Synthesis and Decomposition of the *N*-Alkyl-*N*-nitro-*O*-benzoylhydroxylamines

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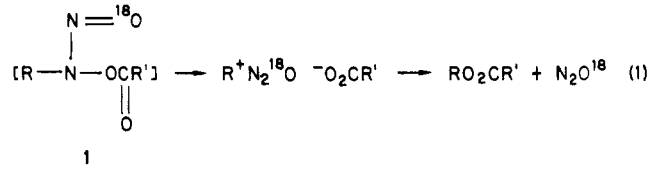
Nitration of *N*-alkyl-*O*-benzoylhydroxylamines yields the corresponding *N*-nitro derivatives. At modest temperatures these compounds decompose to yield alkyl benzoates, alkenes, benzoic acid, and nitrous oxide. In the case of primary alkylnitrohydroxylamines, nitroalkanes and alkyl nitrates are also formed. The alkyl benzoates are products of ionic reactions since skeletal rearrangements characteristic of carbonium ions occur. The insensitivity of the rates of decomposition to solvent polarity suggests that the rate-determining step is a rearrangement rather than direct ionization.

We have shown in earlier studies that *N*-alkyl-*N*-nitroso-*O*-acylhydroxylamines (**1**) yield carbonium ion derived products; the pathway shown in eq 1 is followed.[1]



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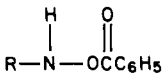
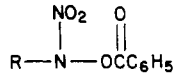
The *N*-nitrosohydroxylamines must be prepared in situ as they are unstable, decomposing as formed even at −50 °C. Since we have found in various deamination series that *N*-nitro compounds are more stable than their corresponding *N*-nitroso analogues,[2] we turned to the *N*-alkyl-*N*-nitro-*O*-acylhydroxylamines. These compounds would be of special interest if they were able to produce a carbonium ion in the rate-determining step. In the present article, we describe the synthesis, isolation, and decomposition of this new class of compounds.

Synthesis. *N*-Isobutyl-*O*-benzoylhydroxylamine (**2b**) and *N*-(*tert*-butyl)-*O*-benzoylhydroxylamine (**2c**) were



2a, R = CH_3
b, R = $CH_2CH(CH_3)_2$
c, R = $C(CH_3)_3$



3a-c

prepared from isobutyl- and *tert*-butylamines and benzoyl peroxide by the method of Zinner.[3] The synthesis of the methyl analogue (**2a**) utilized the second method of Zinner[4] in which *tert*-butyl *N*-methyl-*N*-hydroxycarbamate is treated with benzoyl chloride, and the product is partially hydrolyzed.

Several methods were tried for the nitration of the acylhydroxylamines (**2**). Nitration of **2b** with nitric acid in acetic anhydride[5] gave only a small amount of the desired nitrohydroxylamine (**3b**), and an attempted nitration of **2b** with acetone cyanohydrin nitrate[6] was unsuccessful. Nitronium salts such as nitronium tetrafluoroborate and nitronium hexafluorophosphate[7] did yield the *N*-alkyl-*N*-nitro-*O*-benzoylhydroxylamines (**3**), albeit with complications. The reaction proceeded best when the acylhydroxylamines were treated with 2 equiv of nitronium salt in methylene chloride in the presence of 10 equiv of solid sodium carbonate. Less nitronium salt led to recovery of starting material, whereas a three or larger molar excess, with **2b**, e.g., gave a mixture of butyl benzoates as the major product; nitration of the aromatic ring was also observed in this case. The direct formation of esters during the nitration step may stem from N-nitrosation since we have found that *N*-alkyl-*N*-nitroso-*O*-acylhydroxylamines (**1**) rapidly form nitrous oxide and alkyl esters at temperature below 0 °C (eq 1).[1] Competing nitrosation by nitronium salts has been noted before; the nitration of alkyl ureas with nitronium salts gives *N*-nitrosoureas predominantly.[8] Further, Gidaspov et al.[9] have found nitrosation to compete with nitration in the reaction of secondary amines with nitronium tetrafluoroborate. They proposed that reduction of the NO_2^+ ion by the amine would yield N_2O_4, a nitrosating agent.[10] Although the Russian authors were able to substantially decrease the amount of competing nitrosation by running the reactions at −40 °C, the nitration of **2b** with nitronium tetrafluoroborate at −78 °C and at 25 °C gave similar yields of **3b** (accompanied in each case by isobutyl benzoate).

