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THE CHEMISTRY OF 3-TRIFLUOROMETHYL-PERFLUORO-AZA-2,-BUTENE AND THE SYNTHESIS OF A NEW OXAZIRIDINE: 3,3-BISTRIFLUOROMETHYL,-2-TRIFLUOROMETHYLOXAZIRIDINE

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SUMMARY

Some reactions of $(CF_3)_2C{=}NCF_3$ **1** (3-trifluoromethyl-perfluoro-aza-2-butene) are reported including the isomerisation to $(CF_3)_2CFN{=}CF_2$ **3** (3-trifluoromethyl-perfluoro-2-aza-1-butene) and the formation of $(CF_3)_2CFN(Br)CF_3$ **5** (N-perfluoroisopropyl-N-trifluoromethyl-N-bromoamine). The synthesis and characterization of $(CF_3)_2C(O)NCF_3$ **2** (3,3-bistrifluoromethyl-2-trifluoromethyl-oxaziridine) from **1** is also reported along with its thermal rearrangement to $CF_3C(O)N(CF_3)_2$ **6** (bistrifluoromethyl-trifluoroacetamide) and some selective organic oxidations with **2**.

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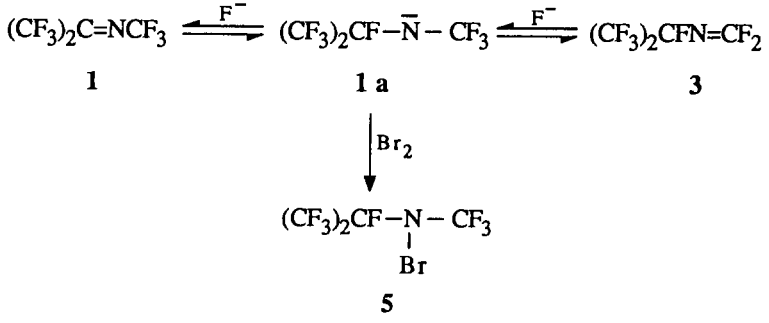
INTRODUCTION

Perfluoroimines are an important class of perfluorocarbon nitrogen compounds and the synthesis and chemical properties have been studied for about thirty years. They are useful intermediates both in organic and organofluorine chemistry because of the high reactivity of the imino functional group. The chemistry of the perfluoroimines has been recently reviewed [1] where synthetic routes to perfluoroimines and their reactions are discussed.

The most studied compounds in this class have been perfluoro-2-azapropene ($CF_2=NCF_3$) and the heavier related imines such as its dimer $(CF_3)_2NCF=NCF_3$, mainly because of the lack of availability of other imines. As a result, most of these imines bear at least a single fluorine atom at the carbon-nitrogen double bond. The limited information on fully substituted perfluorinated imines along with the synthesis of a new oxaziridine provided the purpose for this current study of imine chemistry.

RESULTS AND DISCUSSION

In some respects, $(CF_3)_2C=NCF_3$ **1** was found to behave like other perfluoroimines of general structure $R_fCF=N\text{-}R_f$: for instance (Scheme I) the formation of the corresponding anion $(CF_3)_2CF\bar{N}CF_3$ in the presence of active metal fluorides is highly probable, though not observed directly. Thus the imidic carbon is quite reactive toward nucleophiles, however the anion (**1a**) generated by fluoride attack did not undergo dimerization as in the case of perfluoro-2-azapropene [2,3]. Instead the unusual isomerization of **1** to $(CF_3)_2CF\text{-}N=CF_2$ **3** [4] was observed.



Scheme 1

This isomerization implies an elimination of fluoride from the trifluoromethyl group bonded to nitrogen, whereas for terminal perfluoroimines $R_fCF_2N=CF_2$, the isomerization to an internal position is normally preferred [5]. Furthermore the fact that **3** was always observed in the same 1:2 ratio with **1** under different reaction conditions, suggests that this process may be an equilibrium. Anion **1a** could be trapped, as it is known for other perfluoroimines [6,7,8], by reaction with elemental bromine (Scheme I), giving a new N-bromo derivative, N-perfluoroisopropyl-N-trifluoromethyl-N-bromoamine **5**. The corresponding N-chloro and N-fluoro derivatives are known, although prepared by a different reaction [9]. **5** was readily characterized by its ^{19}F NMR spectrum (Fig. 1).

