in a glass tube and degassed by three freeze–thaw cycles. The tube was placed in an oil bath at 105 °C for 5 days. *n*-Octyl acetate (2.328 mg) was added as standard and the amount of each product was quantitated by GLC (10% SE-30/120 °C). The carbamate **11b** was present in 5% yield and 1-norbornyl chloride in 62%. A very small peak with a retention time the same as norbornane was observed on GLC (5% QF-1/25 °C). From a comparison of the height of this peak with that for 1-norbornyl chloride, it can be estimated that the amount of norbornane was under 0.5%.

In a small bulb blown in the end of an 8-mm glass tube, a second sample of **3b** (2.66 mg, 1.2×10^{-5} mol) was dissolved in 200 μL of CH_2Cl_2 and 29.52 mg (2.1×10^{-4} mol) of K_2CO_3 was added. A small magnetic stir bar was added, the system was degassed by three freeze–thaw cycles, and the tube was sealed under vacuum. The sample was decomposed at 105 °C with stirring for 8 days. Analysis by GLC (10% Se-30 at 120 °C, *n*-octyl acetate was an internal standard) showed 66% norbornyl chloride and 6% of the carbamate **11b**.

Reaction of the Sodium Salt of 1-Norbornylnitramine (15) with *N*,*N*-Dimethylcarbamoyl Chloride (16). The sodium salts of 1-norbornylnitramine[24] (17.2 mg, 0.096 mmol) and *N*,*N*-dimethylcarbamoyl chloride (36.5 mg, 0.34 mmol) were added to methylene chloride (2 mL) in a glass tube. The suspension was degassed by three freeze–thaw cycles and the sealed tube was placed in an oil bath at 105 °C for 6.5 days. The solution turned brown after a few days of heating. GLC (10% Se-30/125 °C) with *n*-octyl acetate (27.9 mg) as an internal standard gave peaks for 1-norbornyl chloride, 1-norbornyl *N*,*N*-dimethylcarbamate, and *N*,*N*-dimethylcarbamoyl chloride (Table II).

Reaction of Dimethylamine with Carbon Tetrachloride. A solution of dimethylamine in CCl_4 was examined periodically by NMR spectroscopy. After 2 days, the signal at δ 2.35 for dimethylamine had disappeared. Two new singlets appeared in at δ 2.78 (tetramethylurea gives a signal at δ 2.78) and 2.15 (unknown). An IR of the solution showed a strong band at 1650 cm^{-1} (the same position as the carbonyl of tetramethylurea). TLC (silica gel, ether) showed a spot that corresponded to tetramethyl urea (R_f 0.2).

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Nitrosation of the *N*-Alkyl-*O*-acylhydroxylamines. A New Deamination Method

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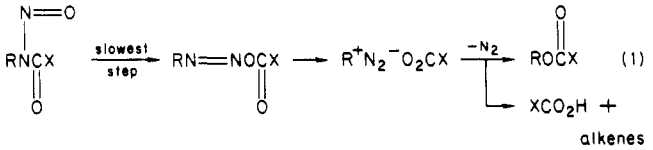
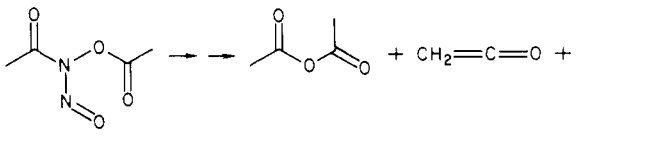
The nitrosation of *N*-alkyl-*O*-acylhydroxylamines leads to immediate decomposition at dry ice temperatures; the corresponding ester and nitrous oxide are formed. An ^{18}O study has shown that the nitroso-*O*-acylhydroxylamines fragment directly rather than undergo a rearrangement reaction (as observed with the nitrosoamides). The product yields are respectable, especially at low temperatures, and the method has promise for the generation of high energy carbonium ions.

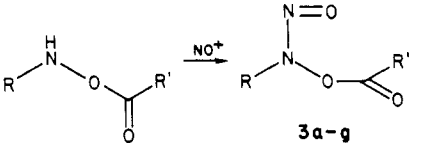
N-Nitrosoamides of various types decompose via a slow rearrangement step (eq 1, X = R, OR, NR_2);[1] *N*-nitrosoamides[2] and *N*-nitroso- and *N*-nitrosulfonamides follow a similar course.[3] We have also observed that *N*-nitrosodiacetylhydroxylamine (**1**) decomposes to yield a similar set of products (eq 2).[4] The present contribution describes our studies of deamination via the related *N*-alkyl-*N*-nitroso-*O*-acylhydroxylamines (**3**).





CH_3CO_2H (2)

Syntheses. The required *N*-alkyl-*O*-acylhydroxylamines (**2**) were prepared by the reaction of alkylamines with diacylperoxides.[5] The nitrosation step, leading to **3**, was carried out principally with dinitrogen tetraoxide[6] or nitrosyl chloride, although nitrosonium tetrafluoroborate was used in a few cases.



2a-g

a, R = isobutyl; R' = phenyl
b, R = *tert*-butyl; R' = phenyl
c, R = benzyl; R' = phenyl
d, R = 1-phenylethyl; R' = phenyl
e, R = 1-phenylethyl; R' = 2-naphthyl
f, R = 1-benzhydryl; R' = phenyl
g, R = 1-norbornyl; R' = phenyl

The Reaction. All of the *N*-alkyl-*N*-nitroso-*O*-acylhydroxylamines that we tested decomposed to the corresponding esters; for nonbridgehead alkyl groups with β-hydrogens, alkenes were also formed. The product set was

(1) White, E. H.; Woodcock, David J. In "The Chemistry of the Amino Group", Patai, S., Ed.; John Wiley and Sons, Inc.: New York, 1968; Chapter 8.
(2) White, E. H.; Grisley, D. W., Jr. *J. Am. Chem. Soc.* **1961**, *83*, 1191.
(3) White, E. H.; Lewis, C. P.; Ribi, M. A.; Ryan, T. J. *J. Org. Chem.* **1981**, *46*, 552–558.
(4) Footnote 12 in ref 2.
(5) Zinner, G. *Arch. Pharm. (Weinheim, Ger.)* **1963**, *296*, 57.
(6) White, E. H. *J. Am. Chem. Soc.* **1955**, *77*, 6008.

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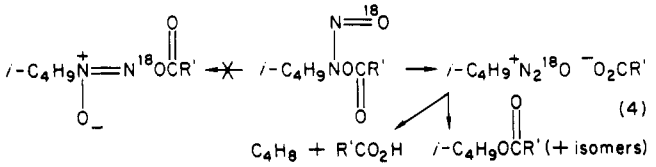
identical with that derived from the nitrosoamides (eq 1), except that nitrous oxide was the gas molecule formed rather than nitrogen (eq 3).

