Aprotic Deamination of Simple Amines
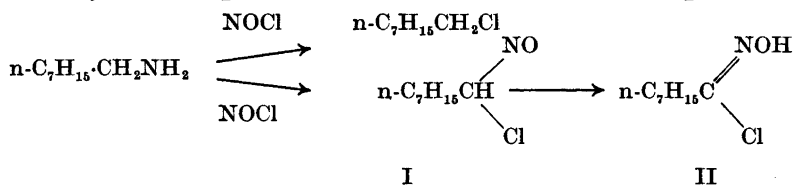
Diazoalkanes as Intermediates

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1-Chloro-1-nitrosooctane (I) was shown to be one of the products from the aprotic reaction between octylamine and NOCl. (I) rearranges to octanoyl chloride oxime, which on refluxing with aqueous H_2SO_4 gave O,N-dioctanoylhydroxylamine. (I) was further shown to be a product from the reaction between NOCl and diazooctane.

A previous investigation[1] showed that the deamination of octylamine with NOCl at $-70°$ gave two main products: 1-Chlorooctane and a compound believed to be 1-chloro-1-nitrosooctane (I). Due to the rapid conversion of I to octanoyl chloride oxime (II, earlier named 1-chlorooctaldoxime[1]) the actually isolated product was believed to be II ("compound A"[1]):

$$\text{n-C}_7\text{H}_{15}\cdot\text{CH}_2\text{NH}_2 \xrightarrow[\text{NOCl}]{\text{NOCl}} \begin{array}{c}\text{n-C}_7\text{H}_{15}\text{CH}_2\text{Cl} \\ \\ \text{n-C}_7\text{H}_{15}\overset{\displaystyle\text{NO}}{\underset{\displaystyle\text{Cl}}{\text{CH}}} \end{array} \longrightarrow \text{n-C}_7\text{H}_{15}\overset{\displaystyle\text{NOH}}{\underset{\displaystyle\text{Cl}}{\text{C}}}$$

$$\qquad\qquad\qquad\qquad\qquad\qquad\text{I}\qquad\qquad\qquad\qquad\text{II}$$

The present work was undertaken to verify the structure of "compound A", and also to investigate the most likely pathway of the formation of I in the deamination reaction.

In their study of the reactions of NOCl with organic substrates, Rheinboldt and Dewald[2] synthesised I using the substrate octaldoxime. In the present work I was prepared by the method of Piloty and Steinbock[3] from the reaction of the oxime with chlorine. This is a rapid method, which gives a good yield (79 %).

1-Chloro-1-nitrosooctane (I) was shown to have the same visible absorption spectrum as the reaction product from octylamine and NOCl (λ_{max} 645 nm, shoulder at 600 nm).[1] The IR spectrum had no bands in the region normally associated with the $C-N=O$ group (1500—1600 cm^{-1}),[4] which may be due to a high proportion of the molecules existing in the dimeric form.

The IR spectrum was rerun every 10 min and the spectrum was gradually replaced by that of II, the change being complete after one hour in the spectrophotometer.

The compound II was prepared by dissolving I in ether and keeping the mixture at 20° overnight. The initially blue solution of I had then turned colourless, and the IR spectrum of the product was consistent with the structure II: Bands at 3200 cm^{-1} (—OH) and 1645 cm^{-1} ($>$C$=$N—), together with a characteristic pattern from 1150 to 950 cm^{-1}. This IR spectrum was almost identical to that of "compound A",[1] except that the latter had two bands (at 1600 and 1500 cm^{-1}) not present in the spectrum of II synthesised in the present work. These two bands are believed to be due to impurities. The presence of impurities in "compound A" worked up from a complex reaction mixture is not surprising, especially in view of the instability of the acyl chloride oximes.[5]

