Reaction of Essentially Free Benzyl Cations with Acetonitrile; Synthesis of Ethanimidic Carboxylic Anhydrides and Unsymmetrical Diacylamines

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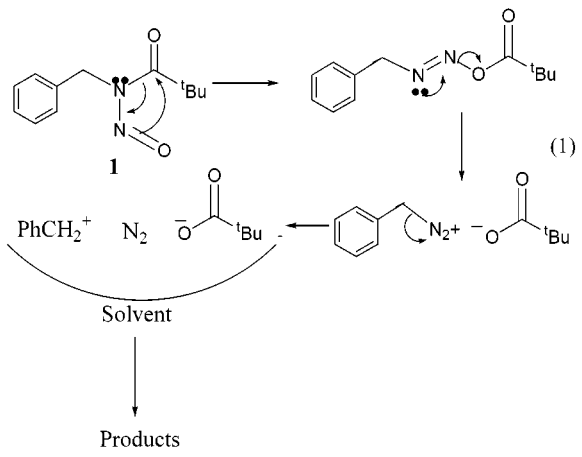
Benzyl cations were generated via the thermal decomposition of *N*-benzyl-*N*-nitrosopivalamide in acetonitrile and acetonitrile−water mixtures at 25 °C. The first-formed (primary) benzylating agent, the benzyl cation, was scavenged competitively by pivalate (trimethyl acetate) ion to yield benzyl pivalate, by acetonitrile to yield the corresponding *N*-benzylnitrilium ion, and by water (when present) to yield benzyl alcohol. The nitrilium ion underwent a cascade of reactions to yield an array of products whose identities and relative yields as a function of time were used to elucidate the mechanistic paths involved. Thus, the *N*-benzylnitrilium ion reacted with pivalate ion to yield the *Z*-isomer of *N*-benzylethanimidic pivalic anhydride, followed by its conversion into the *E*-isomer. This article appears to be the first to document compounds of this type. The *E*-isomer is labile under the reaction conditions, rearranging into *N*-acetyl-*N*-pivalylbenzylamine. In the presence of water as a diluent, a significant fraction of the nitrosoamide was hydrolyzed to benzyl alcohol; hydrolysis of the nitrilium ion yielded *N*-benzyl acetamide. The yield of hydrosylates was directly proportional to the mole fraction of water in the medium.

Introduction

N-Alkyl-*N*-nitrosoamides, e.g., *N*-benzyl-*N*-nitrosopivalamide (**1**), decompose to produce very short-lived nitrogen-separated ion pairs (NSIPs) (**2**) (eq 1).[1] The



unimolecular process[2] generates an ion pair containing a carbenium ion, which is essentially unsolvated and probably represents as free and reactive a carbenium ion as can be formed in the liquid phase.[1,3a−c] The nitrogen molecule shields the carbenium ion from the counterion initially, allowing for surprisingly efficient trapping of the carbenium ions by molecules in the solvent cage.[1,3a−c] No catalysts or other reagents are required for carbocation formation; consequently the reaction is a "clean" one, and only a limited number of low-yielding competing reactions occur.[1a,3c]

The counterion and the solvent compete for the carbenium ion in irreversible reactions, and the high speed of the counterion−carbocation reaction to yield ester, limited by the rate of diffusion of N_2 into the medium, results in the carbenium ion having only a limited time to react with the medium before being scavenged by the counterion;[1a,c] thus, reaction conditions can usually be arranged to lead to kinetically determined products.[1a,c,3a] In these reactions, the yields of solvent-derived products (SDPs) increase with the reactivity of the cation, with the nucleophilicity of the solvent, and in an inverse manner with the nucleophilicity of the counterion.[1a,3d]

In earlier work, it was shown that the decomposition of *N*-benzyl-*N*-nitrosotrifluoromethanesulfonamide in CH_3CN produces *N*-benzylacetonitrilium trifluoromethanesulfonate in quantitative yield. Ostensibly, the nitrilium salt arose principally via the N_2-separated benzyl cation/triflate ion ion pair; some (secondary) benzylation by the labile benzyl triflate was also involved.[1b] The present study was aimed, principally, at the trapping of benzyl cations by acetonitrile in the presence of a more nucleophilic carboxylate ion ($n_{pivalate} \approx 2.7$; $n_{triflate} < 0$)[4] and the investigation of the cascade of subsequent reactions and rearrangements.

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† This paper is dedicated to the memory of Professor Emil H. White, 1926−1999.