The structures of the *N*-nitrohydroxylamines (**3a-c**) follow from the method of synthesis, the elemental analyses, and the physical data. The IR spectra of the nitroacylhydroxylamines show a carbonyl band at ca. 1780 cm^{-1}, shifted from the absorption at 1720 cm^{-1} observed for the parent hydroxylamines (**2**). Similar shifts to higher frequency have been observed in the urea series (from ca. 1650 for the parent urea to ca. 1710 cm^{-1} for the *N*-nitroureas),[7] in the carbamate series (from 1730 for the parent to a doublet at ca. 1740 and 1770 cm^{-1} for the *N*-nitro carbamates),[11] and in the amide series (from 1685 for amides to 1715 cm^{-1} for the *N*-nitro amides).[11] The IR spectra of the nitrohydroxylamines (**3**) have, further, a strong absorption at ca. 1605 cm^{-1} for the asymmetric stretch of the $N-NO_2$ group.[7,11] Similar frequencies have been observed for the latter group in the *N*-nitrocarbamates (ca. 1580 cm^{-1}),[11] the *N*-nitroamides (ca. 1570 cm^{-1}),[11] and the *N*-nitroureas (ca, 1550 cm^{-1}).[7] The NMR

(1) 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. Also: White, E. H.; Ribi, M.; Cho, L. K.; Egger, N.; Dzadzic, P. M.; Todd, M. J. *J. Org. Chem.*, second paper in this series.
(2) White, E. H.; Dolak, L. A. *J. Am. Chem. Soc.* **1966**, *88*, 3790.
(3) Zinner, G. *Arch. Pharm. (Weinheim, Ger.)* **1963**, *296*, 57.
(4) Zinner, G.; *Arch. Pharm. (Weinheim, Ger.)* **1969**, *302*, 916.
(5) White, E. H.; Grisley, D. W. *J. Am. Chem. Soc.* **1961**, *83*, 1191.
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(8) White, E. H.; Ryan, T. J.; Hahn, B. S.; Erickson, R. H. *J. Org. Chem.*, third paper in this series.
(9) Gidaspov, B. V.; Ilyushin, M. A.; Golod, E. L. *Zh. Org. Khim.* **1977**, *13*, 11.
(10) White, E. H.; Feldman, W. R. *J. Am. Chem. Soc.* **1957**, *79*, 5832.
(11) White, E. H.; Chen, M. C.; Dolak, L. A. *J. Org. Chem.* **1966**, *31*, 3038. 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.; Field, K. W. *J. Am. Chem. Soc.* **1975**, *97*, 2148-2153.

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Table I. Thermal Decomposition Products of the *N*-Alkyl-*N*-nitro-*O*-benzoylhydroxylamines (3a–c)

$RN(NO_2)O_2CC_6H_5$ R	solvent[a]	yields, % $ROC(O)C_6H_5$	$C_6H_5CO_2H$	RNO_2	other
Me (3a)	CCl_4	34	36	17[b]	N_2O/NO (16/1), CH_3ONO_2[b]
i-Bu (3b)	CCl_4	11–17	52–56		*t*-Bu benzoate (1%), *sec*-Bu benzoate (2%), N_2O/NO (16/1)
i-Bu	neat	15	54		*t*-Bu benzoate (5%), *sec*-Bu benzoate (3%), isobutene (59%)[c]
i-Bu	$CDCl_3$	30		20	
i-Bu	CF_3CH_2OH (97%), H_2O (3%)[d]				CF_3CH_2O-*t*-Bu, *t*-BuOH (mol ratio = 2/1)
i-Bu	CF_3CH_2OH (87%), H_2O (13%)[d]				ether/alcohol ratio = 1/1
t-Bu (3c)	CCl_4	30		*e*	isobutene (50%)
	$CDCl_3$	14		*e*	isobutene (37%)
	$CDCl_3$[f]	16			isobutene (40%)

[a] Temp 77 °C, except where noted. [b] Compared to authentic samples by GLC. [c] Traces of other butenes were found by GLC. [d] v/v. [e] 2-Methyl-2-nitropropane was detected in trace amounts by IR and NMR. [f] Temp 30 °C.

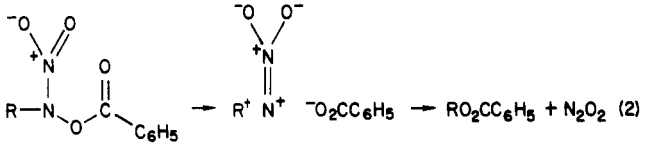
Table II. Decomposition Half-Lives of the *N*-Alkyl-*N*-nitro-*O*-benzoylhydroxylamines (3a–c)

R	solvent	temp, °C	half-life, h
CH_3 (3a)	CCl_4	80	~1
i-Bu (3b)	$CDCl_3$	82	1.3
	CD_3CN	82	2.0
	CF_3CH_2OH, H_2O (97/3)[a]	80	1.2
	CF_3CH_2OH, H_2O (87/13)[a]	80	1.3
t-Bu (3c)	$CDCl_3$	80	0.04
	$CDCl_3$	30	22

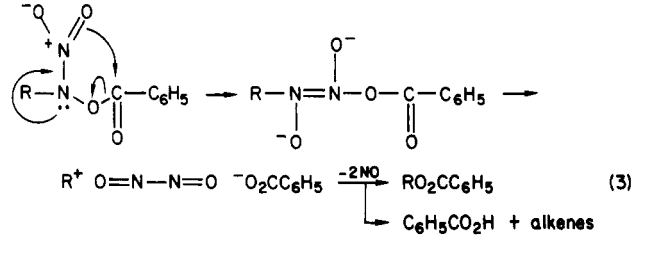
[a] v/v.