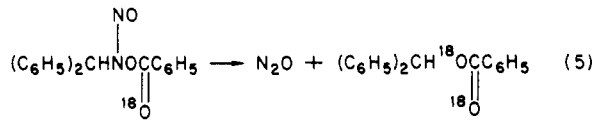
$$3 \rightarrow N_2O + ROC(=O)R' + R'CO_2H + \text{alkenes } [R\text{-}H^+] \quad (3)$$

Reaction Mechanism. The decomposition of the *N*-nitroso-*O*-acylhydroxylamines involves carbonium ion intermediates since the extent of isomerization of the isobutyl group in the decomposition of **3a**, producing *tert*-butyl and *sec*-butyl derivatives, was essentially the same as that observed in the decomposition of the nitrosoamides, a reaction in which it is known that carbonium ions are intermediates.[7] The formation of carbonium ions was also supported by the isolation of diphenylmethane in the decomposition of **3c** in benzene, the formation of *N*-benzhydrylacetamide in the decomposition of **3f** in acetonitrile, and the formation of 1-chloronorbornane in the decomposition of **3g** in methylene chloride (see Experimental Section).

An ^{18}O study showed that the nitrosohydroxylamines did not undergo a "priming" rearrangement as in the case of the amide derivatives (eq 1), but instead fragmented directly to the crucial ions (eq 4).[8] A related result, consistent with the overall fate of the ^{18}O, was obtained in the decomposition of **3f** labeled in the carbonyl group with ^{18}O; all of the isotope in this case ended up in the ester molecule (eq 5).[10]

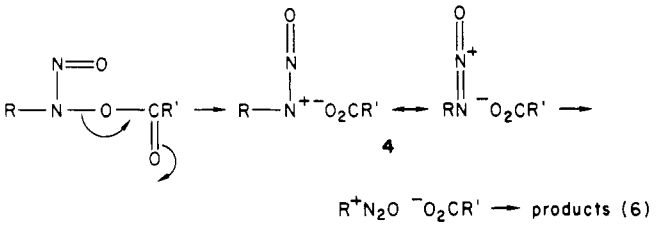


(4)

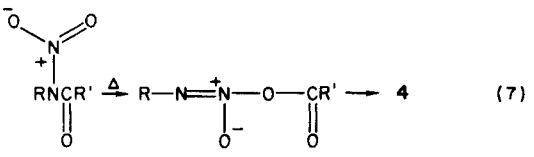


(5)

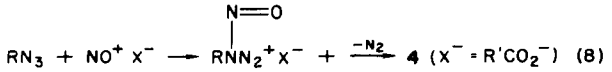
The decompositions are best represented by eq 6. Intermediate **4** accounts for the acyl exchange reactions outlined in the next section; this species has also been prepared via two other routes (eq 7[2] and 8[11]).



$$R^+N_2O\ {}^-O_2CR' \rightarrow \text{products} \quad (6)$$



(7)



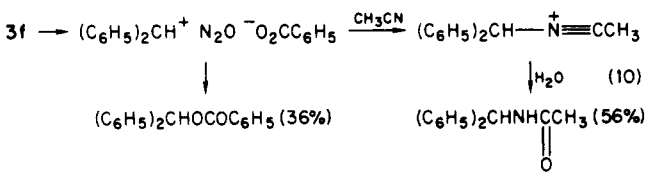
(8)

A surprising aspect of the nitrosohydroxylamine decomposition is the high rate of the ionization step (eq 4). For example, 1-norbornylhydroxylamine **2g** was nitrosated directly in an IR cell at −50 °C; nitrous oxide was observed immediately (intermediates bearing nitroso or azoxy groups were not detected). This reaction thus shows promise as a low temperature method for the generation of high energy carbonium ions (aryl, e.g.) and other ions with unusual properties (e.g., the 2-norbornyl ion, which initially at least, may have a classical structure when prepared via the nitrosohydroxylamine).

Products. Because of the instability of the nitrosoacylhydroxylamines (**3**), deamination reactions were carried out by addition of nitrosating agents to the hydroxylamines, followed by immediate examination of the reaction products. For compounds **2c** and **2f**, without β-hydrogens, and in the presence of bases (sodium acetate or pyridine), the yields of the corresponding esters were effectively quantitative (eq 9). In certain circumstances, however,

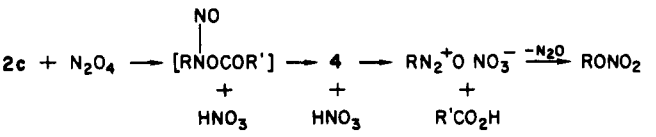
$$\underset{\mathbf{2c}}{C_6H_5CH_2NHOCOC_6H_5} + NO^+ \xrightarrow{-H^+} [\mathbf{3c}] \rightarrow C_6H_5CH_2O_2CC_6H_5 + N_2O \quad (9)$$

the carbonium ions react, in part, with the solvent. For example, diphenylmethane was formed in the decomposition of **3c** in benzene, and the decomposition of **3f** in acetonitrile yielded *N*-benzhydrylacetamide as an acetonitrile capture product (eq 10).[11]



(10)

In the absence of added bases and when N_2O_4 is used as the nitrosating agent, nitrate esters are prominant products. The nitrate esters presumably stem from "front side exchange" reactions (eq 11) with intermediate **4** (see eq 6); it had been observed in the nitrosoamide reaction that strong acids in the medium entered into product formation via proton transfer to basic anions (as in eq 11).[1] With an excess of a strong acid (HX) in the medium, excellent yields of RX would presumably be formed.[1]



(11)

Where elimination reactions are possible (with **3a,b,d,e**) they do occur (as in all deamination reactions[1]) and product distributions are more complex because of subsequent reactions of the alkenes with the nitrosating agents used. To compensate somewhat, the nitrosation of **2** (and decomposition of **3**) can be carried out at low temperatures to favor substitution over elimination and to slow reaction of the nitrosating agent with the alkenes produced in the decomposition. Thus, **3d** at −85 °C gave a 63% yield of 1-phenylethyl benzoate; in comparison, at the higher temperatures required for the nitrosamide method of deamination (25–75 °C) 1-phenylethyl ester yields of ~20–35% are normally observed.[1,12]

(7) White, E. H. *J. Am. Chem. Soc.* **1955**, *77*, 6011.
(8) This result was initially reported in ref 9.
(9) White, E. H.; Todd, M. J.; Ribi, M.; Ryan, T. J.; Sieber, A. A. F.; Dickerson, R. E.; Bordner, J. *Tetrahedron Lett.* **1970**, *51*, 4467-4472.
(10) "A Comparative ^{18}O and Stereochemical Study of Deamination via the Nitrosoamide, Nitroamide, and Nitrohydroxylamine Decompositions", in preparation.
(11) McGirk, R. H.; White, E. H. *J. Am. Chem. Soc.* **1973**, *95*, 3804.
(12) White, E. H.; Aufdermarsh, C. A., Jr. *J. Am. Chem. Soc.* **1961**, *83*, 1179.