(1) (a) Darbeau, R. W.; White, E. H.; Song, F.; Darbeau, N. R.; Chou, J. C. *J. Org. Chem.* **1999**, *64*, 5966. (b) White, E. H.; De Pinto, J. T.; Polito, A. J.; Bauer, I.; Roswell, D. F. *J. Am. Chem. Soc.* **1988**, *110*, 3708. (c) White, E. H.; Field, K. W.; Hendrickson, W. H.; Dzadzic, P.; Roswell, D. F.; Paik, S.; Mullen, P. W. *J. Am. Chem. Soc.* **1992**, *114*, 8023. (d) White, E. H.; McGirk, R. H.; Aufdermarsh, C. A.; Tiwari, H. P.; Todd, M. J. *J. Am. Chem. Soc.* **1973**, *95*, 8107.

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(3) (a) White, E. H.; Darbeau, R. W.; Chen, Y.; Chen, D.; Chen, S. *J. Org. Chem.* **1996**, *61*, 7986. (b) Darbeau, R. W.; White, E. H. *J. Org. Chem.* **1997**, *62*, 8091. (c) Darbeau, R. W. Ph.D. Thesis, The Johns Hopkins University, Baltimore, Maryland. (d) The yield of SDP also rises but to a lesser extent with decreasing temperature and when the nitrogenous molecule is N_2O rather than N_2.[1a,3c]

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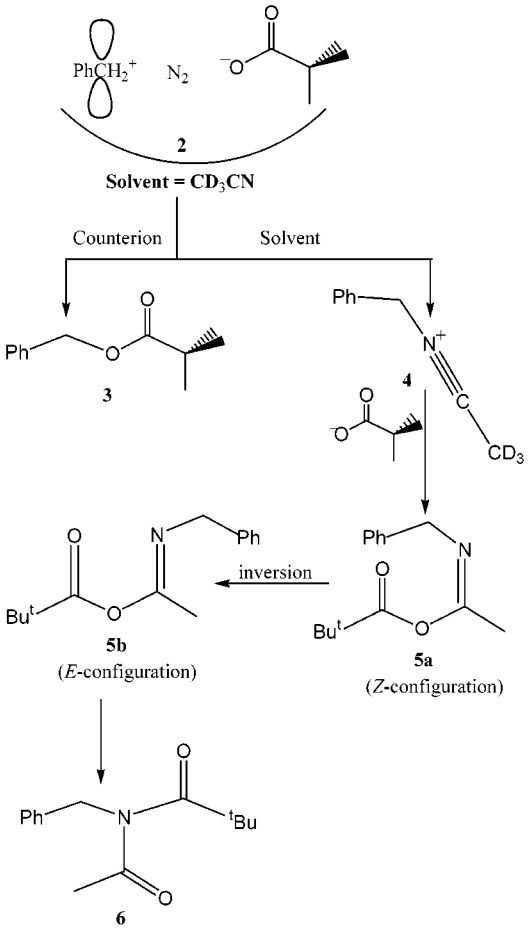
Table 1. Time-Dependent Product Distribution from the Decomposition of *N*-Benzyl-*N*-nitrosopivalamide (1)[a] in CD_3CN at 25 °C

	relative amounts (%)[b]					
			ethanimidic anhydrides			
reaction time (min)	nitrosoamide **1**	benzyl pivalate **3**	**5a**; *Z*	**5b**; *E*	diacyl benzylamine **6**	benzyl alcohol **9**
5	74	23	1.8	0.6	0.0	0.6
15	71	22	2.0	3.0	1.0	1.0
40	42	43	7.0	4.0	3.0	1.0
70	18	58	2.0	6.0	13	3.0
24 h[c]	0	72	0	0	23	5.0

[a] Concentration ≈ 0.045 M. [b] Average of triplicate runs; standard deviation ≈ 0.5. [c] Product distribution was unchanged after a further 2 days at 25 °C.