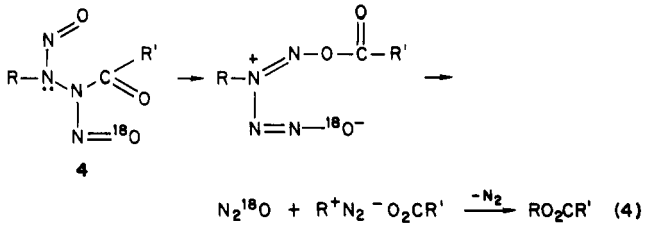
spectra of the nitrohydroxylamines are fully consistent with the assigned structures.

Decomposition Rates. We initially assumed that the nitrohydroxylamines would decompose via a mechanism similar to that followed by the *N*-alkyl-*N*-nitroso-*O*-acylhydroxylamines; tracer studies of the nitroso analogues showed that a simple dissociation was involved (eq 1).[1] The nitro analogues (3a–c) proved to be more stable and their decomposition proved to be more complex than the simple extrapolation of eq 1 to eq 2 would lead one to suspect.

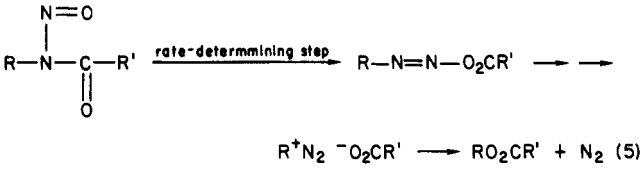


An alternative reaction pathway involving a prior rearrangement (and probably a lower energy pathway for NO formation) was also considered for the reaction (eq 3). A

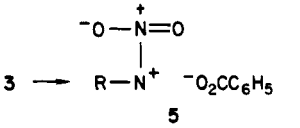




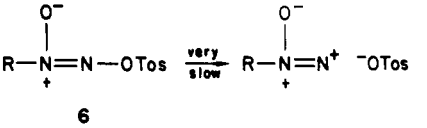
similar rearrangement had been observed in the decomposition of a dinitrosohydrazide (4) (eq 4).[12] Where slow rearrangements are involved in deamination, as in the decomposition of the *N*-nitrosoamides (eq 5), the reaction rates are not sensitive to the electronic nature of R or R′ or to solvent polarity; the reaction rates are increased by bulky R and R′ groups, however.[13] In the present case,



the *N*-nitrohydroxylamine decomposition rates showed very little change with solvent polarity (Table II); the *tert*-butyl/isobutyl rate factor of 30 is also small compared to the corresponding ratio observed in the solvolysis of alkyl bromides, for example.[14] We conclude, therefore, that the *N*-nitrohydroxylamines decompose following a rearrangement, as illustrated in eq 3. The failure of the direct mode of decomposition may stem from the lack of resonance stabilization of the proximal positive charge in 5, representing a probable intermediate in the decompo-

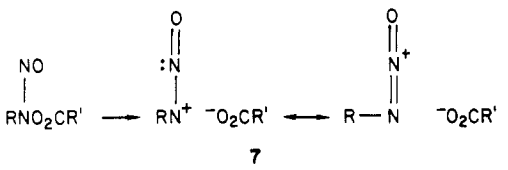


sition mode illustrated in eq 2. A similar effect of full coordination β to a developing charge is presumably responsible for the remarkable stability of the (tosyloxy)-dimide *N*-oxides (6).[1,15] In contrast, the corresponding



species (7) from the nitroso analogue (1) is stabilized by resonance and readily formed.

(12) Ellis, W. D. Ph.D. Thesis, The Johns Hopkins University, 1980.
(13) White, E. H.; Aufdermarsh, C. A. *J. Am. Chem. Soc.* **1961**, *83*, 1174. White, E. H. *J. Am. Chem. Soc.* **1954**, *76*, 4497.
(14) The *tert*-butyl/isobutyl rate factor for the solvolysis of the bromides in ethanol at 55 °C is 10^3. Streitwiesser, A., Jr. "Solvolytic Displacement Reactions"; McGraw-Hill Book Co., Inc.: New York, 1962.
(15) 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. See also ref 1. Note that the isomeric tosyl derivative (corresponding to the acyl analogue 1) is unstable (Freeman, J. P.; Lillwitz, L. D. *J. Org. Chem.* **1970**, *35*, 3107–3110).



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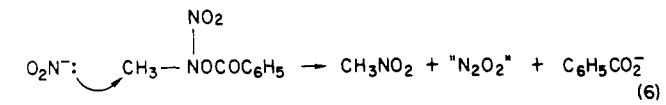
The reaction half-lives were found to be somewhat variable from run to run by a factor of approximately two. Proton and free radical supplying impurities were not the causes of the variability since the decompositions of the methyl compound (**3a**) in carbon tetrachloride with no addend, with added hydrogen chloride, and with added benzoyl peroxide all showed the same half-life within that error factor.

