3$ solution) of precipitate A had bands at 2900 (broad, from 3600 to 2200 cm^{-1}), 1620, 1560, 1460, 1340 (strong, broad), and 1230 (strong, broad) cm^{-1}.

The ether solution kept at −20° afforded a white powder (precipitate B) (0.41 g). The IR spectrum (10 %, $CHCl_3$ solution) of precipitate B had the same bands as that of precipitate A, but the band at 1230 cm^{-1} was somewhat weaker than that at 1350 cm^{-1}. Both precipitates were soluble in $CHCl_3$ and in ether. A white powder appeared when the ether solution of precipitate A or B was placed at −20°, the white powder turned into a jelly again on evaporation of the ether.

The ether phase from the deamination reaction contained 1.4 g of material. IR spectrum of this material showed the presence of octylammonium nitrate (broad band at 3600−2200 cm^{-1} with maximum at 2900 cm^{-1}; broad, strong band at 1350 cm^{-1}). VPC of the ether phase on the XF-1150 column gave 5 peaks of approximately equal areas. One peak had the retention time of octanol and another that of octyl nitrite. The other 3 peaks had retention times different from those of 2-octanol and octyl nitrate. The amounts of octanol and of octyl nitrite were estimated at less than 100 mg of each. VPC on the SE 30 column indicated the presence of less than 100 mg of 1-nitro-octane. This compound did not pass through the XF-1150 column at 150°.

1-Octylammonium nitrate. 10 % aqueous HNO_3 was added to octylamine in water until pH 4 was reached. The water was then removed by freezedrying (p = 0.5 mm Hg). The residue was dissolved in ether and a white powder deposited when the ether was kept at −20°. The ether phase was decanted off and the white powder formed a jelly paste on evaporation of the ether. IR spectrum of the paste (10 % $CHCl_3$ solution) had a broad band at 3600−2200 cm^{-1} (max. 2900 cm^{-1}), 1620, 1510, and 1350 (broad and strong) cm^{-1}.

1-Octylammonium nitrite. This compound was prepared by the method of Ray and Rakshit.[17] 1-Octylammonium chloride (1 g, 6.06 mmoles) and $AgNO_2$ (1 g, 6.5 mmoles) were rubbed together with water (3 ml) in a mortar. The precipitated AgCl was removed by centrifugation. Gas evolution took place in the water solution. The water was removed by freezedrying (p = 0.5 mm Hg). The residue was extracted with ether (20 ml) (not completely dissolved). After drying of the ether phase over Na_2SO_4, evaporation of the ether and re-crystallization of the product from ether, 38 mg of a jelly paste was obtained. IR of this paste (10 %, $CHCl_3$) had a broad band at 3600−2200 cm^{-1} (peak at 2900 cm^{-1}) and strong bands at 1350 and 1230 cm^{-1}. The residue from the ether extraction was dissolved in ether (150 ml) and kept at +2°. A white powder which turned into a jelly paste (400 mg) on evaporation of the ether was obtained. IR spectrum of this jelly (10 %, $CHCl_3$) had a broad band at 3600−2200 cm^{-1} (peak at 2900 cm^{-1}), 1620, 1510, 1460, and 1230 (broad, strong) cm^{-1}. 137 mg more of this precipitate was obtained when the ether solution was kept at −20°. Total yield of octylammonium nitrite: 537 mg (38 %).

Deamination of octylamine with NOCl. After an introductory run where the nitrosyl chloride was passed directly into the ether solution of the amine, the reaction was performed as follows:

Octylamine (1.03 g, 7.97 mmoles) (Fluka, puriss.) in dry ether (150 ml) was cooled to −70° in the apparatus shown in Fig. 2. Nitrosyl chloride (0.6 ml, 12.5 mmoles, 56 % excess) was collected in dry ether (50 ml) in the dropping funnel cooled to −70°. The nitrosyl chloride solution was passed into the amine solution during 8 sec. A precipitate appeared and the solution turned blue. Gas evolution took place. During 70 min 120 ml (standard conditions, 5.3 mmoles) of gas was collected, as shown in Fig. 1. After 70 min the cooling bath was removed and the reaction vessel evacuated at the oil pump (2 mm Hg) during 10 min; 5 ml of brown-coloured ether distilled off. This distillate gave a positive test for Cl^- after shaking with water.

The reaction mixture was then allowed to reach room temperature. During this warming period, the blue colour of the solution faded somewhat; however, no change of the precipitate occurred. The precipitate (330 mg, 2.01 mmoles, 25 %) had an IR spectrum identical with that of octylammonium chloride; it was soluble in water, and the water solution gave a positive test for Cl^-.