Chart 1. Reaction Pathway for the Decompositionof *N*-Benzyl-*N*-nitrosopivalamide in CD_3CN

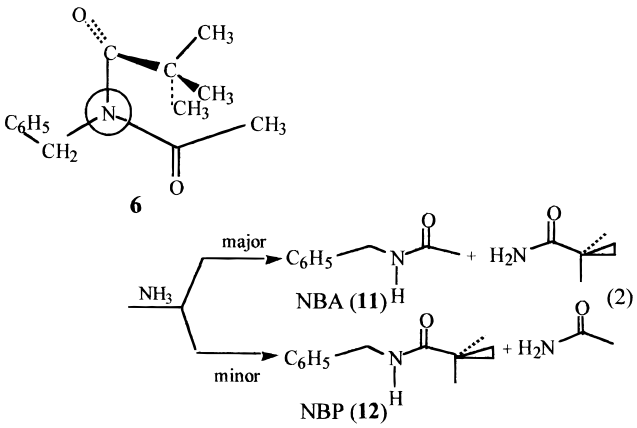


Results and Discussion

N-Benzyl-*N*-nitrosopivalamide (**1**) was used as the source of the benzyl cation because of its convenient rate of decomposition at 25 °C ($t_{1/2}$ is ~30 min in CD_3CN) arising from steric acceleration of the rearrangement step (eq 1) by the *tert*-butyl group.[2] The rapid decomposition of nitrosoamide (**1**) at 25 °C under neutral conditions permits spectroscopic observation of thermolabile, transient intermediates.

The product distribution as a function of time (Table 1) was followed by ^1H NMR spectroscopy. With time, a steadily increasing amount of benzyl pivalate (**3**) was observed along with a small amount of benzyl alcohol (vide infra) (Table 1); in addition, signals were observed at δ 5.21, 4.38, and 4.82. The sum of the integrals for the latter three signals—normalized for the extent of the reaction—was essentially constant. These integrals varied in a manner suggesting that the δ 4.38 signal arose from the compound responsible for the δ 5.21 signal, and that the former compound was converted, in turn, to the compound responsible for the δ 4.82 signal. After 24 h, the decomposition of the nitrosoamide was complete and both intermediates (at δ 5.21 and 4.38) had been fully converted into the δ 4.82 compound, which was stable under the reaction conditions (Table 1).

On the basis of the probable mechanism of the decomposition (eq 1 and Chart 1) it seemed reasonable that the δ 4.82 compound was *N*-acetyl-*N*-pivalylbenzylamine (**6**). The structure of the diacylamine (**6**) was confirmed, in part, through NMR comparison with samples of **6** prepared from the reaction of *N*-benzyl pivalamide and acetyl chloride. Chromatography on silica gel afforded a colorless oil whose physical data and elemental analysis were consistent with the diacylamine structure assigned (**6**). Further, the addition of 20 equiv of NH_3 to diacylamine (**6**) led to the diminution and eventual disappearance of the signal assigned to **6** and the simultaneous appearance of signals due to *N*-benzylacetamide (NBA, **11**) and *N*-benzylpivalamide (NBP, **12**) (eq 2 and Table 2).



Imidic anhydrides **5a,b** are reasonable products to expect from the decomposition of nitrosoamide **1** in acetonitrile because the benzyl cation is known to react with CH_3CN to form the nitrilium ion **4**, which is stable in the presence of weakly nucleophilic counterions.[1b]

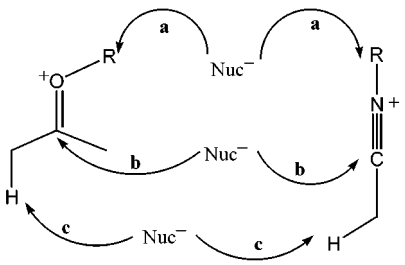
(4) The nucleophilicity, *n*, of a reagent is defined within the linear free energy relationship, $\log(k/k_o) = sn$", where *k* is the rate constant for the S_N2 reaction of a substrate (chosen by Swain and Scott to be MeI) with a particular nucleophile at 25 °C.; k_o is the corresponding rate constant with a standard nucleophile (chosen by Swain and Scott to be water). The term *s* is a parameter that gauges the sensitivity of the substrate toward variation in the nucleophiles. Swain, C. G.; Scott, C. B. *J. Am. Chem. Soc.* **1953**, *75*, 141.

Table 2. Time-Dependent Product Distribution in the Reaction of Ammonia with Diacylamine (6)[a−d]

time (h)	benzyl pivalate (**3**)	diacyl benzylamine (**6**)	benzyl alcohol (**9**)	*N*-benzyl acetamide (**11**)	*N*-benzyl pivalamide (**12**)
0	72	23	5	0	0
2	74	8.0	5	9	4
24[e]	73	0.0	5	15	7

[a] Average of duplicate runs; standard deviation ≈ 0.5%. [b] Acetamide and pivalamide must have been present but were not observed (see text). [c] Twenty equivalents of ammonia were used. [d] Obtained after total decomposition (24 h) of nitrosoamide (**1**) in dry acetonitrile; the diacylbenzylamine (**6**) was the only reactive compound present. [e] Product distribution was unchanged after a further 3 days at 25 °C.