In the deamination of *N*-norbornyl-*O*-benzoylhydroxylamine (**2g**), the high energy carbonium ion formed has sufficient reactivity to wrest a chloride ion from methylene chloride (eq 12, an unusual solvolysis reaction). Several related routes to 1-norbornyl chloride have been reported elsewhere, and the mechanism of the chloride transfer (as shown in eq 12) has been established.[13] When nitrosyl chloride is used, an alkyl chloride could also be formed by the processes outlined in eq 11.

In other studies, we have compared O-18 scrambling and stereochemical changes for the nitrosohydroxylamine reaction and deamination routes involving *N*-nitroso- and *N*-nitroamides; no differences appreciably beyond experimental error were detected.[10]

Acylation of Hydroxylamine Salts. We have also examined the acylation of salts of *N*-isobutyl-*N*-nitrosohydroxylamine (**5**) (eq 13).[14] The results of this approach were similar to those observed in the nitrosation of **2a**, but they were more complex; for example, product 8 derived from nitrosoisobutane was formed (eq 14).[15] The role of intermediate **7** in the reaction (eq 13) is uncertain; if formed, it would probably rearrange to the corresponding nitrosohydroxylamine (**3**) (enroute to the corresponding esters and nitrous oxide). Carboxylic acid derivatives with this structure are unknown, although the corresponding sulfonic acid derivatives are quite stable.[3,9,16-18]

In summary, the nitrosation of *N*-alkyl-*O*-acylhydroxylamines at low temperatures serves as a useful method for the preparation of deaminatively formed carbonium ions and their products.

Experimental Section

Instrumentation. Infrared spectra were obtained on Perkin-Elmer Model 337 and 457 A grating spectrophotometers. Proton magnetic resonance spectra were obtained with Varian Models A-60, T-60, and CFT-20; chemical shifts are reported in δ units with tetramethylsilane as an internal standard. Melting points, obtained on a Thomas-Hoover apparatus, are uncorrected.

***N*-Isobutyl-*O*-benzoylhydroxylamine (2a).** Following the method of Zinner,[5] isobutylamine (29.2 g, 0.4 mol) dissolved in benzene (40 mL) was added to a solution of dibenzoyl peroxide (48.4 g, 0.2 mol) in benzene (200 mL) with stirring and cooling to 0 °C. The yellow colored reaction mixture was then heated to 30 °C for 30 min and 50 °C for 30 min. On cooling to 0 °C, a white precipitate of *N*-isobutylammonium benzoate separated. After filtration the filtrate was washed with water and dried over magnesium sulfate. After filtration anhydrous hydrogen chloride was bubbled through the solution to give a white precipitate of *N*-isobutyl-*O*-benzoylhydroxylamine hydrochloride (12.1 g, 0.053 mol, 26%): mp 120–128 °C (lit.[5] mp 120–125 °C); IR (nujol) 1760 cm^{-1} (lit.[5] 1760 cm^{-1}).

N-Isobutyl-*O*-benzoylhydroxylamine hydrochloride (600 mg) was treated with aqueous sodium carbonate solution (1 N), and the solution was extracted with ether. Drying the ether phase over sodium sulfate and evaporation yielded *N*-isobutyl-*O*-benzoylhydroxylamine which was purified by Kugelrohr distillation: bp 58–65 °C (0.04–0.03 mm); IR (CCl_4) 3235, 1725, 1267, 1088, 1067, 1027 cm^{-1} (lit.[1] as film 1730 cm^{-1}); NMR (CCl_4) δ 0.99 (d, J = 6.5 Hz, 6 H), 1.83 (m, J = 6.5 Hz, 1 H), 2.87 (d, J = 6.5 Hz, 2 H), 7.47 and 7.98 (aromatic m and NH).

***N*-(*tert*-Butyl)-*O*-benzoylhydroxylamine (2b).** The title compound (5.3 g, 28 mmol, 56.0%) was obtained from *tert*-butylamine (7.30 g, 0.10 mol) and 12.1 g (50 mmol) of dibenzoyl peroxide by using the general method of Zinner:[5] IR (CH_2Cl_2) 3220, 1715, 1365, 1260, 1090, 985 cm^{-1} (lit.[5] as film 1720 cm^{-1}); NMR ($CDCl_3$) δ 1.22 (s, 9 H, $[CH_3]_3$), 7.50 and 8.03 (m, 5 aromatic H's and NH). Anal. Calcd for $C_{11}H_{15}O_2N$: C, 68.36; H, 7.84; N, 7.25. Found: C, 68.21; H, 7.74; N, 7.37.

***N*-Benzyl-*O*-benzoylhydroxylamine (2c).** The title compound was prepared in 58% yield as the hydrochloride following the procedure of Zinner.[5] Treatment of the salt with aqueous sodium bicarbonate yielded the free hydroxylamine (74%): IR (film) 3220, 1718 cm^{-1}; IR ($CDCl_3$) same values [lit.[19] ($CHCl_3$) 1725 cm^{-1}]; ^1H NMR ($CDCl_3$) δ 4.24 (s, 2 H), 7.4–7.8 (m, 9 H), 7.8–8.35 (m, 2 H); ^1H NMR (C_6D_6) 3.94 (s, 2 H), 6.8–7.4 (m, 9 H), 7.8–8.1 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) 56.8, 128.0, 128.3, 128.5, 126.6, 129.0, 129.3, 133.4, 135.8, 166.8.

***N*-(1-Phenylethyl)-*O*-benzoylhydroxylamine (2d).** The title compound (2.58 g, 10.6 mmol, 54%) was prepared from 1-phenylethylamine and benzoyl peroxide in methylene chloride following the method of Zinner.[5] The crude product was purified by column chromatography on florisil: IR (CH_2Cl_2) 1720 cm^{-1} (lit.[5] as film 1725 cm^{-1}); NMR ($CDCl_3$) δ 1.52 (d, J = 6.0 Hz, 3 H), 4.30 (*q*, J = 6.0 Hz, 1 H), 7.40 and 7.92 (m, 11 H, aromatic and NH). Anal. Calcd for $C_{15}H_{15}O_2N$: C, 74.67; H, 6.27; N, 5.95. Found: C, 74.34; H, 6.03; N, 5.47.