Similar to other analogues, **1** showed no tendency to undergo radical addition processes; in fact it did not react at +80°C in a passivated stainless steel vessel with fluoroxytrifluoromethane (CF_3OF) which normally adds to olefins in a radical fashion (Scheme II).

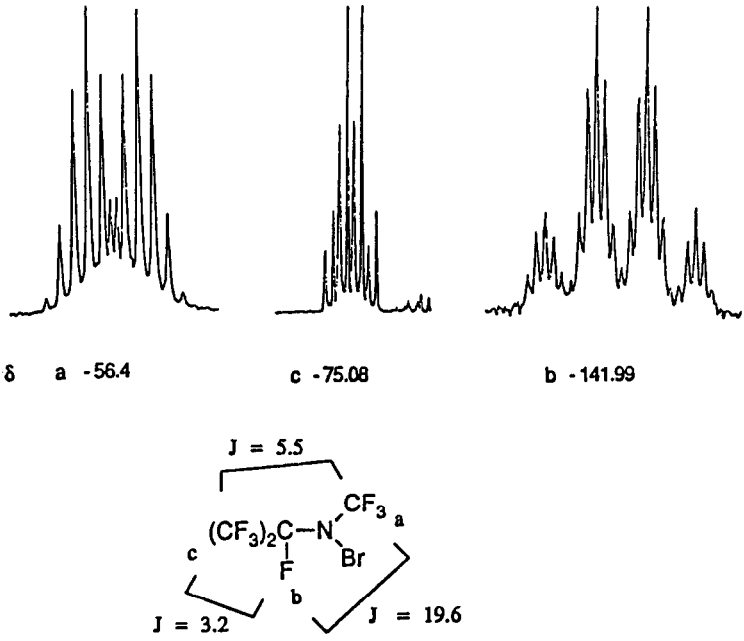


Fig. 1. ^{19}F NMR of N-bromoperfluoro(isopropylmethyl)amine.

$$(CF_3)_2C{=}NCF_3 + CF_3OF \xrightarrow[+\ 80°C,\ 48\ hrs.]{\text{passivated S. S.}} (CF_3)_2CFN{=}CF_2$$

1 3 (28%)

Scheme II.

The hydrolysis of 1 has been reported to be slow [9], whereas for perfluoroazapropene it is so fast that no oxidation reactions can be performed in aqueous media. As was first observed by Navarrini and DesMarteau, imines which have some hydrolytic stability can be

oxidized by aqueous H_2O_2 to the corresponding oxaziridine. They were able to prepare $(CF_3)_2NCF-NCF_3$ (O) by oxidation of $(CF_3)_2NCF=NCF_3$ with H_2O_2 in CH_3CN in the presence of $NaHCO_3$ [10]. In the case of **1** we found that oxidation could also be performed in moderate yield with 50% H_2O_2, but the hydrolysis of the product **2** was a serious problem in this reaction (Scheme **III**).

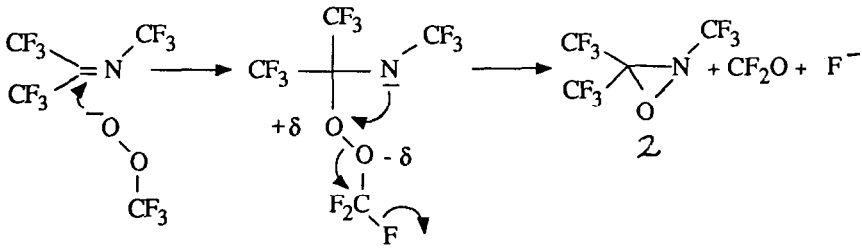
It is known that the reactivity of perfluoroimines toward oxygen nucleophiles (ROH and ROOH) is normally good, leading to the isolation of the corresponding imino-ethers such as $CF_3N=CFOR$ and $CF_3N=C(OR)_2$ [1] and addition products like $CF_3OOCF_2N(H)CF_3$ [11,12]. However, we found that **1** did not react with tert-butyl-hydroperoxide nor with trifluoromethyl-hydroperoxide [13]. Therefore a synthetic route to the oxaziridine **2** through an intermediate addition product as in the case of the perfluoroazapropene was impossible. We achieved however a far better yield (80%) of **2** by reacting **1** and CF_3OOH over active potassium fluoride [14] (Scheme **III**).

