

133 mg (29%) of *p*-(*N*-*tert*-butylamino)benzotrile. The filtrate was concentrated to leave another crystalline solid which was recrystallized from hexane to yield 264 mg (64%) of 3-chloro-4-(*N*-*tert*-butylamino)benzotrile: mp 81–83.5°; ir (KBr) 4.54, 6.24, 6.56, 11.34, and 12.05 μ ; nmr (CCl₄) τ 8.53 (9 H, s), 3.08 (1 H, d), 2.50 (2 H, m).

Anal. Calcd for C₁₁H₁₃N₂Cl: C, 63.31; H, 6.28; N, 13.42; Cl, 16.99. Found: C, 63.39; H, 6.26; N, 13.22; Cl, 16.88.

When the reaction was carried out in pure, unbuffered ethanol the *o*-chloro derivative was isolated in 94% yield. No parent amine was detected in unbuffered ethanol.

Kinetics. Reagents. Commercial absolute ethanol was dried by the reaction with magnesium turnings followed by distillation.¹⁵ Standard sodium thiosulfate solution (*ca.* 0.020 *N*) was used to titrate the liberated iodine.

(15) A. Vogel, "Practical Organic Chemistry," 3rd ed, Wiley, New York, N. Y., 1956, p 167.

Procedure. Stock solutions of the *N*-chloramines in a nonpolar solvent were prepared as indicated above for each compound. For each kinetic run, an aliquot of the stock solution was taken and the solvent was evaporated *in vacuo* to leave the neat chloramine. The chloramine was then dissolved in ethanol buffered 0.1 *N* in anhydrous sodium acetate and 0.1 *N* in acetic acid or in pure ethanol without buffer. The ethanolic solution was quickly thermostated to the desired temperature and aliquots were withdrawn at the desired time intervals. The aliquots were quickly added to 1.0 *N* methanolic potassium iodide solution and acidified with a few drops of 0.1 *N* hydrochloric acid solution to liberate the iodine. The iodometric titrations were quickly done *via* sodium thiosulfate solution using a dead-stop technique employing two platinum electrodes and a Fisher Accumet Model 310 pH meter.

Acknowledgment. We are indebted to the National Cancer Institute of the Public Health Service for a grant which supported this investigation.

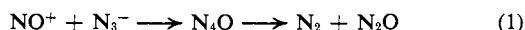
Reactions of the Nitrosonium Ion. II. Reactions of Triphenylmethyl, Benzhydryl, and Benzyl Azides with Nitrosonium Compounds^{1a}

Michael P. Doyle* and Wendell Wierenga^{1b}

Contribution from the Department of Chemistry, Hope College, Holland, Michigan 49423. Received August 4, 1971

Abstract: Triphenylmethyl azide reacts with NO⁺BF₄⁻ in acetonitrile to produce, quantitatively, triphenylmethyl tetrafluoroborate, nitrogen, and nitrous oxide. In acetonitrile benzhydryl azide produces the corresponding cation in equilibrium with the *N*-benzhydrylacetonitrilium ion. Side reactions, including phenyl migration to electron-deficient nitrogen and hydrogen abstraction, are also observed and account for as much as 32% of the reaction products at room temperature. Control over these side reactions has been achieved by variation of the reaction temperature. Benzyl azide reacts with NO⁺BF₄⁻ in acetonitrile to give 1% benzaldehyde and 99% *N*-benzylacetonitrilium tetrafluoroborate. The reactions of alkyl azides with nitrosonium salts are compared with the corresponding reactions of isothiocyanates, sulfanylamines, and amines. These results are discussed in relation to a general mechanism for alkyl azide reactions with the nitrosonium ion.

The reaction between hydrazoic acid and nitrous acid produces an equivalent amount of both nitrogen and nitrous oxide.² In aqueous solution the rate of this reaction is found to be dependent on temperature and ionic strength^{3a} and, under certain conditions, independent of azide concentration. The mechanism can be viewed as an electrophilic attack by the nitrosonium ion on the azide ion to form nitrosyl azide, followed by decomposition to the observed products (eq 1). In this regard, Lucien has obtained evidence,



including physical properties, for the formation of nitrosyl azide from a variety of nitrosonium compounds and either sodium azide or hydrazoic acid.⁴ The

yellow nitrosyl azide decomposes to nitrogen and nitrous oxide even at temperatures as low as -50°. The structure of nitrosyl azide is predicted to be linear, NNNNO, on the basis of ¹⁵N-labeling experiments.⁵