***N*-(1-Phenylethyl)-*O*-(2-naphthoyl)hydroxylamine (2e).** Following the general procedure of Zinner,[5] 1.7 g (16 mmol) of 1-phenylethylamine in 10 mL of benzene was added to a stirred solution of 2.8 g (8.2 mmol) of di-2-naphthoyl peroxide in 10 mL of benzene cooled in a water bath at 0–5 °C. Benzene (25 mL) was added and the mixture was allowed to reach room temperature (benzene was added to keep the pasty mass stirrable). After 15 h, the mixture was filtered to remove 1-phenylethyl naphthoate. The hydroxylamine (**2e**) was either precipitated with hydrogen chloride and then liberated with aqueous sodium carbonate, or else the free hydroxylamine was purified by chromatography on silica gel with benzene–ether or benzene–carbon tetrachloride as eluants. The hydroxylamine (0.8 g, 2.7 mmol, 17%) formed colorless needles: mp 95.5 °C; IR (KBr) 3215, 1725, 1268, 1200, 768, and 710 cm^{-1}; NMR ($CDCl_3$) δ 1.55, (d, J = 6.5 Hz, 3 H), 4.38 (q, J = 6.5 Hz, 1 H), 7.2–8.0 (m, 11 H), 8.5 (br s, 1 H), and 9.0 (br s, 1 H). Anal. Calcd for $C_{19}H_{17}NO_2$: C, 78.33; H, 5.88; N, 4.81. Found: C, 78.41; H, 5.90; N, 4.86.

***N*-Benzhydryl-*O*-benzoylhydroxylamine (2f).** A solution of 18.3 g (0.10 mol) of benzhydrylamine in 30 mL of dry benzene was added dropwise to a solution of 12.1 g (0.05 mmol) of benzoyl peroxide in 50 mL of dry benzene with stirring and cooling at 0 °C. The resulting suspension was heated in a 30–35 °C water bath. The reaction mixture soon became transparent and then formed a thick white precipitate. After 1 h the reaction mixture was filtered, and the benzhydrylammonium benzoate was washed with benzene. The filtrate was dried over magnesium sulfate and concentrated under reduced pressure. The evaporate was recrystallized from absolute ethanol, yielding a first crop of crystals (7.85 g, 0.06 mmol, 52%) and a second crop (0.70 g): IR (CCl_4) 1725 cm^{-1}. Purification was effected by chromatography over 150 g of silica gel (28–200 mesh) eluting with benzene. The hydroxylamine derivative emerged first, and the IR spectrum showed it to be free from *N*-benzhydrylbenzamide; eluting with ether caused the benzamide to appear. Recrystallization from absolute ethanol yielded white crystals: mp 100.5–101.3 °C; NMR ($CDCl_3$) δ 5.4 (d, 1 H, J = 4), 7.2–7.7 (m, 13 H), 7.85–8.05 (m, 2 H), 8.21 (d, 1 H, J = 4). Addition of D_2O caused the doublets at δ 5.4 and 8.21 to collapse to broad singlets. Anal. Calcd for $C_{20}H_{17}NO_2$: C, 79.19; H, 5.65; N, 4.62. Found: C, 79.28; H, 5.64; N, 4.49.

***N*-(1-Norbornyl)-*O*-benzoylhydroxylamine (2g).** The title compound (0.22 g, 0.83 mmol, 29.6%) was obtained from 1-aminonorbornane (0.60 g, 5.4 mmol) and dibenzoyl peroxide (0.67

(13) White, E. H.; Tiwari, H. P.; Todd, M. J. *J. Am. Chem. Soc.* **1968**, *90*, 4734. White, E. H.; McGirk, R. H.; Aufdermarsh, C. A., Jr.; Tiwari, H. P.; Todd, M. J. *J. Am. Chem. Soc.* **1973**, *95*, 8107. White, E. H.; Ryan, T. J.; Hahn, B. S.; Erickson, R. H. *J. Org. Chem.*, third paper in this series.

(14) Preliminary results were listed in ref 2.

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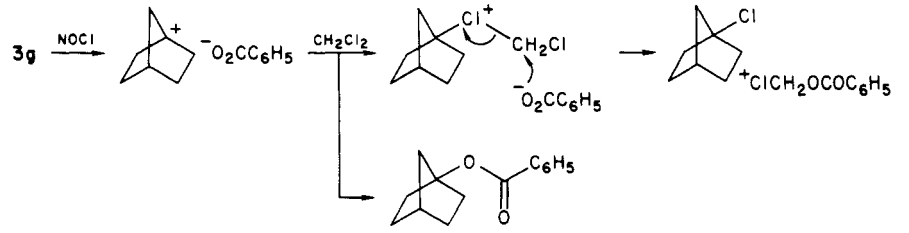
(16) Stevens, T. E. *J. Org. Chem.* **1964**, *29*, 311; *J. Org. Chem.* **1967**, *32*, 1641. Dorko, E. A.; Stevens, T. E. *J. Org. Chem.* **1966**, *31*, 871.

(17) Maskill, H.; Murray-Rust, P.; Thompson, J. T.; Wilson, A. A. *J. Chem. Soc., Chem. Commun.* **1980**, 788.

(18) Freeman, J. P.; Lillwitz, L. D. *J. Org. Chem.* **1970**, *35*, 3107–3110. Freeman and Lillwitz nitrosated *O*-tosyl-*N*-methylhydroxylamine and obtained only methyl tosylate; thus both *N*-nitroso-*O*-acyl- and *N*-nitroso *O*-sulfonylhydroxylamines are unstable species.

(19) Exner, O.; Kakac, B. *Collect. Czech Chem. Commun.* **1960**, *25*, 2530–2538.