A further indication of the identity of "compound A" with II was obtained by refluxing II with aqueous H$_2$SO$_4$ to give a crystalline substance, identical with "compound B", obtained by similarly treating "compound A".
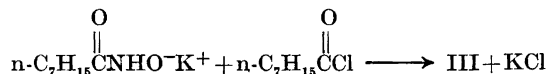
Mass spectrometry of "compound B" showed it to be a C$_{16}$ substance containing no chlorine. As reported previously "compound B" had IR absorption at 3150 cm^{-1} indicating some hydrogen bond H—N$<$ or H—O— to be present. Two bands in the carbonyl region, one at 1785 and one at 1670 cm^{-1} were also present. These two bands seemed to be too far away from each other to arise from the same carbonyl group in two different environments (e.g. hydrogen bound and nonhydrogen bound carbonyl). The band at 1670 cm^{-1} can be assigned to an amide type carbonyl. This, together with the band at 3150 cm^{-1}, suggested the presence of the structural group

$$
\begin{array}{cc}
\text{O} & \text{H} \\
\parallel & \mid \\
\text{R}-\text{C}-\text{N}- &
\end{array}
$$
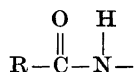
The carbonyl band at 1785 cm^{-1} is of rather high frequency for an open-chain compound. Acyl halides and acyl peroxides absorb in this region, but both are rather unlikely structures here.

However, the structure of the group R—C(O)—O—N$<$ is rather similar to the acyl peroxide structure and thus would probably give a high carbonyl frequency. The combination of these two part structures gives the structure n-C$_7$H$_{15}$C(O)—NH—O—C(O)—n-C$_7$H$_{15}$ (III) for "compound B".

O,N-Dioctanoylhydroxylamine (III) was then synthesised by reacting the potassium salt of octanohydroxamic acid with octanoyl chloride:

$$
\underset{\text{O}}{\overset{\text{O}}{\parallel}}
$$

$$
\text{n-C}_7\text{H}_{15}\overset{\text{O}}{\overset{\parallel}{\text{C}}}\text{NHO}^-\text{K}^+ + \text{n-C}_7\text{H}_{15}\overset{\text{O}}{\overset{\parallel}{\text{C}}}\text{Cl} \longrightarrow \text{III} + \text{KCl}
$$

by analogy with the method of Renfrow Jr. and Hauser,[6] who synthesised O,N-dibenzoylhydroxylamine.

The compound obtained in this synthesis proved to be identical to the one obtained by refluxing of II with aqueous H$_2$SO$_4$.

The structure of "compound B" shows "compound A" to possess the structural grouping n-C_7H_{15}—$\overset{\displaystyle |}{\underset{\displaystyle |}{C}}$—N—O, and this, together with earlier presented evidence, shows "compound A" to be identical with II. The structure of "compound A", together with the evidence of the reported [1] visible absorption spectrum of the deamination reaction product, thus, shows the primary reaction product to be 1-chloro-1-nitrosooctane (I).

The IR spectrum of III at various concentrations in CCl_4 disclosed the presence of intermolecular hydrogen bonds between the amide carbonyl and the nitrogen bound hydrogen. At high concentrations (ca. 0.37 mole/l) the amide carbonyl absorbed at 1670 cm^{-1} and the amide hydrogen at 3180 cm^{-1}. Lowering the concentration to 0.18 mole/l broadened the band of the amide hydrogen and gave the carbonyl band a shoulder at 1710 cm^{-1}. At still lower concentrations, (0.01 mole/l) the hydrogen band was moved to 3360 cm^{-1} and the carbonyl band to 1730 cm^{-1}. The position of the "ester carbonyl" band moved from 1795 cm^{-1} to 1787 cm^{-1} during these manipulations. It is tempting to formulate the hydrogen bound species as a dimer:
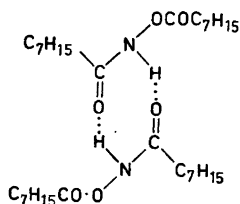
by analogy with the carboxylic acids. However, the experiments do not permit any definite conclusion to be drawn concerning this structure.

Hadži and Prevoršek [7] have discussed the IR spectrum of O,N-dibenzoylhydroxylamine in dilute CCl_4 solution. Due to the rather low N—H frequency (3300 cm^{-1}) they assumed the existence of an intramolecular hydrogen bond:
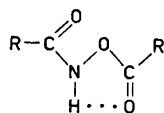
In the case of O,N-dioctanoylhydroxylamine, the existence of this intramolecular hydrogen bound species is further supported by the movement of the "ester carbonyl" frequency from 1795 cm^{-1} to 1787 cm^{-1} on dilution of the sample. The frequency shift is the one expected for an ester carbonyl group going from free to hydrogen bound.[4] As the strong intermolecular hydrogen bond is broken, the new, weak intramolecular one is formed.