Chart 2. Sites of Nucleophilic Attack on Onium Ions[5]



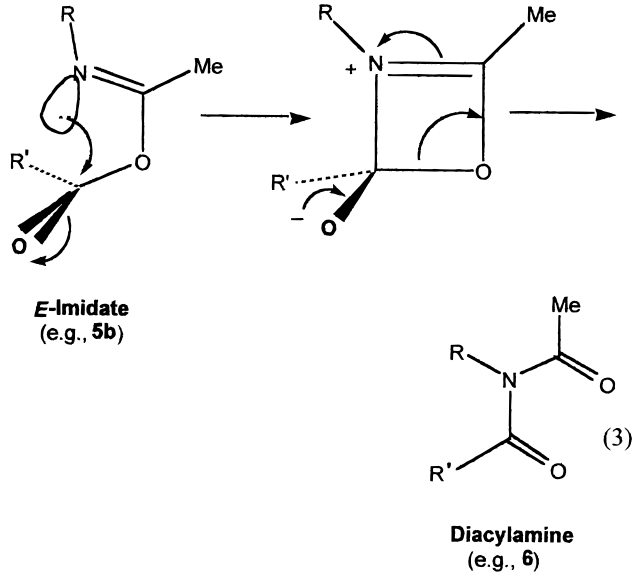
Major path = b

Additionally, the pivalate ion is the major nucleophile in the present system that leads to observable product. Consequently, nitrilium ion/pivalate ion reaction would be expected. In general, reactions between nucleophiles and onium ions appear to be dominated by reaction of the nucleophile at the carbon of the carbon−heteroatom multiple bond (path b, Chart 2).[5] Nucleophilic displacements (path a, Chart 2) and deprotonations (path c, Chart 2) appear to be minor reactions.[5]

Support for the structures of the imidic anhydrides **5a,b** was obtained as follows: (1) The amounts of the imidic anhydrides rose and then fell with time, while that due to the diacylamine (**6**) rose steadily (Table 1). (2) When the integrals of the benzyl signals for all the benzyl compounds present from time = 0 to time = 24 h were prorated to 2 hydrogens, the percentage of the sum of the integrals (benzyl) for **5a**, **5b**, and **6** was constant (24.7 ± 1.4%), which indicates the conversion of **5a,b** into the diacylamine (**6**).

The reaction of pivalate ion (as in path b, Chart 2) with the nitrilium ion (**4**) can lead to two geometric isomers. The product distribution as a function of time (Table 1) shows that the *Z*-isomer is formed initially and subsequently converts to the *E*-form. The stereochemistry of this addition is analogous to that observed in the reactions of good nucleophiles, e.g., methoxide and mercaptides, with acetylenes,[6a] which give the *trans* product.[6] In the present case, the *Z*-isomer is formed more rapidly than the *E*-isomer despite the greater steric strain in the former. Minimization of electronic repulsion between the lone pair of electrons on the nucleophile and the developing negative charge in the sp^2-hybrid of the distal vinylic carbon is probably responsible for this observation. The **5a** → **5b** rearrangement probably occurs via inversion through nitrogen.[7]

The rearrangement of the imidic anhydride **5b** to the diacylamine (**6**) requires overlap of the unshared electrons of nitrogen with the π^* orbital at the carbonyl carbon (eq 3) (a similar orientation of the nitrosyl oxygen



and the carbonyl carbon is required for rearrangement of *N*-nitrosoamides).[1−3] These requirements are met in the *E*- but not in the *Z*-configuration.

The present manuscript appears to be the first to document the formation, stability, interconversion, and rearrangement of imidic carboxylic anhydrides.[8]

Unsymmetrical Diacylamines. Symmetrical diacylamines are readily prepared from the corresponding amine and acid chlorides or anhydrides;[9a] they can also be prepared from amides if the entering acyl group is the same as that already present in the amide.[9b] Unsymmetrical diacylamines, however, are prepared with difficulty and in low yield by the conventional approaches because acylation/deacylation equilibria favor the formation of the symmetrical diacylamine possessing the acyl group of the acylating species.[9] For example, refluxing of NBP with acetyl chloride (∼51 °C) or acetic anhydride (∼140 °C) led to diacetylbenzylamine, even in pyridine as solvent;[3c] with gentle heating (30−50 °C), no reaction occurred.[3c] NBA does not react with pivalyl chloride at 25 °C (72 h) or under reflux (107 °C) in the presence or absence of base (Na_2CO_3 and/or pyridine).[3c] Steric hindrance involving the bulky pivalyl group is probably operating in these cases.