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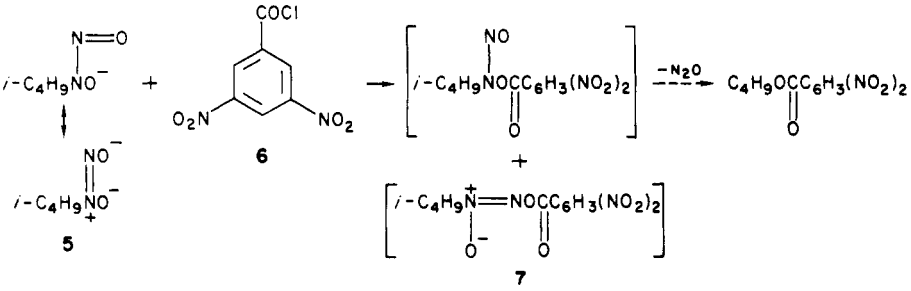

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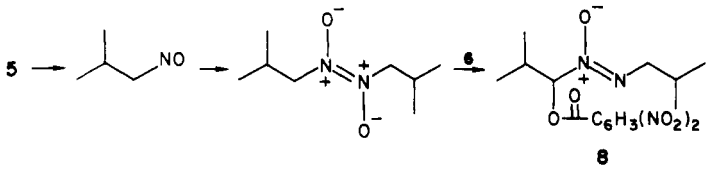

(14)

g, 2.8 mmol) according to the general method of Zinner:[5] mp 165–170 °C; IR (KBr) 3400 (broad, s), 2500 (broad, s), 1765 cm^{-1}. The parent hydroxylamine was obtained by treating the hydrochloride salt with 5% aqueous sodium hydroxide: IR (CH_2Cl_2) 3230, 1720 cm^{-1}.

1-Norbornanol (0.11 g, 1.0 mmol, 20%) was prepared from 0.74 g (5.0 mmol) of 1-aminonorbornane hydrochloride and 1.04 g (15 mmol) of sodium nitrite in acetic acid,[20] mp 152–153 °C (lit.[20] mp 152–154 °C).

1-Norbornyl Benzoate. 1-Norbornanol (32.8 mg, 0.29 mmol) in 2.5 mL (3.0 g, 21.4 mmol) of benzoyl chloride was refluxed for 18 h. Water (7 mL) was added and the reaction mixture was extracted with ether (3 × 15 mL); the combined extracts were washed with water, 10% sodium carbonate solution, and water and then dried over anhydrous sodium sulfate. After removal of the solvent the ester was purified by preparative TLC on alumina with a mixture of carbon tetrachloride and benzene (1:1) as the eluant: yield, 33.8 mg (0.16 mmol, 54%); IR (CCl_4) 1730 cm^{-1}.

Nitrosation of *N*-Isobutyl-*O*-benzoylhydroxylamine (2a). Run 1. To *N*-isobutyl-*O*-benzoylhydroxylamine (70 mg, 0.3 mmol) dissolved in methylene chloride and cooled to −70 °C was added an equimolar amount of dinitrogen tetraoxide dissolved in methylene chloride (−70 °C). A portion of the solution was removed with a dry ice cooled syringe and injected into an IR cell cooled to −50 °C. Starting material and nitrous oxide were observed. A 3 m excess of dinitrogen tetraoxide was then added. The IR cell was washed thoroughly with the new reaction solution and refilled. The nitrous oxide band at 2225 cm^{-1} was now intense. The bands of excess dinitrogen tetraoxide could also be observed but no starting material was seen. No bands of an *N*-nitroso or azoxy intermediate between 1450 and 1580 cm^{-1} or high frequency carbonyl bands (>1720 cm^{-1}) could be found. Heating the IR cell to 0 °C over a period of 1 h did not change the spectrum.

Run 2. *N*-Isobutyl-*O*-benzoylhydroxylamine (1.56 g, 8.07 mmol) was placed in a 50-mL round-bottom flask along with 700 mg (8.54 mmol) of anhydrous sodium acetate. One neck was equipped with a balloon and another with a rubber septum. Carbon tetrachloride (20 mL) was added and the mixture was cooled to −10 °C. Nitrosyl chloride gas (250 mL, ca. 11.2 mmol) was then added in portions over a period of 15 min. The reaction mixture was stirred at that temperature for an additional 15 min and then allowed to warm to room temperature. The gases over the reaction mixture were analyzed for olefin content by GLC with 30% $AgNO_3$/DEG or 80/100 Chrom Q columns (6 ft × $^1/_8$ in.) at room temperature. An aliquot (100 μL) was withdrawn and injected. Isobutylene was detected (23%). A small peak was noted with a retention time corresponding to that of *trans*-butene-2 (estimated yield ca. 1%). *cis*-Butene-2 and butene-1 were not observed (if formed the yield was less than 1%). The reaction mixture was then washed with saturated sodium carbonate solution and the aqueous layers were combined and acidified with concentrated hydrochloric acid. The acidic phase was extracted with methylene chloride to yield 592 mg (4.85 mmol, 60.1%) of benzoic acid, mp 121–122 °C (lit.[21] mp 122 °C). The organic phase after base treatment was light blue in color (nitroso compounds?). It was analyzed by GLC for ester content with a 6 ft × $^1/_8$ in. 5% QF-1 on 80/100 Chrom Q column and benzophenone as an internal standard. The esters obtained: isobutyl benzoate (356 mg, 2.0 mmol, 25%), *tert*-butyl benzoate (50.0 mg, 0.28 mmol, 3.5%), *sec*-butyl benzoate (14.0 mg, 0.08 mmol, 1.0%). Besides the esters, the GLC traces showed four other minor peaks. The IR spectrum of the organic phase [(CCl_4) 1722 (s), 1670 (s), 1557 (w), 1520 (w), 1470 (m), 1272 (s), 1110 (m), 980 (m) cm^{-1}] was basically that of isobutyl benzoate except for minor absorptions at 1640, 1557, and 1520 cm^{-1}. The NMR spectrum [(CCl_4) δ 1.0 (d, J = 6.5 Hz), ca. 2.0 (m, J = 6.5 Hz), 4.05 (d, J = 6.5 Hz), 7.4 (m) and 8.0 (m)] showed isobutyl benzoate; a singlet at δ 1.56 corresponded to the *tert*-butyl group of *tert*-butyl benzoate.

