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Short Communications

A New One Step Synthesis of Diazooctane from Octylamine

BJØRN AUSTIGARD and JAN M. BAKKE

Chemistry Department, College of Arts and Science, University of Trondheim, N-7000 Trondheim, Norway

Precursors for higher homologs of diazomethane are not readily available. Their preparation is therefore time-consuming, and they are not much used in organic synthesis. Diazooctane was reported as an intermediate in the deamination of octylamine with nitrosyl chloride at −70 °C.[1,2] However, an excess of primary amine was necessary if reduction of the yield due to side-reactions between nitrosyl chloride and the diazoalkane was to be avoided. This constitutes a practical disadvantage in the case of less readily available amines. The excess primary amine presumably acts as a base in the diazoalkane formation and the use of a readily available alternative base might allow reduction of the excess of primary amine.

Tertiary amines seemed a possible choice as "foreign base". Reactions between nitrosyl chloride and tertiary amines have been reported,[3] but at low temperatures complex formation predominates.[4,5] Trialkylamines[4] and pyridine[5] were possible candidates, while *N*-alkylated anilines might be subject to substitution by nitrosyl chloride.[3] We now wish to report the influence of added tertiary amines on the reaction between a primary amine and nitrosyl chloride. Octylamine was chosen as a model substance for the deamination.

The reactions were run at −70 °C by adding gaseous nitrosyl chloride to the mixture of octylamine and tertiary amine in the chosen solvent. Formation of diazooctane was established qualitatively by IR spectroscopy. A quantitative estimate was provided by determination of the octyl acetate formed on addition of acetic acid to the reaction mixture.

Three tertiary amines were tried: triethylamine, pyridine and triethylenediamine (1,4-diazabicyclo[2,2,2]octane). Deaminations with triethylamine were most thoroughly studied. The yield of diazooctane was optimized by variations in the excess of triethylamine and nitrosyl chloride and in the reactant concentrations. The optimum condition, an 80 mM solution of octylamine deaminated with nitrosyl chloride (160 mM) in the presence of triethylamine (400 mM) resulted in a 43 % yield of diazooctane (determined as octyl acetate).

Diazooctane proved to be less stable in the preparations with triethylamine than in those with excess octylamine, and to obtain a maximum yield acetic acid should be added within 10 min of the addition of nitrosyl chloride.

The two other tertiary amines tried as bases gave lower yields of octyl acetate than triethylamine: triethylenediamine 25 % and pyridine 15 %. The low yield with triethylenediamine can be explained by its low solubility in ether at −70 °C, and that with pyridine by its lower base strength.

Four different solvents were tried: ethyl ether, tetrahydrofuran (THF), methylene chloride, and triethylamine itself. The etheral solvents gave the best yields[2] (ethyl ether 43 %, THF 35 %, methylene chloride 8 %, and triethylamine 3 %).

In one experiment triethylamine in ethyl ether was allowed to react with nitrosyl chloride before addition of octylamine, but this resulted in a lower yield of diazooctane (30 %) than obtained by the normal procedure.

In addition to octyl acetate, several other compounds were detected from the deamination. The identified substances are given in Table 1.

The presence in the product mixture of octyl chloride and octene has been discussed earlier.[1] Ethyl octyl ether has also been reported,[1] and was now unambiguously identified by MS. Octanol may have been formed in a reaction between the intermediate diazonium ion and hydroxide ions or water. The latter possibility was confirmed by addition of excess water to the deamination product at −70 °C, which increased the yield of octanol from 3 to 13 %. While the identification of pentylcyclopropane was not conclusive due to the low yield, its presence was not unexpected in view of the work of Friedman *et al.*[6]

The ways of formation of octanal and octanal oxime are obscure at present. Octanenitrile was not present as such in the reaction mixture, but formed from precursors in the gas chromatograph. Although octanal oxime gives octane nitrile on gas chromatography, the oxime was not present in sufficient concentration to explain the yield of octane nitrile. It should be noted that octanal, octanal oxime and octane nitrile were only formed when the deaminations were run in the presence of triethylamine.

Table 1. Substances identified from deaminations of octylamine in ethyl ether with triethylamine present (octylamine – triethylamine – nitrosyl chloride 1:5:2).

Substance	Yields (in % of octylamine) After addition of acetic acid	Without acetic acid
Octyl chloride	8[a]	6[a]
Octene	5[b]	1,5[b]
Ethyl octyl ether	< 2[b]	~ 2[b]
Octanol	5 – 6[b]	3[b]
Pentylcyclopropane	< 0.3[d]	trace
Octanal	< 2[b]	~ 2[a](17 – 19[c])
Octanal oxime		< 1[a]
Octane nitrile	~ 2[c]	12 – 13[c]
Octyl nitrate		4[a]
Nitrooctane	2 – 3[a]	2 – 3[a]

[a] Isolated; IR, NMR, GC/MS. [b] Identified and determined by GC/MS. [c] Identified by GC/MS only. Formed in GC. [d] Identified by GC only.

When a fourfold excess of octylamine in ethyl ether was used,[1] only traces of octanal or octane nitrile were detected by gas chromatographic analysis. This suggests that the deaminations in the presence of triethylamine proceed partly by other pathways than those it its absence. Octyl nitrate and nitrooctane may have been formed from traces of nitrogen tetroxide contaminating the nitrosyl chloride. Exclusion of air was without effect on the yield of these two substances.

Two other substances, with molecular formulae $C_9H_{15}NO_2$ and $C_{16}H_{33}NO$, were also formed. While their structures have not yet been elucidated, the former was neither nitrooctene nor nitrosoxy octene, and the latter was different from α-heptyl-*N*-octylnitrone, 2-octyl-3-heptyl-oxaziridine[11] and octanal oxime *O*-octyl ether. Nitrones have been reported to form from diazoalkanes and nitrosoalkanes;[7] both types of substances have been found in aprotic deaminations.[1,2] α-Heptyl-*N*-octylnitrone was synthesised from octanal oxime and octyl bromide.[8] Nitrones have been reported both as dimers[9] and monomers.[7,9,10] Our product was found to be monomeric from spectroscopic evidence.

The deamination of octylamine in the presence of triethylamine thus produces several by-products whose way of formation and significance in the reaction are obscure at present.

Nevertheless, by running the deamination under these conditions, it is possible to transform some aliphatic amines in one step and in acceptable yields to the corresponding diazoalkanes.

Experimental. The general instrumentation used has been described earlier.[12] GC separations were performed on a 3 m × 3 mm, 28 % Pennwalt 223, 4 % KOH, column. Quantitative GC determinations were carried out using 2-heptanone as internal standard. Most of the deaminations were run in a flask equipped with an Ascarite tube and a rubber septum. Nitrosyl chloride was added as gas by a syringe filled directly from a commercial gas flask (Matheson). The described products were not formed from reactions of nitrosyl chloride with 1-octene or triethylamine.

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