(5) Perst, H. *Oxonium Ions in Organic Chemistry*; Verlag Chemie Academic Press: New York,1971; pp 58−59.

(6) (a) Truce, W. E. Nucleophilic Reactions of Thiols and Acetylenes and Chloroethylenes. In *Organic Sulfur Compounds*; Kharasch, N., Ed.; Pergamon Press Ltd.: London, 1961; Vol. 1, (b) Miller, S. I. *J. Am. Chem. Soc.* **1956**, *78*, 6091. (c) Truce, W. E.; Simms, J. A. *J. Am. Chem. Soc.* **1956**, *78*, 2756. (d) The *trans* isomer is equivalent to the *Z*-isomer in the present study.

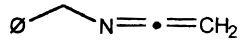
(7) *The Chemistry of Doubly-Bonded Functional Groups;* Patai, S., Ed.; John Wiley and Sons: London, 1977.

(8) (a) We have been unable to find any literature references to this class of compounds. Some of the sources examined follow. (b) Smith, P. A. S. *The Chemistry of Open-Chain Nitrogen Compounds*; W. A. Benjamin, Inc.: New York, 1965; Vols. 1 and 2. (c) Overberger, C. G.; Anselme, J. P.; Lombardino, J. G. *Organic Compounds with Nitrogen−Nitrogen Bonds*; The Ronald Press Company: New York, 1966. (d) Reference 7.

(9) (a) Meyer, H. J.; Nolde, C.; Thomsen, I.; Lawesson, S. O. *Bull. Soc. Chim. Belg.* **1978**, *87*, 621. (b) Mariella, R. P.; Brown, K. H. *J. Org. Chem.* **1971**, *36*, 735.

Decomposition of nitrosoamide (**1**) in dry acetonitrile at 25 °C followed by chromatographic fractionation of the product mixture affords the unsymmetrical diacylamine (**6**) (R_f = 0.7 in 50% ether/CH_2Cl_2) in ~23% yield.

Other Potential Reaction Pathways. Several other pathways and products from the decomposition of **1** in acetonitrile appear feasible in principle but were not observed. Perhaps the most compelling of these pathways are the deprotonation of the nitrilium ion (**4**) to form the azacumulene (or ketenimine) (**7**) and the intramolecular



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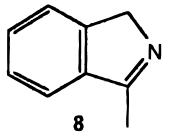
Friedel–Crafts reaction of the onium ion (**4**) to yield the isoindole (**8**). Molecular models of the nitrilium ion show



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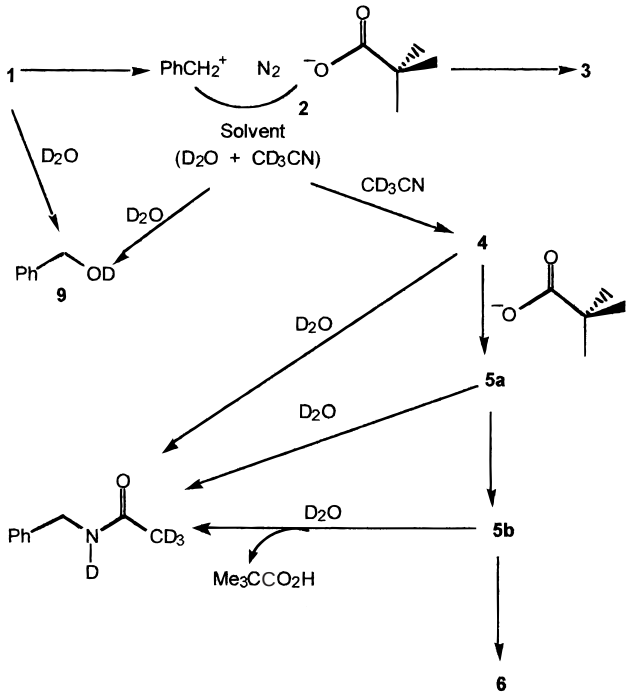
that the π-systems of the aromatic nucleus and the nitrile moiety are poorly aligned for effective overlap. The removal of a proton from the carbon atom β to the heteroatom of an onium ion is rarely observed (Chart 2).[5]

The observed formation of benzyl alcohol (Table 1) from traces of moisture in the "dry" acetonitrile runs must be due to reaction of adventitious water with a benzylating species. In principle, the latter may be the first-formed benzyl cation, the nitrilium ion (**4**), or the starting *N*-nitrosoamide (**1**). The first option is unlikely because of the short lifetime[1c,d] of the cation and the unfavorable distribution of nucleophiles in the medium ($CD_3CN/H_2O > 10^4$).[1a,3b] The second option is also unlikely because alcohol formation would result from an S_N2 displacement reaction (with CH_3CN as the departing group). Displacement reactions, however, would be expected to be slower than nucleophilic attack on the carbon that is multiply bonded to the charged heteroatom,[5] which would produce NBA, **11**. However, no NBA is observed (Table 1), so the alcohol probably does not arise from a water/nitrilium ion reaction.