As the structure of the blue reaction product from the deamination reaction was firmly established as 1-chloro-1-nitrosooctane, the mechanism of its formation was made the object of further studies.

Previously,[1] the possibility of a radical reaction between NOCl and 1-chlorooctane was discussed and considered to be less likely. Experiment has

now shown that 1-chlorooctane is stable towards NOCl under the deamination condition used.

Rheinboldt et al.[2] synthesised (I) from octaldoxime and NOCl. This points towards 1-nitrosooctane or octaldoxime being possible intermediates. When octaldoxime and NOCl were brought together at $-70°$, a blue-green solution was indeed obtained. The visible absorption spectrum of this solution clearly indicated the presence of (I) (λ_{max} 645 nm, shoulder at 600 nm). However, the colour did not fade with time. This behaviour was not the same as that observed for the deamination reaction, nor for the 1-chloro-1-nitrosooctane (I) synthesised in the present work. Instead, it indicated (I) to be formed from some intermediate reaction product between octaldoxime and NOCl.
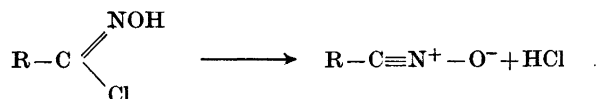
The IR spectrum of a sample of the reaction product gave further support to this interpretation. The IR spectrum run directly after concentration was different from the IR spectra of (I) and (II), but when the concentrated sample was kept at 20° overnight, the IR spectrum showed the characteristic bands of (II), together with other bands. A band at 1670 cm^{-1} was present in both these spectra, however, no absorption at this frequency was found in the deamination product.[1]

The sample had evolved water and nitrogen oxides when kept at 20° overnight. Although one may formulate the intermediate as the addition product between octaldoxime and NOCl:

$$C_7H_{15}-\overset{\displaystyle H}{\underset{\displaystyle Cl}{\overset{|}{C}}}\diagdown\overset{\displaystyle NO}{\underset{\displaystyle OH}{N}}$$
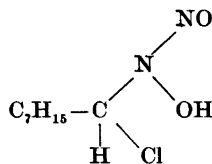
no definite conclusion can be drawn at present. One point, however, is quite clear from these experimental data. The 1-chloro-1-nitrosooctane from the deamination has not arisen from a reaction between octaldoxime and NOCl.

Another intermediate, which could possibly yield I by reaction with NOCl is diazooctane. There are a few reports in the literature of the reaction between relatively stable diazo compounds and NOCl. Kissinger, McQuistion, and Schwartz [8] reacted perfluoroalkyldiazomethanes and NOCl and obtained the corresponding acyl chloride oximes and also some furoxanes. They did not mention the chloro-1-nitroso compounds as possible intermediates. Skinner [9] reacted NOCl with ethyl diazoacetate and isolated a polymer believed to have arisen from the corresponding nitrile oxide. Nitrile oxides are known degradation products from acyl chloride oximes:[5]

$$R-C\diagdown\overset{\displaystyle NOH}{\underset{\displaystyle Cl}{}} \longrightarrow R-C\equiv N^+-O^- + HCl$$

Thus, both these works and other [10] suggest that acyl chloride oximes and therefore also 1-chloro-1-nitroso compounds could be possible reaction products from diazoalkanes and NOCl.

Accordingly, the reaction between diazoethane and NOCl was tried under the conditions used for the deamination reaction. Due to the high volatility of the reaction products none of them were isolated. However, one compound had the same retention time on vapor phase chromatography (VPC) as ethyl chloride, and another had the same visible light spectrum as 1-chloro-1-nitrosoethane (made by the method of Wieland [11]). This spectrum is very similar to that of I: λ_{max} 641 nm and shoulder at 600 nm.