Nitrosation of *N*-Isobutyl-*O*-benzoylhydroxylamine with Dinitrogen Tetraoxide-^{18}O. The labeled oxygen was obtained by electrolysis of deuterium oxide enriched in ^{18}O (~3%). One drop of sulfuric acid was added and the mixed deuterium and oxygen were collected by displacement of sulfuric acid. The mixed gases (300 mL) were injected into an evacuated 500-mL flask fitted with a serum cap. Nitric oxide (100 mL) was then injected and the mixture allowed to stand for 12 h at room temperature. The base of the flask was immersed in liquid N_2 until the brown color of NO_2 disappeared. Deuterium and excess oxygen were pumped off. A sample of the labeled NO_2 was removed and a mass spectrum was recorded to determine the ^{18}O enrichment. (Mass spectra were also recorded for samples of NO_2 and N_2O with natural abundances of ^{18}O.) The labeled NO_2 was frozen at −80 °C, and carbon tetrachloride (50 mL) was injected into the flask to give, after warmup, a solution containing roughly 2.2 mmol of

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N_2O_4. The hydroxylamine (0.473 g, 2.45 mmol) and pyridine (0.380 g, 4.8 mmol) were dissolved in CCl_4 (30 mL) in a flask fitted with a serum cap, a system for nitrogen flushing, and a reflux condenser. The top of the condenser was connected to a collection train consisting of a tube of Ascarite (to absorb any CO_2) and a collection tube cooled in liquid N_2. The hydroxylamine solution was chilled in an ice bath and the solution of N_2O_4[18] was slowly injected below the surface of the liquid. The brown color of the gas disappeared immediately and a white precipitate gradually formed. The mixture was warmed to room temperature and allowed to stand for 1 h. A slow stream of nitrogen was then bubbled through the solution for 30 min, and the stopcocks on the cold trap were closed. The large amount of solid material in the trap indicated that a considerable quantity of solvent vapor had reached the trap. Still cooled in liquid N_2, the trap was then attached to a vacuum line and evacuated. The pump was isolated and the trap warmed to −80 °C, any material volatile at this temperature being collected in a mass spectrometer gas sample tube cooled to liquid N_2 temperature. The major peaks of the mass spectrum of the gas collected were identical with those of pure N_2O.

The nitrosation and decomposition were then repeated with unlabeled N_2O_4 (40 mL in 50 mL CCl_4), hydroxylamine (0.320 g, 1.66 mmol), and pyridine (0.280 g, 3.04 mmol). The N_2O formed in this case contained 0.30 atom % ^{18}O. The following ^{18}O concentrations were found (atom % ^{18}O): unlabeled NO_2 (0.24), unlabeled N_2O (0.23), N_2O isolated from unlabeled NO_2 and the hydroxylamine (0.30), enriched NO_2 (1.6), N_2O isolated from labeled NO_2 and the hydroxylamine (2.1). The abnormally high values found for recovered N_2O may stem from the presence of some NO_2 (note: m/e $NO_2 = N_2{}^{18}O = 46$).

A mass spectral comparison of the isobutyl benzoates from each decomposition was then made. The reaction mixture from the ^{18}O run was filtered to remove the white precipitate (probably pyridinium nitrate). The filtrate was extracted with 2 N hydrochloric acid (30 mL) and washed with distilled water (2 × 30 mL). After drying for 8 h ($MgSO_4$), the solvent was removed leaving an oily residue containing some solid material. This mixture was distilled in a short tube (55–60 °C (10 microns)) to yield a colorless oil (0.145 g, 33.0%) which was shown by GLC (2% NPGS/140 °C) to be mainly (ca. 90%) isobutyl benzoate. There were smaller amounts of *n*-, *sec*-, and *tert*-butyl benzoates (2% each) and also some more volatile components (probably small amounts of solvent and butanols). In the same way, a second sample of isobutyl benzoate was isolated from the products of nitrosation with unlabeled N_2O_4. Since the parent peaks were very small, the prominent peak at m/e 123 corresponding to protonated benzoic acid was chosen for the analysis and its height compared with that at m/e 125 corresponding to $PhCO^{18}OH_2^+$. These peaks rise from rearrangement of two hydrogen atoms with elimination of an allylic type radical and are prominent in the spectra of medium and long chain esters of aromatic acids. The ester isolated from the nitrosation with $N_2{}^{18}O_4$ gave a value average of 0.43 for the atom % excess of ^{18}O [125/(123 + 125) × 100/2] whereas the sample isolated from the nitrosation with unlabeled N_2O_4 gave an average value of 0.42.

Nitrosation of *N*-*tert*-Butyl-*O*-benzoylhydroxylamine (2b). To the title compound (287 mg, 1.5 mmol) dissolved in 1 mL of $CDCl_3$ was added 0.33 equiv of N_2O_4 gas (10 mL) and an NMR spectrum was measured within 4 min. The ratio of isobutylene (δ 1.68) to *tert*-butyl benzoate (δ 1.61) to a signal at δ 1.52 (unknown) was 5/1/0.5; two thirds of the starting material remained. A second 0.33 equiv of N_2O_4 led to a ratio of products of 7.5/1/0.5. After addition of the third 0.33 equiv of N_2O_4 (total elapsed time ~30 min), a new peak appeared at δ 1.58; the product ratio (in order of decreasing δ) was 2.5/1/2.5/1 (the latter two products probably stem from reaction of isobutylene with N_2O_4[22]). At this point the yield of isobutylene was 25% and that for *tert*-butyl benzoate 11%. In more dilute runs (0.1 M) made in the presence of 2 mol equiv of pyridine, ester and benzoic acid yields of 20% and 84%, respectively, were observed.

Nitrosation of *N*-Benzyl-*O*-benzoylhydroxylamine (2c). CH_2Cl_2 + Pyridine Run. Hydroxylamine **2c** (95 mg, 0.42 mmol) and pyridine (67 μL, 0.84 mmol) were dissolved in 5 mL of methylene chloride. The solution was cooled to 0 °C, and 10.2 mL (0.42 mmol) of gaseous dinitrogen tetraoxide was added with stirring over a 2-min period of time. After 5 min, the organic phase was washed with 5% hydrochloric acid, dried, and evaporated to yield 88 mg of a yellowish oil. Analysis by NMR (vs. standard samples) led to the following yields: benzyl benzoate (78%), benzyl nitrate (2%). No benzaldehyde was detected.

C_6D_6 Run. N_2O_4 (2 molar equiv) was added to the hydroxylamine as described for the CH_2Cl_2 run, except that no pyridine was used. The product distribution was determined from the NMR spectrum measured in C_6D_6: benzyl benzoate (δ CH_2 5.13, 45%), benzyl nitrate (δ CH_2 4.67, 40%), diphenylmethane-d_5 (δ CH_2 3.74, 7%), benzaldehyde (δ CHO 9.6, 7%). Essentially the same product distribution was observed at an early stage in the reaction when 0.4 equiv of N_2O_4 had been added per 1 equiv of hydroxylamine.

Nitrosation of *N*-(1-Phenylethyl)-*O*-benzoylhydroxylamine (2d). In a 50-mL round-bottomed flask equipped with a mechanical stirrer, a drying tube, and a rubber septum were placed 0.50 g (2.07 mmol) of *N*-(1-phenylethyl)-*O*-benzoylhydroxylamine and 0.50 g (6.33 mmol) of pyridine in 30 mL of methylene chloride. The solution was chilled to −85 °C and while the solution was stirred, 100 mL (4.46 mmol) of nitrosyl chloride gas was injected. After stirring for 1 h at −85 °C, 55 mL (2.45 mmol) of ammonia gas was injected to destroy excess nitrosyl chloride. After the reaction vessel was allowed to warm to room temperature, the methylene chloride solution was washed with water and dried over anhydrous Na_2SO_4. Removal of the methylene chloride at 30 °C gave 0.48 g of product. This was dissolved in $CDCl_3$ which contained 0.033 g (0.36 mmol) of toluene as a standard; the NMR spectrum showed that 0.296 g (1.31 mmol, 62%) of 1-phenylethyl benzoate was present.