5 ml of the ether solution evaporated at the aspirator showed the total solution (200 ml) to contain 0.78 g of material. 20 ml of the ether solution was concentrated to 3 ml, and

a visible light spectrum was run, λ_{max} 645 mμ, shoulder at 605 mμ. The rest of the ether solution was washed with $NaHCO_3$/water, dried over Na_2SO_4 and the volume made up to 180 ml with ether. VPC of this solution showed the following 5 compounds to be present (retention time in min on 10′ SE 30 column, t = 114°, area as percentage of total area): octene (1.1 min, 5 %); 2-chloro-octane (3.0 min, 1.2 %); 1-chloro-octane (4.7 min, 85 %); octyl ethyl ether (6.0 min, 5 %); octyl nitrate (12.5 min, 4 %). The amount of 1-chloro-octane was determined by comparing the peak height in the chromatogram with the peak height of 1-chloro-octane (Fluka, puriss.) from a standard solution of this compound. Total yield of 1-chloro-octane was found to be 370 mg (31 % of total amine, 42 % of reacted amine). Neglecting differences in the ionising power of the four other compounds in the chromatogram, the yields were found to be: octene 1.9 % (2.5 % of reacted amine); 2-chloro-octane 0.4 % (0.6 % of reacted amine); octyl ethyl ether 1.9 % (2.5 % of reacted amine); octyl nitrate 1.5 % (2 % of reacted amine).

Approximately 100 mg of substance from the ether solution from the reaction was separated by preparative TLC with 10 % ether/petroleum ether as eluent. By inspection in UV light the chromatogram was separated into 8 different zones. These zones were scraped off the chromatostrip and extracted with ethanol. The following amounts were obtained:

Zone	1	from	start:	0.6	mg	0.7	%	as isolated	by	TLC
»	2	»	»	4.6	»	6.0	»	»	»	»
»	3	»	»	2.6	»	3.0	»	»	»	»
»	4	»	»	29.7	»	36.5	»	»	»	»
»	5	»	»	6.6	»	8.0	»	»	»	»
»	6	»	»	5.0	»	6.0	»	»	»	»
»	7	»	»	27.1	»	33.4	»	»	»	»
»	8	»	»	5.0	»	6.0	»	»	»	»

The zones were overlapping, and total separation was probably not achieved. The separation by preparative TLC was repeated to increase the amount of the zone 4-compound (compound A in the text section and later in this experimental part). Compound A was sublimed at 65°/0.05 mm Hg as a colourless oil. IR spectrum of compound A (liquid film) had bands at 3280, 2900, 1640, 1600, 1500, 1460, 1375, 1140, 1090, 965, and 720 cm^{-1}. The NMR spectrum of compound A had a singlet at 1.0 τ, triplet at 7.54 τ, and broad peaks at 8.71 and 9.13 τ.

Total amount of compound A from the reaction: 0.78 g × 36.5 % = 0.28 g, corresponding to 27 % yield of 1-chloro-octaldoxime (based on reacted amine).

Reaction between compound A and aqueous H_2SO_4. Compound A (24.9 mg) was refluxed with aqueous H_2SO_4 (5 ml, 10 %) for 15 min. The product was extracted with ether, the ether washed with aqueous $NaHCO_3$ solution and dried over Na_2SO_4. Yield 18.9 mg. Crystallization of the product from ether at −20° gave 7 mg of crystals after 3 crystallizations (compound B). Compound B had m.p. 66.5−68.5°; IR spectrum (10 %, CCl_4) with bands at 3150, 2900, 1785, 1670, 1500, 1460, 1370, 1135, and 1080 cm^{-1}; and NMR spectrum (CCl_4) with signals at 0.49, 6.60 (quartet), 7.76 (quartet), 8.73, 8.86, and 9.03 τ.

Lithium aluminum hydride reduction of compound A. Sublimed compound A (12.4 mg) was dissolved in dry ether (10 ml) and solid lithium aluminum hydride (large excess) added. The mixture was stirred at 20° for 30 min. After addition of water, the mixture was acidified to pH 3 and extracted with ether. TLC of the ether extract showed the presence of starting material together with two spots with R_F-values identical to those of octaldoxime.

Reaction between octaldoxime and chlorine. Chlorine gas was passed through octaldoxime (1 g) in dry ether (25 ml) in the dark. The mixture first turned blue and a precipitate appeared. When the precipitate had dissolved and the colour turned bluish-green, the chlorine stream was stopped, and the ether phase washed 4 times with 2 N NaOH. The colour faded during this working up procedure. The ether solution was dried over Na_2SO_4, the ether removed at the aspirator and the product sublimed at 70°/0.05 mm Hg. TLC of the product showed one spot with R_F identical to that of compound A, and one with a larger R_F-value.

IR spectrum (liquid film) of the product showed bands at 3280, 2900, 1640 (shoulder), 1600 (very strong), 1460, 1430 (shoulder), 1140, 1090, 1020, 965, 850, and 720 cm^{-1}.