On this evidence it seemed to be a clear possibility that diazooctane was an intermediate in the formation of (I) in the deamination reaction. The over-all reaction for the formation of diazooctane would then be:

$$2 \text{ n-C}_7\text{H}_{15}\text{CH}_2\text{NH}_2 + \text{NOCl} \longrightarrow \text{n-C}_7\text{H}_{15}\text{CHN}_2 + \text{H}_2\text{O} + \text{n-C}_7\text{H}_{15}\text{CH}_2\text{NH}_3{}^+\text{Cl}^-$$

In the deamination reactions, an excess of NOCl was used,[1] and from both the reaction scheme above and from the reaction between diazoethane and NOCl there seemed to be a possibility of stopping the reaction at the diazo-octane stage by adding less than an equimolecular amount of NOCl.

NOCl in ether solution cooled to $-70°$ was therefore added dropwise into a four-fold excess of octylamine in ether cooled to $-70°$. At the end of the addition, the solution was colourless. An IR spectrum of a sample of the solution showed a band at 2050 cm^{-1}, characteristic of a diazo compound, and the sample had visible light absorption in the same region as diazoethane: λ_{max} 464 nm (λ_{max} diazoethane: 466 nm). To further prove the presence of diazooctane, benzoic acid was added to the rest of the solution kept at $-70°$, and octyl benzoate was isolated after working up the reaction products. From the IR and visible light spectrum and from the amount of octyl benzoate, the amount of diazooctane was estimated to be 40 % of the added NOCl. In addition to the diazooctane, the reaction mixture contained 1-chlorooctane (27 % of added NOCl).

The deamination reaction could thus be formulated:

Scheme 1

$$\text{RCH}_2\text{NH}_2 + \text{NOCl} \longrightarrow \text{RCH}_2\text{N}_2{}^+\text{X}^- + \text{HY} \quad (+\text{RCH}_2\text{NH}_2 \longrightarrow \text{RCH}_2\text{NH}_3{}^+\text{Y}^-)$$

V,   a: X=Cl,   Y=OH
      b: X=OH,   Y=Cl

$[\text{RCH}_2{}^+ \ \text{X}^-] + \text{N}_2$ $\text{RCHN}_2 + \text{HX} \quad (+ \ \text{RCH}_2\text{NH}_2 \rightarrow \text{RCH}_2\text{NH}_3{}^+\text{X}^-)$

| VI,
| a: X=Cl
↓   b: X=OH $\text{RCH}_2\text{NH}_3{}^+\text{Cl}^-$ |

RCH$_2$X
and other products
derived from carbonium
ion intermediates   NOCl

                                                              NO
                                                            /
                                          RCH   +[RCH$_2$Cl]
                                            \
$\text{RCH}_2\text{Cl} + \text{RCH}_2\text{NH}_2$ Cl
(R=n-C$_7$H$_{15}$)

A key intermediate from the reaction between NOCl and the amine is probably the diazonium compound (V) or the covalent equivalent $\text{R}\cdot\text{CH}_2\text{N}=\text{N}-\text{X}$. In the cases where HX or HY represents HCl, this is as-

sumed to be removed as the ammonium salt as indicated by the parenthesis. It is not possible at present to make a choice between (Va) and (Vb) as to which is the more likely structure for the diazonium compound. Müller, Haiss, and Rundel [13] have presented evidence for N-nitrosomethylamine as an intermediate in the reaction between methylamine and NOCl. The N-nitrosoamine should then rearrange to the diazonium hydroxide (as Vb). However, in ether, an aprotic medium with low dielectric constant, the ion-pair (VIb) formed from (Vb) would most probably, collapse to the alcohol. As octyl alcohol was formed only in trace amounts by the deamination reaction [1] ($RCH_2OH/RCH_2Cl < 0.01$), (Vb) must be less important than (Va) as intermediate in that instance. That is, if we assume the chlorooctane to have been formed solely by the break-down of (V) and (VI).

In the reaction between diazoethane and NOCl, some ethyl chloride was produced together with 1-chloro-1-nitrosoethane, indicating that some of the chlorooctane in the deamination reaction may have been formed from the reaction between NOCl and diazooctane.