After removal of $CDCl_3$ by rotary evaporation, the solid was dissolved in 100 mL of benzene and eluted through a silica gel column. The first 60 mL contained a single compound (0.75, TLC on SiO_2, benzene eluant), which after removal of benzene by rotary evaporation at 30 °C, afforded 0.30 g (1.33 mmol, 63%) of liquid, identified as 1-phenylethyl benzoate on the basis of the following data: IR (CH_2Cl_2) 2900, 1710, 1560, 1490, 1320, 1175, 1110, 1060, 990, 860 cm^{-1}; NMR ($CDCl_3$) δ 1.60 (d, J = 6.0 Hz, 3 H), 6.08 (q, J = 6.0 Hz, 1 H), 7.32 (m, 8 H), 8.02 (m, 2 H).

Elution with a further 140 mL of benzene yielded 0.17 g of solid, which was dissolved in 5% NaOH and precipitated with HCl. Ether extraction afforded 0.15 g (1.23 mmol, 32%) of benzoic acid, mp 121.5 °C (lit.[21] mp 122 °C).

Nitrosation of *N*-(1-Phenylethyl)-*O*-(2-naphthoyl)-hydroxylamine (2e). The title compound (217 mg, 0.746 mmol) in 25 mL of methylene chloride was nitrosated with nitrosyl chloride gas (40 mL, 1.77 mmol) in the presence of sodium acetate (150 mg, 1.83 mmol) as described above except that the nitrosyl chloride was injected at room temperature. The mixture was stirred for 1 h; the solvent was distilled keeping the receiving flask at −78 °C. The distillate (17 mL) did not contain styrene (UV spectroscopy). The solid residue was worked up as in previous runs to give 68.5 mg (0.398 mmol, 53%) 2-naphthoic acid, mp 180–182 °C (lit.[21] mp 158 °C), and a neutral phase, 101 mg. An aliquot of the latter (43.5 mg) was analyzed by NMR with toluene (9.6 mg, 0.10 mmol) as the internal standard; 85 mg (0.31 mmol, 41%) of 1-phenylethyl naphthoate was found. The NMR sample was combined with the remainder of the ester and applied on a preparatory TLC alumina plate (with fluorescent indicator). The plate was developed in benzene, and the ester band was removed and extracted with ether (3 × 50 mL) and methylene chloride (3 × 50 mL). The solvents were removed to give 76.1 mg (0.276 mmol, 37%) of ester. The ester was found to be pure by NMR spectroscopy [δ 1.70 (d, 6.5 Hz, 3 H), 6.26 (q, J = 6.5 Hz, 1 H), 7.2–8.3 (m, 11 H), 8.70 (br s, 1 H)]. In a second run, 56% naphthoic acid and 39% of the ester was obtained. The yield of ester was also determined from the λ_{max} 237 (ε 59800),[23] 37% yield of the ester was found by this technique.

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(23) 1-Phenylethyl 2-naphthoate that was found pure by NMR spectroscopy has λ_{max} 237 (ε 58800) nm.

Nitrosation of N-Benzhydryl-O-benzoylhydroxylamine (2f). In Methylene Chloride. The title compound (1.50 g, 4.94 mmol), sodium acetate (5.0 g, 61 mmol), anhydrous sodium sulfate (2.0 g), and dry methylene chloride (150 mL) were stirred at 0 °C. Nitrosyl chloride gas (150 mL, 6.70 mmol) was added slowly. The mixture was allowed to warm to room temperature (22 °C), then stirred for 1 h. The organic phase was washed with aqueous sodium bicarbonate, then dried, and evaporated to yield 1.31 g (4.54 mmol, 92%) of benzhydryl benzoate, mp 85–87 °C (lit.[21] mp 88 °C). The IR spectrum (1720, 1105 cm^{-1} in CH_2Cl_2) was superimposable in detail on that of the pure ester. Recrystallization from 95% ethanol yielded 1.01 g (3.51 mmol, 71%) of the pure ester, mp 88–89 °C. A single run with nitrosonium tetrafluoroborate as the nitrosating agent gave the ester in a yield of 69%.

In Acetonitrile. Nitrosonium tetrafluoroborate (0.132 g, 1.13 mmol) as a slurry in 5 mL of dry acetonitrile was added over several minutes to the hydroxylamine (0.307 g, 1.02 mmol) in 5 mL of acetonitrile under N_2. After 30 min at room temperature, TLC showed no hydroxylamine. Water was added (0.2 mL) and then CH_2Cl_2 (30 mL) and additional water (15 mL). The organic phase was washed, then dried, and evaporated. The evaporate contained benzoyl fluoride; the IR (CCl_4) 1820 cm^{-1} and mass spectra (*m/e* 124) were identical with those of authentic benzoyl fluoride. Treatment of the residue with CCl_4 yielded a residue of *N*-benzhydrylacetamide, mp 148–149 °C (IR and melting point identical with those of authentic amide). Evaporation of the CCl_4 yielded benzhydryl benzoate (0.102 g, 0.37 mmol, 36%), which after recrystallization from ethanol gave mp 83.5–85.5 °C and an IR spectrum identical with that of authentic ester. Analysis of the initial reaction mixture by GLC showed benzoyl fluoride, 20%, *N*-benzhydrylacetamide, 60%, and benzhydryl benzoate, 20%. In a second run with equivalent amounts of the reactants, NMR analysis of the products showed *N*-benzhydrylacetamide (56%) and benzhydryl benzoate (36%).

Nitrosation of N-(1-Norbornyl)-O-benzoylhydroxylamine (2g). The hydroxylamine (41.5 mg, 0.180 mmol) in 5 mL of CCl_4 was nitrosated with nitrosyl chloride gas (4.5 cm^3, 0.20 mmol) at −15 °C. After 10 min, an aliquot showed N_2O by IR (2215 cm^{-1}). After a water workup, the products were analyzed by GLC (6 ft × $^1/_8$ in. 5% QF-1 on Chromosorb Q column, column temperature 70 °C). Absolute calibration was used. The yield of 1-chloronorbornane was 9.4 mg (0.072 mmol, 40.0%) and the yield of 1-norbornyl benzoate was 17.5 mg (0.081 mmol, 45%). No other products were observed.