Benzyl alcohol, **9**, probably originates from hydrolysis of the starting nitrosoamide (**1**). Reaction of water at the pivalyl group would lead to pivalic acid and benzyldiazoic acid (**10**) ($C_6H_5CH_2N{=}N{-}OH$), which then would yield benzyl alcohol by subsequent reactions. Low yields (<1%) of benzyl alcohol have been observed during the thermolyses of other *N*-benzyl-*N*-nitrosoamides in benzene–toluene[3c] and chloroform,[3c] and the same mechanism involving trace moisture is probably involved in the present case.

Reaction of Ammonia with *N*-Acetyl-*N*-pivalylbenzylamine (6). A 20-fold excess of ammonia was added to the diacylamine. More NBA (**11**) than NBP (**12**) was formed (Table 2). The formation of these amides from the reaction of NH_3 with the diacylamine, **6**, (Table 2) is consistent with the structure of **6**. Acetamide and pivalamide must also have formed from the treatment of the product mixture with ammonia (eq 2). However, the former possesses a trideuteriomethyl group and is thus not visible in the ^1H NMR spectrum, while the *tert*-butyl signal of the latter is unresolved from that of the nitrosoamide (**1**) or the ester (**3**).

Chart 3. Reaction Pathways for Decomposition of Nitrosoamide (1) in Acetonitrile–Water Mixtures



The larger yield of NBA over NBP is somewhat surprising. This result indicates that NH_3 *apparently* attacks the more sterically hindered pivalyl group in *preference* to the acetyl group. A reasonable interpretation of this observation follows. Molecular models show that nonbonded interactions operating in the diacylamine, **6**, force the *tert*-butyl group out of the plane of the acetamide moiety (eq 2). Thus there is little overlap of the n-electrons of the nitrogen and the π^* orbital of carbonyl group of the pivalyl moiety. Resonance interaction involving the n-electrons of the nitrogen would thus occur within the acetyl function but not within the pivalyl group, rendering the latter more reactive than the fomer. Additionally, the bulky pivalyl group is oriented such that the *tert*-butyl moiety physically obstructs one face of the acetyl group from nucleophiles (eq 2) and blocks solvation of the developing negative charge if a nucleophile reacts with the opposite face. This steric feature also provides an explanation for difficulties in the synthesis by the acid chloride.

Decomposition of *N*-Benzyl-*N*-nitrosopivalamide (1) in Acetonitrile–Water Mixtures. In dry acetonitrile, the only nucleophiles that compete for the cation are acetonitrile and the pivalate ion. When the mole fraction of water is increased, it can effectively enter into bimolecular reactions and compete against other nucleophiles.

N-Benzyl-*N*-nitrosopivalamide (**1**) was decomposed in CD_3CN-D_2O mixtures in the presence of 2 equiv of pyridine at 25 °C. The half-life of the nitrosoamide (**1**) in CD_3CN-D_2O was ~30 min at 25 °C, essentially unchanged from the value in dry acetonitrile, ($t_{1/2}$ in CD_3CN was also ~30 min at 25 °C).

Benzyl pivalate (**3**), the imidic anhydrides (**5a,b**), the diacylamine (**6**), benzyl alcohol (**9**), and pivalic acid were observed. In addition, in this case, NBA was formed. Competition by water for the nitrilium ion, **4**, is now