Another possible mode of formation of chlorooctane is by a reaction between diazooctane and octylammonium chloride. This possibility was tested by reacting diazoethane and octylammonium chloride under the conditions used for the deamination in the present work. After 40 min benzoic acid was added to the mixture. VPC analyses of the solution showed it to contain ethyl chloride corresponding to *ca.* 20 % of the diazoethane added and ethyl benzoate corresponding to 80—90 % of the diazoethane, giving a ratio between reacted and unreacted diazoethane = 0.25. The mole ratio between chlorooctane and diazooctane in the deamination reaction was *ca.* 0.7. In the present deamination reaction, there did not seem to be any reaction between the diazooctane and NOCl as judged from the absence of the 1-chloro-1-nitroso compound. A major part of the chlorooctane formed has therefore probably been produced by a break-down of the diazonium compound, which indicates the diazonium chloride (Va) to be an important intermediate.

White and Aufdermarsch [14] showed diazoalkanes to be intermediates in the decomposition of N-nitrosoamides of primary carbinamines.

Müller and Rundel [15] obtained diazomethane in the reaction between methylamine and NOCl. These points, together with the present work, show the diazoalkanes to be important intermediates in the aprotic deamination of primary carbinamines.

The presence of diazoalkanes points at the possibility of carbenes as intermediates in aprotic deaminations. Jurewicz and Friedman [16] have shown that carbenes are not intermediates in protic and aprotic deaminations when alkane nitrites and acids are used as deaminating agents. However, due to the presence of acid, any diazo compounds formed are removed as cationic species, before they can form any carbenes. Under more strictly aprotic conditions, carbenes can not be excluded as intermediates.

The present work also indicates a simple method for the production of diazoalkanes for purposes where interference is not caused by the presence of unreacted amine.

EXPERIMENTAL

The IR spectra were recorded on a Perkin-Elmer infrared spectrophotometer, Model 257. The electronic spectra were recorded on a Beckman DK-2 spectrophotometer. NMR spectra were recorded on a Varian A 60 spectrometer using tetramethylsilane as internal standard. Gas chromatograms were recorded on a Perkin-Elmer F 11 gas chromatograph, equipped with a hydrogen flame ionisation detector.

NOCl [17] was refluxed in a stream of dry N_2 and distilled twice from P_2O_5 filled tubes before use. Melting points are uncorrected. Ether used in the reactions was distilled from lithium aluminium hydride.

1-Chloro-1-nitrosooctane (I). Octaldoxime (4 g) was dissolved in hydrochloric acid (25 %, 100 ml) and the solution cooled to $-3°$. Dry chlorine gas was passed through the solution for 5 min and the white-green precipitate formed was filtered off, washed three times with ice water, three times with ethanol (cooled to $-25°$), and dried at $20°/0.05$ mm Hg for 30 min. Yield 3.9 g (79 %). The crystals had m.p. $35.5-37.6°$, Cl content: $19.04-19.15$ %, (calc. 20.0 %) and visible light spectrum with λ_{max} 645 nm ($\varepsilon \sim 6$) and 321 nm ($\varepsilon \sim 1600$). The extinction coefficients are only approximate, due to the rapid rearrangement of the chloro-nitrosooctane to the octanoyl chloride oxime, and to the equilibrium: nitroso monomer $\rightleftharpoons$ nitroso dimer.

IR spectrum (5 %, $CHCl_3$) had bands at 2930, 2860, 1460, 1390, and 1190 cm^{-1}.

The IR spectrum was rerun every 10 min and after 1 h it had changed into the spectrum of octanoyl chloride oxime (see below).

Octanoyl chloride oxime. 1-Chloro-1-nitrosooctane (0.39 g) was dissolved in ether (100 ml) and kept at $20°$ for 15 h. The solution was then colourless and on evaporation gave 0.38 g of octanoyl chloride oxime, b.p. $70°/0.05$ mm Hg. The IR spectrum (liquid film) had bands at 3250, 2930, 2860, 1640, 1470, 1380, 1140, 1090, 965, and 720 cm.$^{-1}$.