Reaction Products. The formation of carboxylate esters in these reactions (Table I) and especially the formation of the isomeric alkyl esters (from **3b**) indicate that carbonium ions are reaction intermediates (eq 3). The isomer distribution in the butyl benzoates from **3b** is quite close to that observed in the ionic decomposition of *N*-nitroso-*N*-isobutylbenzamide, which decomposes via similar intermediates (eq 5).[16] The decomposition products of the *tert*-butylnitrohydroxylamine (**3c**) may be readily accounted for on this basis (Table I and eq 3).

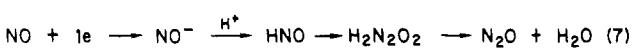
The decompositions of the primary alkylnitrohydroxylamines (**3a,b**) are considerably more complex. Nitrogen dioxide was observed in decompositions in sealed, evacuated tubes, conditions under which the very rapid formation of nitrogen dioxide from nitric oxide and oxygen is not possible. Further, nitroalkanes are formed, and also, in the case of the methyl compound **3a**, the alkyl nitrate. Displacements on primary centers are facile reactions, and possibly a direct displacement occurs in the formation of the nitroalkanes (e.g., eq 6) and in the formation of methyl



(6)

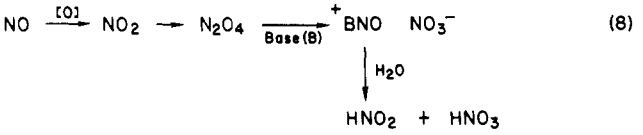
nitrate. Free radical reactions do not appear to be involved since the decomposition of **3b** in chloroform did not yield isobutane and the decomposition in carbon tetrachloride did not produce isobutyl chloride; both products would have been expected had isobutyl radicals been formed.[17] On the other hand, any free radicals formed may well have been scavenged by the nitric oxide (and nitrogen dioxide) produced.

One of the more perplexing aspects of the nitrohydroxylamine decompositions is the fate of the "N_2O_2" formed (eq 3). Instead of the expected nitric oxide, nitrous oxide was the major gas molecule formed even when the gas formed in sealed tubes was transferred (via break-off seals) directly into a mass spectrometer. Further, in several runs on neat **3b** at 80 °C and under vacuum, the volatiles were pumped off during the decomposition, trapped with liquid nitrogen, and subsequently allowed to expand into a gas IR cell; some nitric oxide was detected, but >90% of the material was nitrous oxide. Searches for isobutyraldehyde and isobutene epoxide in the decomposition of **3b** were negative, suggesting that an oxygen atom donation by the "N_2O_2" was not occurring.[18] Nitric oxide reacts rapidly with organic compounds[19] to produce nitrous oxide, possibly as shown in eq 7. Most of the nitric oxide formed



(7)

in the decomposition (eq 3) could, in principle, be converted into nitrous oxide in this way; however, our control runs with several products of the decomposition indicate that the conversion of nitric oxide into nitrous oxide is not fast enough with those compounds to account for the formation of all of the nitrous oxide in the decomposition of the nitrohydroxylamines. On the other hand, it is possible that exceptionally good reducing agents may be present in the complex mixture of reaction products from **3a–c**. Finally, the nitrite and nitrate ions, which may be precursors of the nitroalkanes and alkyl nitrates formed in the primary alkyl cases may stem from the reactions shown in eq 8.[10]



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In summary, the *N*-alkyl-*N*-nitro-*O*-acylhydroxylamines (**3a–c**) decompose via intermediates closely related to those involved in the decomposition of nitrosoamides, nitroamides, and related compounds. Since a reactive gas, NO, is produced in the decomposition of the nitrohydroxylamines (**3a–c**), a wider spectrum of products is formed as compared to, e.g., the nitrosoamide case.

Experimental Section

General Methods. Spectra were measured on a Perkin-Elmer Model 457A IR spectrophotometer, Varian A-60, and Jeol JNM-MH-100 NMR spectrometers (with tetramethylsilane as an internal standard), a Varian Techtron 635 UV–vis spectrophotometer, and a Hitachi-Perkin-Elmer RMU-6E mass spectrometer (70 eV). Gas-liquid chromatography was performed on a Varian Aerograph Model 1800 instrument. Melting points were obtained on a Thomas-Hoover apparatus and are reported uncorrected. Elemental analyses were determined by Galbraith Laboratories, Inc. of Knoxville, TN.