The Ammonium Salt of N-Isobutyl-N-nitrosohydroxylamine. An aqueous solution of the magnesium salt of *N*-isobutyl-*N*-nitrosohydroxylamine, prepared as previously described,[2] was poured onto water and acidified with aqueous hydrochloride solution (2 N). The aqueous phase was extracted with ether and the ether layer was washed with water and dried over anhydrous sodium sulfate. After filtration, anhydrous ammonia (dried with sodium hydroxide) was bubbled through the solution from which a crystalline product (3.19 g, mp 58–60 °C) separated after half an hour. The mother liquid was concentrated and further ammonium salt (3.47 g, mp 58–60 °C) was isolated after having bubbled ammonia through again. The total yield was 6.66 g (50 mmol, 12%): IR ($CHCl_3$) 2960 s, 2870 m, 1465, 1395, 1140, 1059 vs, 975 s cm^{-1}.

The copper salt of N-isobutyl-N-nitrosohydroxylamine was prepared as previously described:[2] mp 81–82 °C (lit.[2] mp 80–82.5 °C); IR (CCl_4) 2960 s, 2865 m, 1420, 1277, 1230 s, 1190 s, 954 cm^{-1}.

The Potassium Salt of N-Isobutyl-N-nitrosohydroxylamine. Potassium hydroxide (1.46 g, 85% pure, 22.3 mmol) dissolved in a small amount of water and methanol was added to an aqueous solution of the ammonium salt (3 g, 22.3 mmol) containing one drop of ethanolic phenolphthalein. The solution became slightly reddish. The solvents were removed and alternate additional of methanol and evaporation was done until crystallization occurred. The salt residue (very hygroscopic) was dried over calcium chloride under vacuum: IR (Nujol) 3460 m, 1267–1262, 1250, 1206, 1108 m, 954, 898 m cm^{-1}.

The Silver Salt of N-Isobutyl-N-nitrosohydroxylamine. To the ammonium salt (0.8 g, 6 mmol) dissolved in water was added silver nitrate (1 g, 6 mmol) dissolved in water while stirring at room temperature. The white precipitate was filtered, washed three times with water, methanol, and ether, and then dried in vacuum over calcium chloride at room temperature. Yield: 0.767 g (57%). The silver salt was stored in darkness.

Reaction of the Potassium Salt of N-Isobutyl-N-nitrosohydroxylamine with 3,5-Dinitrobenzoyl Chloride. To the potassium salt of *N*-isobutyl-*N*-nitrosohydroxylamine (312 mg, 2 mmol) suspended in methylene chloride (20 mL) was added 3,5-dinitrobenzoyl chloride (550 mg, 2.38 mmol) dissolved in methylene chloride (15 mL) at 10 °C with stirring over a period of 5 min. After 30 min the precipitate had changed character and an infrared spectra of the solution showed nitrous oxide (2225 cm^{-1}). The reaction mixture was kept at −10 °C for 12 h and then filtered. The filtered was evaporated to dryness and divided in an ether soluble (375 mg) and an ether insoluble crystalline part (3,5-dinitrobenzoic anhydride, 72 mg, mp 220–222 °C (lit.[24] 219–221 °C)). The ether soluble part was resolved by TLC (3 plates, 20/20 cm, 20 g of PF_{254} silica gel (Merck)); first development, cyclohexane:diethyl ether (10:1); second development, cyclohexane:diethyl ether (10:2.5). The zones were detected by UV (254 nm) and eluted with chloroform. The products are arranged in order of decreasing R_f values: fraction 1, 12 mg of an oil; fraction 2, 140 mg, 22% yield of isobutyl dinitrobenzoate and *sec*-butyl 3,5-dinitrobenzoate (ratio ~10); fraction 3, 20 mg (3% yield) of 1-((3,5-dinitrobenzoyl)oxy)-1,1′-ONN-azoxyisobutane (8);[15] fraction 4, 6 mg (IR in CCl_4 at 1765 cm^{-1}); fraction 5 24 mg (0.11 mmol) of 3,5-dinitrobenzoic acid.

Reaction of the Copper Salt of N-Isobutyl-N-nitrosohydroxylamine with 3,5-Dinitrobenzoyl Chloride. To the copper salt (743 mg, 5 mmol) dissolved in methylene chloride (10 mL) was added 3,5-dinitrobenzoyl chloride (1.15 g, 5 mmol) in methylene chloride (20 mL) at 0 °C with stirring. After 5 min the mixture was warmed to room temperature and allowed to stand for 12 h. The precipitate (961 mg) was removed and the filtrate was evaporated to dryness. The residue was only partially resoluble in methylene chloride. The soluble part was separated by TLC as described for the potassium salt reaction: fraction 2, 20 mg (largely isobutyl 3,5-dinitrobenzoate); fraction 3, 29 mg (recrystallization from ether/cyclohexane gave 12 mg, mp 93–94 °C; IR (CCl_4) 1744 cm^{-1}); fraction 4, 87 mg; fraction 5, 20 mg of an oil. Fraction 4 was rechromatographed by TLC on two 20/20 cm plates bearing 20 g of PF_{254} silica gel (Merck); the first development was cyclohexane:benzene (1:3) and the second development was cyclohexane:benzene (1:6). Two fractions were obtained: fraction 4, 9 mg (IR (CCl_4) 1775 cm^{-1}); fraction 4′, 30 mg (1.5%) of compound 8 (mp 58–60 °C (lit.[15] mp 59–60 °C); UV (EtOH) λ_{max} 222 nm (log ϵ 4.37)).

Reaction of the Silver Salt of N-Isobutyl-N-nitrosohydroxylamine with 3,5-Dinitrobenzoyl Chloride. To the silver salt (224 mg, 1 mmol) suspended in methylene chloride (10 mL) was added 3,5-dinitrobenzoyl chloride (230 mg, 1 mmol) dissolved in methylene chloride (10 mL) at 0 °C. The reaction mixture was kept at 0 °C overnight. A sample of the crude material was filtered directly into an IR cell. Nitrous oxide, 3,5-dinitrobenzoic anhydride, isobutyl 3,5-dinitrobenzoate, and traces of *sec*-butyl 3,5-dinitrobenzoate could be detected by comparison with IR's of authentic samples. The crude material was worked up as described for the potassium salt reaction. Separation by TLC gave only isobutyl 3,5-dinitrobenzoate and *sec*-butyl 3,5-dinitrobenzoate in reasonable quantities (46 mg, 17% yield); the iso/sec ratio was ~9.

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