Reaction between octanoyl chloride oxime and aqueous H_2SO_4. Octanoyl chloride oxime (139 mg) was refluxed with aqueous H_2SO_4 (10 %, 27 ml) for 15 min. The reaction mixture was extracted with ether, the ether phase washed with $NaHCO_3$ solution, dried over Na_2SO_4, and concentrated. The yield of partly crystalline substance was 105 mg, which after three crystallisations from ether gave 15 mg of a substance with IR spectrum and m.p. identical to those of *O,N*-dioctanoylhydroxylamine (see below). Mixed m.p. of the crystals with the authentic material showed no depression.

O,N-Dioctanoylhydroxylamine. This compound was prepared by the same method as that used for *O,N*-dibenzoylhydroxylamine [6] by reacting octanoyl chloride and the potassium salt of octanohydroxamic acid. The product had m.p. $73.2-73.8$ after four crystallisations from petroleum ether. IR spectra in CCl_4 at various concentrations had the following absorption maxima: 10 % solution: 3180, 2930, 2860, 1795, 1670, 1500, 1470, 1380, 1130, and 1090 cm^{-1}; 5 % solution: 3200 (broad), 2930, 2860, 1792, 1710 (shoulder), 1670, 1500 (shoulder), 1470, 1380, 1130, and 1090 cm^{-1}; 0.3 % solution: 3360, 2930, 2860, 1787, 1730, 1470, 1380, 1140, and 1090 cm^{-1}.

The NMR spectrum (5 % CCl_4) had signals at 0.06 τ (varies with concentration); multiplet (5 bands visible) with center at 7.75 τ, 8.70 τ, and a triplet with center at 9.22 τ. The NMR spectrum of "compound B" [1] was reported to have a quartet at 6.60 τ and band at 8.86 τ in addition to those bands. These signals were due to ethyl ether present in the sample caused by inadequate drying of the crystals (crystallised from ethyl ether).

1-Chlorooctane and NOCl. To 1-chlorooctane (1.00 g) in ether (200 ml) cooled to $-70°$ the equivalent amount of NOCl was passed with dry N_2 gas. After 0.5 h at $-70°$ the cooling bath was removed and the solution evacuated (0.1 mm Hg) for 15 min. IR spectrum of the product (0.98 g) after removal of the ether was identical to that of 1-chlorooctane.

Octaldoxime and NOCl. Octaldoxime (1 g, 7.0 mmoles) in ether (100 ml) was cooled to $-70°$ in the apparatus described earlier.[1] The oxime partly crystallised. NOCl (0.6 ml, 12 mmoles) was collected in ether (100 ml) at $-70°$ and the solution added to the octaldoxime solution over a period of 10 sec. No gas evolution was noticed. The solution was initially brown, but turned yellow and the precipitate disappeared after 15 min. After 0.5 h at $-70°$ the cooling bath was removed and the solution evacuated (0.1 mm) for 10 min. A brown ether solution (6 ml) was collected in the cold trap. After 0.5 h at $-25°$ UV and visible light spectra were run on the solution. λ_{max}: 645 nm [$\log(I_0/I)$

$=0.62$], 600 nm [shoulder, $\log(I_0/I)=0.32$], and 323 nm [$\log(I_0/I)=7.05$]. After 30 min at 0° the absorbance at 645 nm had increased to $\log(I_0/I)=0.75$. After 48 h at 20° the absorbance at 645 nm had $\log(I_0/I)=0.46$. After 2 days at $-25°$ a 50 ml sample of the solution was placed at 20° for 2 h and the ether removed. The sample (0.45 g) was then blue-green. IR spectrum of the sample had bands at 2940, 2860, 1720, 1670, 1570, 1470, 1390, 1300, and 1215 cm^{-1}. The bands at 2940, 1670, and 1390 cm^{-1} were the strongest in the spectrum. When the sample was kept at 20° overnight and the IR spectrum rerun, there were bands at: 3300, 2940, 2860, 1720, 1670, 1640, 1570, 1470, 1380, 1140, 1090, 1040, and 965 cm^{-1}. Water and nitrogen oxides had evolved from the sample during the night.