***N*-Alkyl-*O*-benzoylhydroxylamines (2a–c).** *N*-Isobutyl-*O*-benzoylhydroxylamine (**2b**) and *N*-(*tert*-butyl)-*O*-benzoylhydroxylamine (**2c**) were prepared by the method of Zinner[3] from the reaction between dibenzoyl peroxide and the appropriate amine at 0 °C. The products were first isolated as their hydrochloride salts and then neutralized by dilute aqueous NaOH to give **1b** and **1c** in 20–30% overall yields (based on dibenzoyl peroxide). *N*-Methyl-*O*-benzoylhydroxylamine (**2a**) was prepared by the method of Zinner;[4] *tert*-butyl *N*-hydroxy-*N*-methylcarbamate and benzoyl chloride in the presence of triethylamine yielded *N*-(*tert*-butyloxycarbonyl)-*N*-methyl-*O*-benzoylhydroxylamine which was treated with HCl gas, and the product (**2a**·HCl) was neutralized with dilute aqueous $NaHCO_3$ to give **2a** in ca. 70% overall yield. The use of dilute aqueous NaOH to neutralize the hydrochloride salt of **2a** resulted in hydrolysis of the benzoyl group.

(**2a**): IR (CH_2Cl_2) 3240 and 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.91 (s, 3 H), 7.40 (m, 3 H), 7.90 (m, 3 H) (C_6H_5 + NH). The hydrochloride: mp 135–136 °C dec (lit.[3] mp 123–124 °C); IR (KBr) 1770 cm^{-1} (lit.[3] 1770).

(**2b**): bp 58–65 °C (0.04 torr); IR (CCl_4) 1725; ^1H NMR ($CDCl_3$) δ 1.00 (d, J = 6 Hz, 6 H), 1.95 (sept, J = 6, 1 H), 2.98 (d, J = 7 Hz, 2 H), 7.23–7.70 (m, 3 H), 7.77–8.23 (m, 3 H). The hydrochloride: mp 120–128 °C (lit.[3] mp 120–125 °C); IR (Nujol) 1760 cm^{-1} (lit. 1760 cm^{-1}).

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(18) White, E. H.; Wilson, A. A.; Anhalt, J. P.; Baumgarten, R. J.; Choca, J. I. *J. Org. Chem.* **1982**, *47*, 2892–2896 (ref 22). White, E. H.; Egger, N. *J. Am. Chem. Soc.* **1984**, *106*, 3701–3703.

(19) Brown, J. F., Jr. *J. Am. Chem. Soc.* **1957**, *79*, 2480–2488. The production of nitrous oxide in the reaction of nitric oxide with isobutylene was apparently not noted by Brown. Nitrous oxide has been reported in the reaction of nitric oxide with 1,3- and 1,4-hexadiene (Shaw, R.; Cruickshank, F. R.; Benson, S. W. *J. Phys. Chem.* **1967**, *13*, 4538–4543).

(2c): ^{1}H NMR ($CDCl_3$) δ 1.22 (s, 9 H), 7.20–7.57 (m, 4 H), 7.80–8.07 (m, 2 H) [lit.[20] ($CDCl_3$) δ 1.24 (s, 9 H), 7.3–7.6 (m, 3 H), 7.99–8.09 (dd, 2 H, J = 1.8 and 7.9 Hz)].

N-Isobutyl-N-nitro-O-benzoylhydroxylamine (3b). In a nitrogen-filled flask conncected to a mineral oil bubbler, 204 mg (1.05 mmol) of N-isobutyl-O-benzoylhydroxylamine (**2b**), 1.10 g (10.5 mmol) of sodium carbonate, and 402 mg (2.10 mmol) of nitronium hexafluorophosphate were stirred at room temperature in 25 mL of dry CH_2Cl_2 (distilled from P_2O_5). After 60 min, no starting material remained by TLC (silica gel, benzene eluate) and ca. 5 mL of H_2O was added to the stirred mixture. After a few minutes, the organic layer was separated and washed with 5% aqueous sodium bicarbonate (10 mL) and then with H_2O (2 × 10 mL). After drying the organic layer with sodium sulfate, the solvent was removed on a rotary evaporator to give 162 mg (0.68 mmol, 64%) of N-nitro-N-isobutyl-O-benzoylhydroxylamine as a pale yellow liquid: IR (CH_2Cl_2) 3050, 1780, 1605 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.03 (d, J = 6.5 Hz, 6 H), 2.06 (sept, J = 6.5 Hz, 1 H), 3.87 (d, J = 6.5 Hz, 2 H), 7.50 (m, 3 H), 8.05 (m, 2 H). Analytically pure material was obtained by short-path distillation in a sublimer (ca. 2-mm path length, 40 °C oil bath, ca. 0.05 mm) to give N-nitro-N-isobutyl-O-benzoylhydroxylamine as a clear, colorless liquid. Anal. Calcd for $C_{11}H_{14}N_2O_4$: C, 55.46; H, 5.92; N, 11.76. Found: C, 55.46; H, 6.30; N, 11.65.

Old samples of nitronium hexafluorophosphate yielded isobutyl benzoate directly in these reactions. An attempted nitration of **2b** with a mixture of acetic anhydride and nitric acid produced a small amount of the desired compound (IR in CH_2Cl_2 at 1601 cm^{-1}) plus what appeared to be N-isobutyl-N-acetyl-O-benzoylhydroxylamine (IR 1675 and 1760 cm^{-1}).