Table 3. Time-Dependent Product Distribution[a] from Decomposition of *N*-Benzyl-*N*-nitrosopivalamide (1)[b] in CD_3CN−Water at 25 °C

	yields (%)						
			imidic anhydrides				
time[c]	nitrosoamide **1**	benzyl pivalate **3**	**5a**; *Z*	**5b**; *E*	diacyl benzylamine **6**	benzyl alcohol **9**	NBA **11**
			$X_{D_2O}{}^d = 0.0079$				
24 h	0.0	72	0.0	0.0	23.0	5.0	0.0
			$X_{D_2O}{}^d = 0.25$				
10	77	18	1.1	0.4	0.2	3.0	0.3
20	60	25	3.4	1.0	1.2	8.0	1.4
40	40	34	6.0	1.2	3.6	13.0	2.2
70	19	43	3.0	0.0	8.0	23.0	4.0
24 h	0.0	52	0.0	0.0	13.0	28.0	7.0
			$X_{D_2O}{}^d = 0.5$				
24 h	0.0	49	0.0	0.0	2.0	36.0	15.0

[a] Averaged from triplicate runs; standard deviation ≈ 0.5%. [b] Concentration ≈ 0.045 M. [c] Time in min unless otherwise stated. [d] Mole fraction.

observed in the formation of NBA[10] (Chart 3, Table 3). The yield of the imidic anhydrides (**5**) is lower that in the anhydrous runs (Table 1) because of diversion of the nitrilium ion by water to NBA and because the anhydrides are probably hydrolyzed by water (Chart 3).

Finally, the yield of benzyl alcohol increases with water concentration (Table 3), most likely because of the increase in the hydrolysis of the nitrosoamide. Direct competition by water for the benzyl cation is probably also responsible, though to a smaller extent.

Experimental Section

Materials and Methods. Benzylamine, pivalyl chloride, acetyl chloride, pyridine, acetonitrile-d_3 (99.5% atom D), deuterium oxide (99.8% atom D), sodium acetate, phosphorus pentoxide, and benzyl benzoate were obtained from the Aldrich Chemical Co. Ammonia and dinitrogen tetroxide were purchased from The Matheson Gas Company. Commercial reagents were used without further purification. Spectra were recorded on 300 MHz FT-NMR, FT-IR and UV−vis spectrometers. TLC analyses were performed on UV-fluorescent silica gel plates.

Stability of *N*-Benzyl-*N*-nitrosopivalamide. Handling and Storage. N-Benzyl-*N*-nitrosopivalamide is thermolabile and was prepared as needed. It is labile in the presence of acids, bases, and moisture; being photolabile it was handled in the dark. **Caution!** Nitrosoamides should be handled with extreme care because of their possible mutagenicity[11a] and carcinogenicity (local and systemic).[11b] Efficient fume hoods and appropriate personal protection (chemical-resistant gloves, safety glasses, lab coat, etc.) are recommended when handling these compounds.

***N*-Benzylpivalamide** was prepared from the method of Heyns and von Bebenburg:[12a] mp 81−82 °C (lit.[12b] mp 81−82 °C); IR (KBr) 3309, 1689, 1510, 1390, 1375 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.27 (s, 9H), 4.44 (d, 2H, J = 7 Hz), 5.90 (bs, 1H), 7.26−7.32 (m, 5H); UV (ET_2O) λ_{max} = 284 nm (ϵ = 209).

***N*-Benzyl-*N*-nitrosopivalamide (1).** A mixture of *N*-benzylpivalamide (95.5 mg, 0.5 mmol), NaOAc (250 mg, 3.0 mmol), and Na_2SO_4 (0.5 g) was dried at oil pump vacuum. Methylene chloride (3.0 cm^3) freshly distilled from P_2O_5 was added to the solid material (under N_2), and the suspension was cooled to −78 °C. A solution of $N_2O_{4,(l)}$ (0.2 cm^3, 3.1 mmol) in CH_2Cl_2 (1.0 cm^3) at −78 °C was then added at −78 °C to the stirred suspension, which was then allowed to warm to −25 °C over 10 min. After a further 15 min at −25 °C, the suspension was evaporated in vacuo for ∼15 min until a lemon yellow color was observed. Ether at −20 °C was then added, and the suspension was washed in turn with saturated solutions of NaCl, Na_2CO_3, and NaCl at −5 °C. The organic phase was dried over Na_2SO_4 at −30 °C and then evaporated in vacuo (at −30 °C) to yield 0.11 g (0.5 mmol, 100%) of a lemon yellow oil. The synthesis and isolation were performed in the dark: IR (neat) 1720, 1605, 1502, 1390, 1375 cm^{-1}; ^1H NMR (CD_3CN) δ 1.45 (s, 9H), 4.97 (s, 2H), 7.05−7.40 (m, 5H). UV (CH_2Cl_2) λ_{max} 275 nm (ϵ = 500), 400 nm (ϵ = 63) 394 nm (sh), 422 nm (ϵ = 66).

