Nitrolysis of Tertiary Alkylamines

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Several secondary nitramines can be used for explosives and propellants as high energetic materials.[1] Secondary nitramines can be prepared by the nitration of dialkylamine, or by the nitrolysis of dialkylamide, dialkylcarbamate, or dialkylsulfonamide.[2,3] Converting one of alkyl groups in tertiary alkylamines to nitro group is not a general synthetic strategy in the synthesis of secondary nitramines.

In the synthesis of cyclic secondary nitramines (*N*-nitroazacycloalkanes), a *N*-blocking group is often required to control the ring formation, and subsequently the *N*-blocking group is removed by nitrolysis to give the nitramines.[4,5]

Acyl blocking group may be replaced by NO_2^+ on the basis of the previously suggested S_E2 mechanism, which the reaction is sensitive to steric hindrance and electronic factor (eq. 1).[2b]

$$R_2N-\overset{\overset{O}{\|}}{C}-X \xrightarrow{NO_2^+} R_2N-NO_2 + X-C=O \qquad (1)$$

Among alkyl blocking groups, isopropyl and *t*-butyl groups have been used for this purpose with varying success.[4,6] Although *t*-butyl blocking group can also be replaced by NO_2^+ under the similar condition to acyl blocking group, the reaction mechanism might be different, nitronium ion attacks the tertiary amine to give the quarternary ammonium salt followed by the release of carbocation to afford nitramines (eq. 2).[4]

$$R_2N-Bu^t \xrightarrow{NO_2^+} R_2N\overset{NO_2}{\underset{Bu^t}{<}} \longrightarrow R_2N-NO_2 + t\text{-}Bu^+ \qquad (2)$$

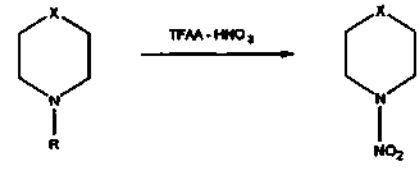
Nitrating power of the nitrating agents and basicities of the amine was known to be important. Generally TFAA-HNO_3 gave better yield than HNO_3, but the role of the bascities was not conclusive.[4]

In this work, we examined the nitrolysis of *N*-alkyl piperidine and *N*-alkyl morpholine.The nitrolysis proceeded with TFAA-HNO_3, but it did not with HNO_3. As shown in Table 1, *t*-butyl group can be replaced by nitro group better than other alkyl groups, even though the reaction preceeded in much lower yield.

Recently hexanitrohexaazaisowurtzitane was synthesized presumably from hexabenzylhexaazaisowurtzitane.[5,7] Thus the nitrolysis of piperidine and morpholine with benzyl blocking groups was studied. The reaction varies with substituents; the methoxy proceeds in moderate yield, and the chlorine, or hygrogen does in very poor yield if at all, as shown in Table 2. Because the electron donating group stabilizes the benzyl cation,the methoxy substituent increases the nitrolysis. The major reaction pathway was the nitration on the aromatic ring.

In the nitrolysis of 1-*t*-butyl-3,3-dinitroazacyclobutane, 1,3,3-trinitroazacyclobutane (TNAZ) was obtain in good yield even at 0 °C using TFAA-HNO_3.[3,8] With HNO_3 or HNO_3-H_2SO_4, the reaction proceeded in the same yield, but it did at much higher temperature. On the other hand, TNAZ was

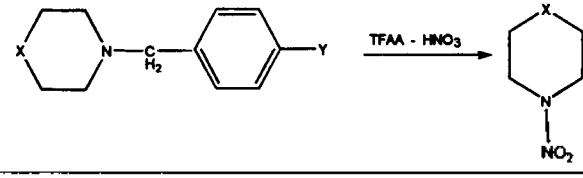
Table 1. Nitrolysis of *N*-alkylpiperidine and *N*-alkylmorpholine with TFAA-HNO_3



X	R	Yield (%)[a]
CH_2	Me	3.1
	i-Pr	4.1
	t-Bu	10.3
O	Me	3.7
	i-Pr	4.0

[a] Yields were determined by G.C.