N-Methyl-N-nitro-O-benzoylhydroxylamine (3a). A mixture of N-methyl-O-benzoylhydroxylamine (1.60 g, 10.6 mmol), anhydrous sodium acetate (2.50 g, 25 mmol), and methylene chloride (75 mL) was cooled to 0 °C under N_2. Nitronium hexafluorophosphate (4.73 g, 24.8 mmol) was added slowly with stirring, and the mixture was allowed to reach room temperature. After 2 h, 200 mL of water was added and the organic phase was washed with saturated sodium bicarbonate solution, then dried, and evaporated to give the nitrohydroxylamine as a yellow liquid (1.89 g, 9.64 mmol, 90%), which solidified on standing at 4 °C, mp 29–30 °C. Pure material was obtained by sublimation at 10^{-2} torr and 60 °C: mp 48–50 °C; IR (CH_2Cl_2) 3060, 1778, 1605 cm^{-1}; UV (CH_2Cl_2) λ_{max} 237 (13 300), 270 sh (2140), 280 sh (1530) nm; ^{1}H NMR ($CDCl_3$) δ 3.68 (s, 3 H) 7.55 (m, 3 H), 8.10 (m, 2 H); mass spectrum, m/e (relative intensity) 28 (75), 30 (35), 77 (51), and 105 (100, C_6H_5CO). Anal. Calcd for $C_8H_8N_2O_4$: C, 48.98; H, 4.11; N, 14.28. Found: C, 49.06; H, 4.10; N, 14.13. More vigorous nitration led to ring nitrated compounds (IR 1530 and 1350 cm^{-1}).

N-(tert-Butyl)-N-nitro-O-benzoylhydroxylamine (3c). The title compound was prepared by using the method described for the isobutyl analogue (**3b**); it was purified by sublimation, followed by recrystallization from hexane: mp 35–35.5 °C (yield, 17%); IR (film) 1770, 1600, and 1450 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.50 (s, 9 H), 7.23–7.67 (m, 3 H), 7.90–8.17 (m, 2 H). Anal. Calcd for $C_{11}H_{14}N_2O_4$: C, 55.46; H, 5.92; N, 11.76. Found: C, 55.83; H, 5.94; N, 11.69.

General Prccedure for Decompositions. Unless stated otherwise, all decompositions were carried out in glass tubes that were sealed under vacuum after degassing by three freeze–thaw cycles at ca. 0.01 mm. The sealed tubes were fully immersed in a thermostated water bath. The kinetics of the decompositions were followed in the NMR by the disappearance of the following signals: the methyl singlet at δ 3.60 for **2a**, the methylene doublet at δ 3.87 for **2b**, and the t-Bu singlet at δ 1.50 for **2c**.

Decomposition of N-Nitro-N-methyl-O-benzoylhydroxylamine (3a). A solution of the title compound (250 mg, 1.3 mmol) in 2.5 mL of CCl_4 was degassed and sealed off in a glass tube. After heating at 85 °C for 12 h, a brown gas (NO_2) was observed above the liquid in the tube. The gas was allowed to expand into an IR cell; the spectrum showed strong bands at 2220 (N_2O), 1730 (N_2O_4), 1695, 1450, 1280, 1108, 1024, and 710 cm^{-1}. The liquid remaining in the tube was diluted with a few more milliliters of CCl_4 and the solution was washed with aqueous saturated sodium carbonate solution (4 × 50 mL). The aqueous layers were combined, acidified, and extracted with CH_2Cl_2 to give 56 mg (36%) of benzoic acid. The organic phase was dried over anhyrous sodium sulfate. Filtration and removal of the solvent by rotary evaporation gave 92.7 mg of an oil, the IR spectrum of which showed benzoic acid, methyl benzoate, and methyl nitrate (1640 cm^{-1}). When toluene was used as an internal standard, it was determined by NMR that 84.0 mg (34%) of methyl benzoate was present.

A second sample (20 mg) was heated to 80 °C directly inside an evacuated IR gas cell; brown fumes were formed. After 15 min, the spectrum was that of N_2O and some N_2O_4; NO was not observed. After 2 h the spectrum was similar but more intense.

A third sample of the hydroxylamine (50.0 mg) was decomposed in 1.5 mL of CCl_4 in a sealed NMR tube at 80 °C. The reaction was essentially over in 3 h, with a half-life of ca. 1 h. Final ^{1}H NMR δ 3.82 (s), 3.95 (s), 4.17 (s), 7.40 (m), 8.00 (m), and 13.00 (br s). The integration of the peaks at δ 3.82 and 13.00 (the CH_3 of methyl benzoate and the COOH of benzoic acid) and comparison to the integration of the aromatic region showed that the compounds responsible for the signals at δ 3.95 and 4.17 contained no aromatic ring. The compound resonating at δ 4.17 was identified by peak enhancement as nitromethane. Using toluene as an internal standard, the yield of nitromethane was found to be 2.5 mg (17%). IR spectra and GLC traces vs. an authentic sample confirmed the identification of the nitromethane.