Diazoethane and NOCl. Diazoethane (from 1 g of *N*-nitroso-*N*-ethyl urea) in ether (44 ml) was dried over KOH pellets and cooled to $-70°$. NOCl (0.2 ml, 4 mmoles) in dry ether (50 ml) cooled to $-70°$ was dropped into the diazoethane solution. After 30 min at $-70°$ the cooling bath was removed and the solution evacuated (0.1 mm) for 5 min. A yellow ether solution (3 ml) was collected in the cold trap. Electronic spectra of the solution were run when it reached room temperature. λ_{max}: 641 nm, [$\log(I_0/I)=0.15$), shoulder at 600 nm [$\log(I_0/I)=0.08$]. 1-Chloro-1-nitrosoethane made by the method of Wieland [11] had λ_{max} 641 nm [$\log)I_0/I)=0.21$], shoulder at 600 nm [$\log(I_0/I)=0.12$]. By using the absorption coefficient of 1-chloro-1-nitrosooctane at 645 nm, the concentration of 1-chloro-1-nitrosoethane in the reaction mixture was 2.5×10^{-2} mmoles/ml, corresponding to 2.4 mmoles in the whole solution. VPC of the reaction mixture showed it to contain $0.1-0.3$ % ethyl chloride, corresponding to 0.13 g (2 mmoles) ± 50 % ethyl chloride.

Octylamine and NOCl. Octylamine (2.01 g, 15.4 mmoles) was dissolved in dry ether (100 ml) and cooled to $-70°$. The solution became cloudy. NOCl (0.2 ml, 4 mmoles) in dry ether (40 ml) cooled to $-70°$ was dropped into the amine solution over a period of 5 min. The brown colour of the NOCl disappeared immediately, and when addition of the NOCl solution was complete, the cloudy solution was colourless. A sample (25 ml) of the solution was withdrawn and raised to room temperature. The IR spectrum of this ether solution had a sharp band at 2050 cm^{-1} [$\log(I_0/I)=0.32$]. The IR spectrum of an ether solution of diazoethane (4.8×10^{-2} mmoles/ml) had an identical sharp peak at 2050 cm^{-1} [$\log(I_0/I)=1.32$]. From this the concentration of diazooctane in the solution was calculated to be 1.2×10^{-2} mmoles/ml, total amount 1.7 mmoles.

The visible spectrum of the solution had $\lambda_{max}=464$ nm [$\log(I_0/I)=0.06$]. A visible spectrum of diazoethane (4.8×10^{-2} mmoles/ml) had λ_{max} 466 nm [$\log(I_0/I)=0.33$]. From this, the concentration of diazooctane in the solution was 0.9×10^{-2} mmoles/ml, total amount 1.3 mmoles. To the rest of the reaction mixture (115 ml) kept at $-70°$ benzoic acid (1 g) was added and the solution kept at $-25°$ overnight. The solution was then shaken once with hydrochloric acid (6 %), twice with NaHCO$_3$ solution, dried over Na$_2$SO$_4$ and the ether removed. A yield of 0.45 g was recorded, corresponding to 0.55 g for the total reaction mixture. The IR spectrum of this product was almost identical to that of octylbenzoate. VPC of the mixture (2,4-dinitrotoluene as internal standard) showed it to contain: octyl benzoate (67 %, 0.37 g, 1.6 mmoles, corresponding to 40 % of added NOCl) and 1-chlorooctane (31 %, 0.17 g, 1.1 mmoles, corresponding to 27 % of added NOCl).

Diazoethane and octylammonium chloride. Diazoethane (3.4 mmoles) in ether (70 ml) was dried over KOH for 3 h at $-25°$, cooled to $-70°$ and added dropwise to a slurry of octylammonium chloride (0.430 g, 2.67 mmoles, crystallised twice from ethanol) and octylamine (2.07 g) in ether (70 ml) cooled to $-70°$. The mixture was stirred for 40 min and benzoic acid (1 g, 8 mmoles) added. After 5 min at $-70°$, the reaction mixture was kept at $-25°$ overnight. VPC showed it to contain ethyl benzoate (2,4-dinitrotoluene as internal standard, 0.45 %, 0.45 g, 3 mmoles, 88 % of added diazoethane) and ethyl chloride (run without internal standard, less than 0.05 %, 50 mg, 0.8 mmole, 25 % of added diazoethane).

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