Considering the instability of nitrosyl azide, the rate of reaction of nitrosonium compounds with substituted azides should depend only on how readily the substituted nitrosyl azide is formed. Reactions of azido-pentaamminecobalt(III)⁶ and azidopentaquochromium(III)⁷ ions with sodium nitrite, for example, are easily effected in aqueous acid solutions to give both nitrogen and nitrous oxide in equal amounts. Use of stable nitrosonium salts such as NO⁺BF₄⁻, NO⁺SbF₆⁻, and NO⁺PF₆⁻ in anhydrous nonhydroxylic media would certainly be expected to effect similar reactions with aliphatic azides.

With substituted azides (A-N₃), unlike the azide ion which has two equivalent sites for attack, reaction with

(1) (a) A preliminary communication of this work, part I, has been reported: M. P. Doyle and W. Wierenga, *J. Amer. Chem. Soc.*, **92**, 4999 (1970); (b) National Science Foundation Undergraduate Research Participant, summer 1969.

(2) (a) H. Thiele, *Ber.*, **41**, 2681 (1908); (b) F. Sommer, *ibid.*, **48**, 1884 (1915); (c) T. Werner, *Proc. Roy. Soc. (London)*, **28**, 257 (1911); (d) E. Oliveri-Mandala, *Gazz. Chim. Ital.*, [I] **51**, 101 (1922).

(3) (a) F. Seel and R. Schwaebel, *Z. Anorg. Allg. Chem.*, **274**, 169 (1953); (b) F. Seel, R. Wölfe, and G. Zwarg, *Z. Naturforsch. B.*, **13**, 136 (1958); (c) C. A. Bunton and G. Stedman, *J. Chem. Soc.*, 1702 (1960), and preceding papers.

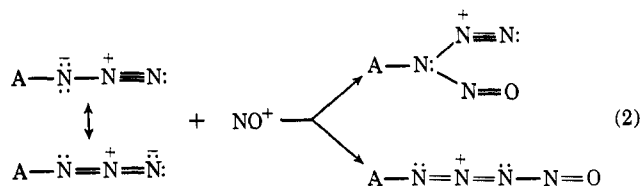
(4) H. W. Lucien, *J. Amer. Chem. Soc.*, **80**, 4458 (1958).

(5) K. Clusius and H. Knopf, *Chem. Ber.*, **89**, 681 (1956).

(6) (a) A. Hiam and H. Taube, *Inorg. Chem.*, **2**, 1199 (1963); (b) R. B. Jordan, A. M. Sargeson, and H. Taube, *ibid.*, **5**, 1091 (1966); (c) D. A. Buckingham, I. I. Olsen, A. M. Sargeson, and H. Satrapa, *ibid.*, **6**, 1027 (1967); (d) R. G. Pearson and J. W. Moore, *ibid.*, **3**, 1334 (1964).

(7) R. C. Thompson and E. J. Kaufmann, *J. Amer. Chem. Soc.*, **92**, 1540 (1970).

the nitrosonium ion may occur either at the internal substituted nitrogen or the external nitrogen (eq 2).

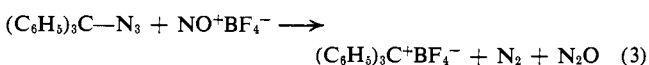


Attempts to differentiate between these two modes of attack have been unsuccessful. In the nitrous acid reactions with azidocobalt(III) complexes studied by Taube and coworkers^{6b} there appears to be either a very short time lag between nitrogen and nitrous oxide loss or no difference at all.

This paper reports the reactions of three representative aliphatic azides with stable nitrosonium salts. The expected loss of nitrogen and nitrous oxide is observed with concurrent formation of carbenium ions.⁸ Two competing reactions, however, have been identified. The control of these side reactions by temperature variation and a comparison with similar methods of carbenium ion production are also reported.