$$\underset{\mathbf{1}}{(CF_3)_2C=NCF_3} + H_2O_2 \;\; 50\% \xrightarrow[-10°C,\ 15\ min.]{CH_3CN/NaHCO_3} \underset{\mathbf{2}\ (22\%)}{(CF_3)_2C(O)-NCF_3} + \text{hydrolysis products}$$

$$\mathbf{1} + CF_3OOH \xrightarrow[0°C]{\text{active KF}} \underset{(80\%)}{\mathbf{2}} + (CF_3OO)_2CO + CF_3OOC(O)F + CF_2O$$

Scheme III.

This result along with other available data [15] and the fact that CF_3OOH is quite acidic (the proton is at δ 9.14 ppm in ^1H-NMR) and the formation of the salt $K^+ OOCF_3$ has been postulated in the past [16], indicate (Scheme **IV**) that hydroperoxides in their anionic conjugated form ROO^- can be fairly good oxidants for the preparation of perfluorinated oxaziridines from the parent imines.



Scheme IV.

The structure of oxaziridine **2** was confirmed by its mass spectrum, ^{19}F NMR (Fig. 2) and other properties given in the experimental section. Compound **2** also behaved differently compared to the related oxaziridines obtained from perfluoroazapropene and perhalo-1-aza-2-butenes [17,18]; in fact it did not give a cycloadduct with tetrafluoroethylene up to +160°C as was readily observed for these oxaziridines. However **2** initiated the polymerization of C_2F_4 already at +85°C, and much faster at +160°C, with $CF_3C(O)N(CF_3)_2$ **6** (78% yield) found to be the only byproduct. We found that **6** is also formed by isomerization of **2** alone in the gas phase and at +160°C conversion of **2** to **6** is quantitative in 2 days. A radical process (Scheme **V**) is involved in this isomerization, but the possibility of a

more highly concerted mechanism or an acid catalysis cannot be ruled out.

In contrast to the gas phase decomposition of **2**, a solution of **2** in 1,1,2,2-tetrachloroethane at +150°C gave only a slow decomposition (26% in 5 hours and 51% in 19 hours) releasing its oxygen atom to give **1**.

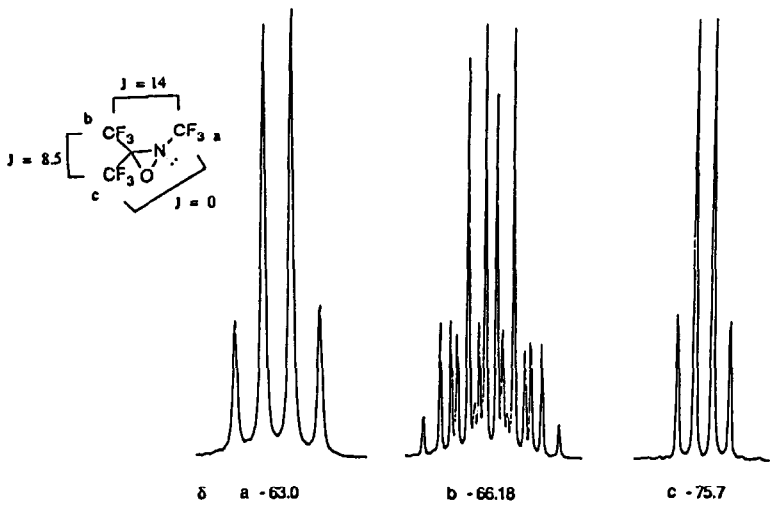
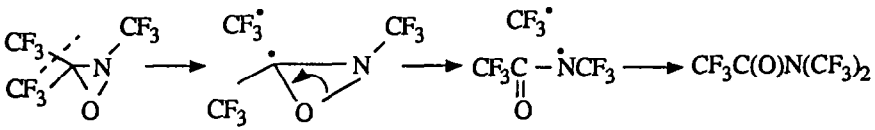
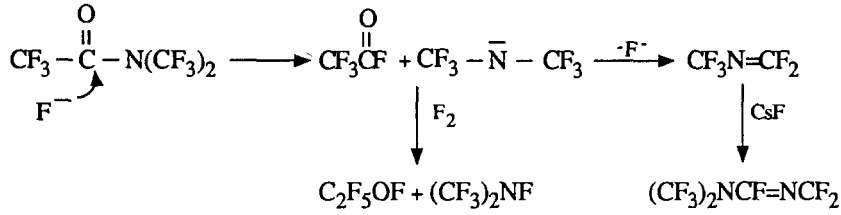


Fig. 2. ^{19}F NMR of 3,3-bistrifluoromethyl-2-trifluoromethyloxaziridine.