A fourth sample (50 mg, 0.26 mmol) was dissolved with benzoyl peroxide (5 mg) in 1.5 mL of carbon tetrachloride and the solution was degassed at 10^{-2} torr; the glass tube was then sealed off with a torch. Upon heating to 80 °C, brown fumes (NO_2) were seen and the half-life was found to be about 1 h (based on the NMR spectra). Nitromethane was apparent from the NMR resonance at 4.17 ppm (confirmed by spiking). The principal products were nitromethane (17%) and methyl benzoate (34%). GLC at 100 °C confirmed the presence of nitromethane and methyl benzoate, while at 66 °C, a peak was seen which coeluted with methyl nitrate (prepared by the method of Black and Babers).[21] The yield of methyl nitrate is low since a resonance for this compound was not observed in the NMR spectrum of the reaction mixture (CH_3ONO_2 in $CDCL_3$ shows a singlet at 4.11 ppm).

Decomposition of N-Nitro-N-isobutyl-O-benzoylhydroxylamine (3b). The title compound (70 mg, 0.294 mmol) was decomposed in 5.5 mL of CCl_4 at 77 °C for 36 h: IR (CCl_4) strong bands at 2960, 2220, 1725, 1700, 1640, 1450, 1270, 1110, and 1025 cm^{-1}. The solution was heated to 80 °C and the volatile fraction was analyzed by GLC ($_1/^8$ in. × 6 ft 80/100 Chrom Q with 5% QF-1 as the support, temperatures column 55 °C, injector 210 °C, detector 250 °C). The volatile fraction contained seven unknowns. The nonvolatile material was washed with saturated sodium carbonate solution (2 × 20 mL). The aqueous phase was acidified with concentrated HCl and then extracted with CH_2Cl_2 (3 × 20 mL). The solvent was removed on a rotary evaporator to give 20.0 mg (0.164 mmol, 56%) of benzoic acid; the IR (CCl_4) shows strong bands at 3000, 1700, 1420, and 1290 cm^{-1}. The organic phase was analyzed by GLC (same conditions as above except column temperature 110 °C, benzophenone was the internal standard) which showed the presence of isobutyl benzoate (5.90 mg, 0.033 mmol, 11%), sec-butyl benzoate (1.16 mg, 0.0065 mmol, 2%), tert-butyl benzoate (0.52 mg, 0.0029 mmol, 1%), and four unknowns.

A second sample of **3b** (103 mg) was decomposed in a tube fitted with a break-seal at 80 °C for 20 h. The tube was connected to a mass spectrometer and cooled with liquid nitrogen; the break-seal was broken and the spectrum recorded: MS, m/e 18 (12), 28 (100), 30 (3) (NO), 44 (32) (N_2O). The spectrum was recorded next at −78 °C: MS, m/e 28 (19), 30 (12), 39 (10), 41 (26), 44 (100) 56 (16). Then the spectrum was recorded at room temperature: MS, m/e 18 (25), 27 (18), 28 (25), 29 (14), 39 (30), 41 (100) (C_3H_5), 42 (11), 43 (10), 44 (34), 55 (22), 56 (45) (C_4H_8). The residue in the glass tube was dissolved in 5 mL of CH_2Cl_2 and the solution was washed with saturated sodium carbonate (3 × 15 mL). The aqueous and organic phases were worked up

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and analyzed as above to give 28.3 mg (54%) of benzoic acid, 11.2 mg (14.5%) of isobutyl benzoate, 2.7 mg (3.5%) of *sec*-butyl benzoate, and 3.7 mg (4.8%) of *tert*-butyl benzoate.

A third sample of **3b** (99 mg) was decomposed neat at 80 °C for 20 h. the volatile portion of this decomposition was analyzed by GLC (6 ft, $^1/_8$ in., 30% $AgNO_3$/DEG on 80/100 Chrom Q, temperatures column −30 °C, injector −80 °C, detector −80 °C). Isobutylene was found to be present (0.245 mmol, 59%, by direct calibration). Trace amounts of *trans*-2-butene and of 1-butene were also found.

A fourth sample of **3b** (115 mg, 0.483 mmol) was decomposed neat at 80 °C for 20 h. The volatile portion was collected and analyzed by IR (gas phase): 3510 (m), 2980 (s), 2580 (m), 2360 (w), 2240 (s) (N_2O), 2210 (s) (N_2O), 1900 (w) (NO), 1670 (m), 1310 (s), 890 (s) cm^{-1}. The spectrum showed that the ratio of N_2O:NO was ca. 16:1. The residue was worked up and anlyzed by GLC to search for the presence of 1,2-epoxyisobutane; none was found. In a similar experiment, neat **3b** was heated to 80 °C at 0.01 torr for 6 h while being pumped on through a "U" tube cooled with liquid nitrogen. The contents of the "U" tube were allowed to expand into a gas IR cell as the tube was warmed to room temperature. Only N_2O was detected (2240 and 2210 cm^{-1}). Tests showed that nitric oxide could be condensed and transferred essentially quantitatively in this manner.