Reaction between the chlorinated oxime and H_2SO_4. The chlorinated oxime (94 mg) was refluxed with 10 % aqueous H_2SO_4 for 15 min, and extracted with ether. On concentration, the ether extract gave 11 mg of crystals, m.p. 65–67°, with IR spectrum identical to that of compound B.

The mother liquor from the crystallization (73 mg) had an IR spectrum with bands at 2900, 1600 (very strong), 1460, 1430 (shoulder), 1140, 1090, 1020, 850, and 725 cm^{-1}.

1-Octene and nitrosyl chloride. 1-Octene (from heptanal and triphenylphosphonium iodide) (100 mg, 1 mmole) in dry ether (25 ml) was cooled to −70° and nitrosyl chloride (0.1 ml, 2 mmoles) carried into the solution by dry N_2 gas. VPC of the reaction mixture after 24 h at −70°, showed all of the octene to be present at that time.

Deamination of butylamine with nitrosyl chloride. Butylamine (1.00 g, 13.7 mmoles) (Fluka, puriss.) in dry ether (100 ml) was cooled to −70° in the apparatus shown in Fig. 2. Nitrosyl chloride (0.72 ml, 15.0 mmoles, 10 % excess) was collected in dry ether (100 ml) in the dropping funnel cooled to −70°. The nitrosyl chloride solution was added to the amine solution during 15 sec. A precipitate appeared and the solution turned blue. During 45 min 133 ml of gas (standard conditions, 5.9 mmoles) was evolved as shown in Fig. 1. After 45 min the cooling bath was removed, 10 ml of ether (colourless) removed *in vacuo* (2 mm Hg) and the precipitate (0.535 g, 4.9 mmoles, 36 %) filtered off when the mixture reached 20°. The precipitate had an IR spectrum identical to that of butylammonium chloride. The ether phase was washed with aqueous $NaHCO_3$ solution and dried over Na_2SO_4. The amounts of butyl chloride and isobutyl chloride was determined by VPC, analogously to the determination of the octyl chlorides. The yield of butyl chloride was 330 mg (3.6 mmoles, 26 %, 41 % of reacted amine) and the yield of isobutyl chloride 10 mg (0.1 mmole, 0.8 %, 1.2 % of reacted amine). Total yield of butyl chlorides was thus 340 mg, 97 % of which was butyl chloride. The available columns for VPC were not able to separate butenes from the large amounts of ether in the reaction mixture.

Acknowledgements. I am grateful to Professor N. A. Sørensen for his interest in this work and to *Norges tekniske høgskole* for a fellowship.

REFERENCES

1a. Ridd, J. H. *Quart. rev. (London)* **15** (1961) 418.
1b. Zollinger, H. *Azo and Diazo Chemistry*, Interscience, New York and London 1961.
1c. Streitweiser, Jr., A. *J. Org. Chem.* **22** (1957) 861.
2. Solonina, V. *J. Soc. Phys.-Chim. Russe* **30** (1898) 431.
3. Smith, P. A. S., Baer, D. R. and Ege, S. N. *J. Am. Chem. Soc.* **76** (1954) 4564.
4. Felkin, H. *Compt. Rend.* **236** (1953) 298.
5. Felkin, H. *Bull. Soc. Chim. France* **1960** 1582.
6. Müller, E., Haiss, H. and Rundel, W. *Chem. Ber.* **93** (1960) 1541.
7. Roedig, A. and Grohe, K. *Tetrahedron* **21** (1965) 2375.
8. Curtin, D. Y., Kampmeier, J. A. and Farmer, M. L. *J. Am. Chem. Soc.* **87** (1965) 87.
9. Friedman, L., Bayless, J. H. and Mendicino, F. D. *J. Am. Chem. Soc.* **87** (1965) 579.
10. Wilhelm, M. and Curtin, D. Y. *Helv. Chim. Acta* **40** (1957) 2129.
11. Bartlett, P. D. In Gilman, H. *Organic Chemistry*, Wiley, New York 1953, Vol. 3, p. 44.
12. White, E. H. and Aufdermarsch, Jr., C. A. *J. Am. Chem. Soc.* **83** (1961) 1179.
13. White, E. H. and Feldman, W. R. *J. Am. Chem. Soc.* **79** (1957) 5832.
14. Müller, E., Metzger, H. and Fries, D. *Chem. Ber.* **87** (1954) 1449.
15. *C. Brauer's Handbuch der präparativen anorganischen Chemie*, Enke, Stuttgart 1954.
16. Kharasch, M. S. and Brown, H. C. *J. Am. Chem. Soc.* **61** (1939) 2142.
17. Ray, P. C. and Rakshit, J. *J. Chem. Soc.* **101** (1912) 141.

Received January 10, 1967.