Scheme V.

Since little information was previously available about this amide [19,20,21], **6** was fully characterized and its physical properties along with some reactions which further prove its structure (Scheme **VI**), are given in the experimental section.

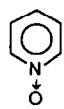


Scheme VI.

Besides being a polymerization initiator, **2** showed interesting properties as an oxidizing reagent for organic molecules such as olefins, sulfides and pyridines, with a remarkable reactivity and selectivity at low temperatures. In this respect **2** behaves like other known three member ring systems such as dioxiranes [22-26], peroxocomplexes of transition metals [27,28], N-sulfonyl-oxaziridines [29,30,18] and $CF_3N(O)CF_2$ but its selectivity is truly remarkable. As shown in Table 1, **2** reacts rapidly with propylene, cis-2-butene and dimethyl-sulfide to give the corresponding epoxides and sulfoxide at low temperatures with very good yields and conversions. Indeed the absence of higher oxidized or cleavage products in these reactions indicates that the oxygen transfer takes place in a highly concerted fashion. Compound **2** also gave pyridine-N-oxide but in this case the reaction mechanism must be more complicated because, while **2**

reacted quantitatively, 1 could not be detected in the reaction mixture, whereas for the other oxidations this was the only coproduct formed.

TABLE 1

Substrate	Product	% yield	% conversion of 2	temp. °C	time
		91	56	20	3 hrs
		92	96	-10	15 min
Me_2S	Me_2SO	75	100	-30	20 min
		24	100	-10	15 min

EXPERIMENTAL

All the compounds were handled in a conventional Pyrex and 316-stainless steel vacuum line and purified by trap-to-trap fractionation, or preparative GLC when needed, on a Halocarbon K-352/Chromosorb PAW column. ^{19}F and ^{1}H-NMR spectra were recorded on a Bruker AC 200E NMR spectrometer. Mass spectra were run on a HP 5985B GC/MS system. Infrared spectra were recorded either on a Perkin-Elmer model 1650 FT-IR or a model

1430 instrument with a 7500 data station. GLC analyses were done on a Perkin-Elmer 8500 gas chromatograph on the same type of column used for preparative GLC.

All the ^{19}F NMR data reported are referred to $CFCl_3$, assigning negative values to signals resonating at higher field than $CFCl_3$. The imine **1** was prepared, according to R. L. Kirchmeier and J. M. Shreeve [9], by photolysis of a gaseous mixture of $(CF_3)_2CO$ and CF_3CN in the molar ratio 50/28 for 20 hours. The product was separated and collected at -120°C (passes -90°C) by trap-to-trap fractionation from the photolysis byproducts $(CF_3)_3CN{=}NCF_3$, $(CF_3)_3CN(CF_3)_2$ and unreacted CF_3CN.

CF_3OOH was prepared according to DesMarteau and co-workers [31-34]. All other chemicals were purchased from commercial sources.

3,3-bistrifluoromethyl-2,trifluoromethyl-oxaziridine 2. 4.0 ml of acetonitrile and 1.2 ml of H_2O_2 (50%) were placed in a 100 ml Pyrex flask fitted with an Ace-thread connection and a Teflon-glass valve containing 1.8 g of $NaHCO_3$ and 1.8 g of $MgSO_4$. Then 8 mmol of **1** was added to the flask by vacuum transfer and the reactor was held at -10°C with stirring for 20 minutes.

The volatile materials were fractionated in a vacuum line and in the trap at -125°C (passes -75°C) 1.72 mmol of pure **2** was collected; 4.9 mmol of CO_2 from hydrolysis was found in the trap at -196°C.