***N*-Acetyl-*N*-pivalylbenzylamine (6).** A solution of *N*-benzyl pivalamide (95.5 mg, 0.5 mmol) in acetyl chloride (1 cm^3, 14 mmol) was cooled to −20 °C and was then treated with pyridine (40 mL, 0.5 mmol) with stirring; a white precipitate of pyridine hydrochloride formed. The solution was then refluxed for 12 h. The acetyl chloride was removed in vacuo, and the residue was fractionated by preparative TLC using 50% ether/CH_2Cl_2. The band at R_f = 0.7 was eluted with ether; removal of the ether in vacuo yielded a pale yellow oil (5.5 mg, 0.025 mmol, 5%): ^1H NMR ($CDCl_3$) δ 1.26 (s, 9H), 2.24 (s, 3H), 4.89 (s, 2H), 7.21−7.32 (m, 5H).

The major product of the above reaction was diacetylbenzylamine [^1H NMR ($CDCl_3$) δ 2.23 (s, 6H), 4.97 (s, 2H), 7.21−7.32 (m, 5H)]. With gentle heating (30−50 °C), no reaction occurred. NBA did not react with pivalyl chloride at 25 °C or under reflux regardless of the presence of base (Na_2CO_3 and/or pyridine).

Decomposition of Nitrosoamide (1). In a typical run, ∼5 mg of **1** was dissolved in 500 μL of solvent (CD_3CN or CD_3CN−D_2O) in an NMR tube. The solution was frozen with liquid N_2, and the tube was degassed at oil pump vacuum, evacuated, and flame-sealed. The sealed tube was then incubated at 25 °C, and the reaction was followed by NMR. The half-life was ∼30 min. The products observed were benzyl pivalate, **3**, (δ 5.07); *E*-ethanimidic anhydride, **5b**, (δ 4.38); *Z*-ethanimidic anhydride, **5a**, (δ 5.21); *N*-acetyl-*N*-pivalylbenzylamine, **6**, (δ 4.82); and benzyl alcohol, **9**, (δ 4.56). Only the benzyl signals are reported (in CD_3CN); acetyl signals are fully deuterated and thus not visible in the ^1H NMR spectrum. The methyl signals of the pivalyl groups of the compounds in this study are indistinguishable from each other.

Isolation of *N*-acetyl-*N*-pivaloylbenzylamine (6) from Decomposition of Nitrosoamide (1) in CH_3CN. In a typical run, nitrosoamide (**1**) (50 mg, 22.7 mmol) was dissolved in 1 cm^3 CH_3CN (dried over Na_2SO_4), and the solution was set aside in the dark at 25 °C for 24 h. The solution was concentrated in vacuo and was then fractionated by preparative TLC using ether/CH_2Cl_2. Ethereal elution of the band at R_f = 0.7 followed

(10) (a) A semilog plot of % NBA (y) vs mole fraction of water (x) yields a straight line: $\log y = 26.5x - 0.20$; $R^2 = 1.00$. (b) A product mixture from a run that had been allowed to stand at 25 °C until all of the nitrosoamide had decomposed and all of the imidic anhydrides (**5a,b**) had rearranged to the diacylamine (**6**).

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by removal of the solvent in vacuo yielded a pale yellow oil (42 mg,. 182 mmol). Anal. Calcd for $C_{14}H_{19}N0_2$: C, 72.11; H, 8.15; N, 6.01; O, 13.73. Found: C, 72.28; H, 8.05; N, 6.09; O, 13.58. ^{1}H NMR ($CDCl_3$) δ 1.26 (s, 9H), 2.24 (s, 3H), 4.89 (s, 2H), 7.21−7.32 (m, 5H). Due caution must be exercised during the separation because benzyl pivalate elutes with an R_f of ∼0.8 under the same conditions.

Treatment of a Decomposed Sample of Nitrosoamide (1) in CD_3CN with Ammonia. A product mixture from a decomposition run was analyzed by ^{1}H NMR to ensure the absence of anhydrides, **5**, (at δ 5.02 and 4.36) and nitrosoamide, **1**, (at δ 4.93) and the presence of the diacylamine, **6**, (at δ 4.80). Ammonia (20 equiv) was injected into the NMR tube through a serum stopper whose underside was copiously lined with Teflon tape. The tube was shaken for ∼30 s and NMR spectra were taken after 2 and 24 h; the relative yields of benzyl pivalate (**3**), *N*-acetyl-*N*-pivalylbenzylamine (**6**), benzyl alcohol, NBP, and NBA were measured (Table 2).

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