A fifth sample of **3b** (80 mg) was decomposed in 0.5 mL of $CDCl_3$ in a sealed NMR tube at 80 °C. The half-life was found to be 1.3 h. The yield of isobutyl benzoate (methylene doublet at δ 4.09) and 1-nitro-2-methylpropane (methylene doublet at δ 4.14) was determined by NMR after the reaction was complete (Table I).

A sixth sample of **3b** (73 mg) was decomposed in 0.5 mL of CD_3CN in a sealed NMR tube at 80 °C. The half-life was found to be 2.0 h. The yield of ester and nitroalkanes was determined by NMR (Table I).

A seventh sample of **3b** (44 mg) was dissolved in 0.5 mL of 97% trifluoroethanol/3% H_2O (v/v). The sample was sealed in an NMR tube and heated in an 80 °C water bath. The half-life was determined from the rate of disappearance of the doublet for the two methyls of the isobutyl group in the starting material at δ 1.05. The half-life was found to be 1.2 h. The major products were *tert*-butyl trifluoroethyl ether (*t*-Bu singlet at δ 1.27) and *tert*-butyl alcohol (*t*-Bu singlet at δ 1.23) in a ratio of ca. 2:1.

An eighth sample of **3b** (40 mg) was decomposed in 0.5 mL of 87% trifluoroethanol/13% H_2O (v/v) in an NMR tube at 80 °C. The half-life was found to be 1.3 h. The major products were *tert*-butyl trifluoroethyl ether and *tert*-butyl alcohol (in a ratio of ca. 1:1).

A ninth sample decomposed in benzene at 60 °C in a degassed and sealed glass tube yielded isobutyl benzoate (48%) and isobutylene (14%); a small spike was seen in the NMR spectrum at δ 1.22 suggesting the formation of <1% *tert*-butylbenzene. No signal was detected at δ 2.34 (CH_2 of isobutylbenzene).

Decomposition of *N*-(*tert*-Butyl)-*N*-nitro-*O*-benzoylhydroxylamine (3c). A sealed NMR tube containing 80 mg of **3c** in 0.5 mL of CCl_4 (containing ca. 0.3% Me_4Si) was heated at 80 °C for 15 min, at which time the NMR spectrum showed the decomposition was complete. The final spectrum showed the presence of *tert*-butyl benzoate (δ 1.58, s) isobutylene (δ 1.68 (t, J = 1 Hz, 6 H), 4.55 (m, 2 H), and two small singlets at δ 1.23 and 1.27. A TLC of the final reaction mixture (silica gel, CH_2Cl_2) showed the presence of *tert*-butyl benzoate (R_f 0.52, UV), benzoic acid (R_f 0.07, UV), and 4 additional spots (two by UV, two by I_2). 2-Methyl-2-nitrosopropane was not detected by TLC.

A second sample of **3c** (51 mg in 0.5 mL of $CDCl_3$) was decomposed at 80 °C for 5 min. The tube was removed and plunged into ice water for 1 min. Then an NMR spectrum was taken which showed that the half-life was 2–3 min. The tube was returned to the water bath for 15 min more to fully decompose the sample and then the product yields were determined by NMR (Table I).

A third sample of **3c** (40 mg in 0.5 mL of $CDCl_3$) was decomposed at 30 °C. The reaction had a half-life of 22 h. The product yields were determined by NMR.

Control Reaction. Nitric Oxide. A glass tube was evacuated to 0.02 mm, then NO was introduced to a pressure of 100 mmHg. The tube was immersed in liquid nitrogen and sealed. Into a second glass tube was placed 20 mg of benzoic acid, 15 drops of isobutyl benzoate, and 15 drops of oleic acid. The tube was evacuated, NO was introduced as above, and the tube sealed. Both tubes were heated at 80 °C for 18 h. An IR spectrum of the gases after heating showed that the NO/N_2O ratio in the tube containing no organics was ca. 8:1. The gases in the tube that contained organics had an NO/N_2O ratio of ca. 2:1. When NO was heated with isobutene in a gas IR cell at 60 °C for 3 days, it was completely converted into N_2O.

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Registry No. **1b**, 92844-62-7; **1c**, 92844-63-8; **2a**, 1943-79-9; **2a**·HCl, 27130-46-7; **2b**, 92787-70-7; **2c**, 51339-03-8; **3a**, 92844-59-2; **3b**, 92844-60-5; **3c**, 92844-61-6; MeN(OH)C(O)OBu-*t*, 19889-97-5; PhC(O)Cl, 98-88-4; NO, 10102-43-9; $PhCO_2H$, 65-85-0; PhC(O)OBu-*i*, 120-50-3; *N*-(*tert*-butyoxycarbonyl)-*N*-methyl-*O*-benzoylhydroxylamine, 28330-55-4; oleic acid, 112-80-1.