The reaction of 6 mmol of **1** and 12 mmol of CF_3OOH in a glass tube fitted with a glass-Teflon valve and containing 22 mmol of active KF was a much more convenient route to **2**. The reaction

mixture was kept for 4 hours at 0°C with occasional shaking, and after pumping off the volatile materials and a careful distillation, **2** was collected in 80% yield. Byproducts were found to be ca. 3.4 mmol of $(CF_3OO)_2CO$, 1.6 mmol of $CF_3OOC(O)F$ which could be eventually recycled to CF_3OOH, and 2 mmol of CF_2O. The bp of **2** was determined with the use of an isoteniscope. Vapor pressure (torr, °C) 3.8, -75; 24, -47.4; 72.5, -25.4; 118, -16.80; 245, -3; 377, 6.7; 546, 16.5; 749, 249; bp=24.98°C, ΔHvap = 6.72 Kcal/mol, ΔSvap = 22.5 e.u.; IR 1421w, 1326s, 1280s, 1250vs, 1234m, 1194s, 1023m, 979m, 755, 729, 701, 663, 540 cm^{-1}; MS (CI, CH_4) m/z, 250 (MH^+, 100%), 234 (MH^+-O, 13.6), 230 ($M-F^+$, 19.5), (EI) 230 ($M-F^+$, 3.1), 180 ($M-CF_3^+$, 2.8), 97 (CF_3CO^+, 8.7), 69 (CF_3^+, 100), 50 (CF_2^+, 8.7). ^{19}F NMR ($CFCl_3$) see Figure 2. Homodecoupling experiments confirmed the assignments.

Reaction of 2 with $CF_2=CF_2$: Compound **2** (2.19 mmol) and 3.30 mmol of C_2F_4 were condensed into a 100 ml Pyrex flask fitted with a glass-Teflon valve and the mixture was allowed to warm gently to room temperature and placed in an oil bath heated at 60°C. No reaction was observed (NMR check) over a 12 h period. The temperature was then raised to 85°C and after two hours a waxy polymer started to form at the surface of the glass. The temperature was finally raised to 160°C and held overnight. The distillation of the volatiles gave 1.73 mmol of **6** and in the -30°C trap a few mg of a liquid with very low vapor pressure. This was observed by NMR to be a complex mixture of perfluorinated materials. A white and waxy polymer (1.4 g) remained on the walls of the reactor.

Isomerization of 2 to $CF_3C(O)N(CF_3)_2$ 6: Compound **2** (3 mmol) was placed in a glass tube fitted with a glass-Teflon valve and held at 160°C for two days. The volatile materials were then separated yielding the pure amide **6** in quantitative yield. Since little information was available in the literature on this compound, its properties are given here. The bp was determined by the same method used for **2:** vapor pressure (torr, °C) 3, -60.9; 26, -34.2; 57.5, -23.3; 91, -15.2; 150, -6.4; 199, -1.1; 264, 4.8; 343, 10.7; 434, 16.1; 592, 23.6; 714, 28.4; 800, 31.9; bp = 29.49°C, ΔHvap = 7.26 Kcal/mol, ΔHvap =23.9 e.u.; IR 1800s, 1781m, 1313vs, 1256vs, 1232vs, 1203m, 1176, 1134, 1007s, 894s, 767, 734, 710 cm^{-1}. MS (CI, CH_4) m/z 250 (MH^+, 100%), 230 ($M-F^+$, 15.3); (EI) 180 ($M-CF_3^+$, 11.8), 114 ($C_2F_4N^+$, 18.2), 97 (CF_3CO^+, 22), 92 ($C_2F_2NO^+$, 17.7), 69 (CF_3^+, 100), 50 (CF_2^+, 4.2). ^{19}F NMR at 20°C, δ-55.66(q), -72.36(septet); J = 5.58 Hz.

Some reactions were also done with **6** which confirm its structure (Scheme VI): i) 0.1 mmol of **6** and 1.3 mmol of F_2 were condensed in a 75 ml stainless steel cylinder containing 3.1 mmol of active CsF[14]. The reaction was allowed to warm slowly from -150°C to -40°C and allowed to stand for 8 hours. The excess of fluorine was then removed at -196°C. The remaining volatile materials were distilled and analyzed by ^{19}F NMR and found to be: $(CF_3)_2NF$ >95% (δ -71.02 (d), -87.74 (septet); J=15.8 Hz), and a mixture (ratio 51/38) of $CF_3C(O)F$ δ138 (m), -81.42(d), -97.24 (d)[35]. All NMR signals gave the expected integrals. ii) 0.51 mmol of **6** was condensed in a glass tube containing 0.8 mmol of active CsF and let stand at 50°C overnight. Analysis of the volatile products

gave only $CF_3C(O)F$ and $(CF_3)_2NCF{=}NCF_3$ in quantitative yield. The oxaziridine **2** did not give this reaction with CsF.