Table 2. Nitrolysis of benzylamines



X	Y	Yield (%)[b]
CH_2	Cl	<1
	H	<1
	OMe	37
O	Cl	<1
	H	<1
	OMe	25

[b] Yields were determined by G.C.

Table 3. Nitrolysis of 1-alkyl-3,3-dinitroazacyclobutane

R	Yield (%)[c]
t-Bu	90
i-Pr	7

[c] Yields were determined by

given in much lower yield when isopropyl group was used instead of *t*-butyl group (Table 3).

In conclusion, three factors are important in the nitrolysis of *N*-alkly protected amine; NO_2^+ concentration (nitrating power), basicity of the amine, and the carbocation stability of the leaving alkyl group. Among them,the influence of basicity is not quite understood. In synthetic point of view, the nitrolysis can be applied to the cyclic compound having other nitro groups in the cyclic skeleton, as in the preparation of TNAZ. Otherwise the reaction proceeds in much lower yield.

Experimental

Caution. Some of the compounds reported herein should be handled with appropriate care. Most of the compounds were previous reported.

General procedure for the nitrolysis. To 20.2 mL (0.143 mol) of TFAA was added 6.4 mL (0.143 mol) of 100% HNO_3, cooling being required to maintain the temperature at −5 °C to 0 °C. This solution was cooled to −20 °C and amine (0.00204 mol) was added cautiously. The resulting solution was stirred for 1-2 hr, and poured into ice-water. The aqueous mixture was extracted with ether several times.The ether extracts were dried and concentrated in vacuo to give a nitramine.[9]

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9. N-Nitropiperidine[2a]; ^{1}H NMR ($CDCl_3$) 1.54-1.81 (m, 6H), 3.80 (m, 4H). N-Nitromorpholine[2a]; ^{1}H NMR ($CDCl_3$) 3.85 (s). ^{13}C NMR ($CDCl_3$) 48.6, 65.1. TNAZ[3]; mp 101 °C. ^{1}H NMR ($CDCl_3$) 5.2 (s).

Electrochemical Behavior of Safranine O in a Thick Lipid Film

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During last two decades, much attention has been paid to the microbial fuel cell[1-3] as a means of direct energy conversion. Electricity is produced by confining living microorganisms in an anodic compartment of the cell and feeding them with substrates. Electrons yielded from the catabolic action of microorganisms are transferred through the cell wall to the anode, and thus electrical energy can be drawn with a suitable cathode. Microbial fuel cells are promising as future energy sources because they are very environment friendly and the operation with a high efficiency is possible.[4,5] For example, electricity can be obtained during the waste treatment. Other than this, many advantages[6] over conventional methods have been pointed out. Among efforts that optimize the cell operational conditions, it has been found that a remarkable enhancement[7,8] in the efficiency can be achieved by adding redox mediators in an anodic part of the cell. The role of the mediator is believed to help electrons produced from the oxidation of substrates to be transferred to the anode, with itself undergoing a redox reaction. Although many have attempted to find suitable mediators and tested cell performance with them, the basic research on the interaction between mediators and lipids which consist of cell membranes is scarce. Only Bennetto *et al.*[9,10] measured rates of reduction of phenothiazine derivatives by *E. coli* and NADH as far as we know.

In this paper we report our preliminary results on the electrochemical behavior of safranine O(SFO) in a thick film of phosphatidylethanolamine (PE) as a model system for the study of mediator-lipid interaction. To our knowledge, there have been no reports on this subject although Petrova *et al.*[11] studied redox properties of phenazine-derivatives such as phenazine ethosulfate, phenosafranine and safranine T. SFO is a well known staining agent[12] in a Gram test and its redox potential is negative enough so that an appreciable cell potential could be achieved in combination with a suitable cathode. Moreover, the strong absorption of light in a visible region makes it possible to follow microbial activities spectrophotometrically. PE is known as a main con-