N-Perfluoroisopropyl-N-trifluoromethyl-N-bromoamine 5. Compound **1** (1.2 mmol) and 2.18 mmol of Br_2 were condensed in a glass tube containing 4.4 mmol of active CsF and left at 20°C for 15 hours. Fractionation of the volatile materials through traps at -80°C and -196°C gave 0.95 mmol of **1** and 27% of **3** in the trap at -196°C and 0.7 mmol of $(CF_3)_2CFN(Br)CF_3$ mixed with Br_2 in the -80°C trap, which could not be further separated.

$(CF_3{}^a)_2CF^bN{=}CF_2{}^{cd}$: IR ν C=N 1806; ^{19}F NMR δ cd -31.19 and -42.05 (broad AB pattern), b =155.7(m), a -80.44 (d); J_{ab}=3.9 Hz.[4].

$(CF_3)_2CFN(Br)CF_3$: ^{19}F NMR see Figure 2. Homodecoupling experiments gave the expected pattern and J value for each signal.

Isomerization of 1 to 3 with CsF. Compound **1** (2 mmol) was condensed into a Pyrex tube fitted with a glass-Teflon valve, containing 0.26 mmol of CsF and 0.8 ml of anhydrous grade diglyme. The mixture was stirred at 90°C for 28 hours and the volatile materials were then collected in a trap at -196°C and analyzed by ^{19}F NMR. The spectra indicated the formation of **3** in a 28% yield along with unreacted **1**. The same isomerization was also effected without the solvent at 70°C. After seven days, **3** was formed in 30% yield. Formation of **3** was also achieved in 27% yield during the attempted reaction of **1** with CF_3OF at 80°C for two days in a 316 stainless steel cylinder, previously passivated with elemental fluorine.

Organic oxidations with 3,3 bistrifluoromethyl-2,trifluoromethyl-oxaziridine. Epoxidation of propene: Equimolar amounts of **2** and propene were condensed into a Pyrex glass tube and the mixture was allowed to slowly warm to 20°C and kept for 3 hours. The contents were then expanded into the vacuum line and a sample was analyzed by ^{1}H and ^{19}F NMR. No acetaldehyde nor formaldehyde could be detected; the conversion of **2** to **1** was found to be 56% and the propylene oxide yield was 91%. The reaction was complete in 12 h at 45°C with an 81% yield of propylene oxide and complete conversion of **2** to **1**.

Epoxidation of cis-2-butene: Equimolar amounts of alkene and **2** were condensed with $CDCl_3$ and a small amount of $CFCl_3$ into a NMR tube which was sealed under vacuum. After standing at -10°C for 15 min., ^{1}H and ^{19}F NMR analysis indicated a 96% conversion of **2** to **1** and a 92% yield of cis-2-butene oxide as the only products. No trans-epoxide or higher oxidation products were detected.

Oxidation of dimethylsulfide: A violent reaction of equimolar amounts of $(CH_3)_2S$ and **2** without solvent could be partially controlled at -20°C and led to the formation of $(CH_3)_2SO$ and $(CH_3)_2SO_2$ in the ratio 1: 2.3. The same reaction carried out in an NMR tube at -30°C for 20 min. in $CDCl_3/CFCl_3$ gave $(CH_3)_2SO$ in 75% yield and a trace of $(CH_3)_2SO_2$ (0.4%) with complete conversion of **2** to **1** as indicated by NMR..

Oxidation of pyridine: Equimolar amounts of pyridine and **2** were condensed into an NMR tube with $CDCl_3/CFCl_3$ as solvent and held at -10°C. The solution turned blue in a few minutes. The ^{1}H and ^{19}F NMR spectra taken after 15 min. indicated the formation of pyridine-N-oxide in 24% yield as the only oxidation product, but the coproduct **1** could no longer be detected in the reaction mixture.

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