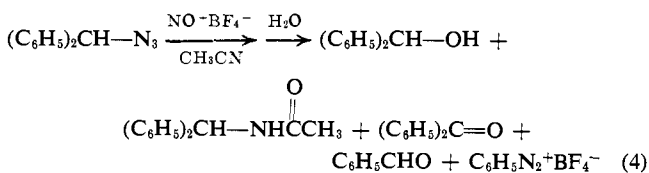
Results

Triphenylmethyl Azide. Treatment of triphenylmethyl azide with 1 equiv of nitrosonium tetrafluoroborate produces a stoichiometric amount of nitrogen, nitrous oxide, and triphenylmethyl tetrafluoroborate (eq 3). A typical procedure involves the addition of



the nitrosonium salt in an appropriate anhydrous nonhydroxylic solvent to the azide in the same solvent. When carried out in anhydrous acetonitrile at room temperature, this reaction, as well as those of the nitrosonium salts with benzhydryl and benzyl azides, is characteristically rapid. The rate of gas evolution under these conditions depends only on the rate of addition of nitrosonium salt to the azide and no difference in either product formation or product yield is observed when the azide is added to the nitrosonium salt.

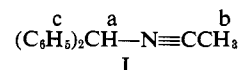
Benzhydryl Azide. Unlike triphenylmethyl azide, which when treated with NO^+BF_4^- in acetonitrile followed by addition of water produced only triphenylmethanol, benzhydryl azide yielded benzhydryl, *N*-(diphenylmethyl)acetamide, benzophenone, benzaldehyde, and benzenediazonium tetrafluoroborate under the same conditions (eq 4). Benzaldehyde and benzo-



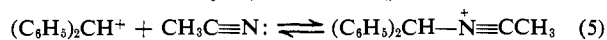
phenone were detected by both glpc analysis and ir spectroscopy prior to the addition of water. The stretching frequency in the infrared of the benzenediazonium ion at 2300 cm^{-1} was also observed prior to quenching. The gas evolved was composed of both nitrogen and nitrous oxide. Prior to addition of the

(8) The nomenclature for carbocations suggested by G. A. Olah, *J. Amer. Chem. Soc.*, **94**, 808 (1972), is used here.

water the pmr spectrum at 41° showed, in addition to several other absorptions, broadened singlets at δ 6.94 (a) and 2.56 (b) in an integral ratio of 1:3 and a singlet at δ 7.55 (c), all attributable to the *N*-benzhydryl-acetonitrilium ion (I). These assignments are reason-



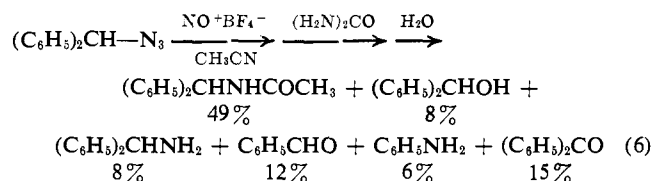
able in comparison to the data of Olah and Kiovsky⁹ for *N*-alkylnitrilium salts in sulfur dioxide solution and by analogy to the *N*-benzylacetonitrilium ion discussed later. The broadening of the absorptions at δ 6.94 and 2.56 may be attributed to the rapid exchange of acetonitrile with the benzhydryl cation (eq 5). However, no



spectral evidence was obtained for the independent existence of the benzhydryl cation, as observed by Olah^{10a} and Farnum,^{10b} under the pmr conditions employed in this study. The absorptions assigned to I were also obtained from the pmr spectrum obtained when benzhydryl chloride was treated with silver tetrafluoroborate in acetonitrile.¹¹

Control over the relative yields of products can be achieved through variation of the reaction temperature. As shown in Table I the yields of benzaldehyde and benzophenone increase with increasing temperature while the yields of those products derived from the benzhydryl cation, alcohol and amide, increase with decreasing reaction temperature. At -30° the reaction between benzhydryl azide and NO^+BF_4^- in acetonitrile produces only 8% of carbonyl products; 92% of the benzhydryl azide reacts to form the benzhydryl cation. Surprisingly, the yield of carbonyl products does not change appreciably whether NO^+BF_4^- is added to the azide or the azide is added to NO^+BF_4^- (for example, reactions at 10 and 0° , respectively). Except for the run at 55° , the ratio of alcohol to amide does not change appreciably with temperature. The reaction times for the reactions run at temperatures below room temperature were noticeably longer; reaction at -30° , for example, required 3 hr for completion.

The reaction between urea and nitrous acid is well known.¹² We expected that the use of urea would quench any further reaction of intermediate product(s) with excess nitrosonium ion. Addition of 0.15 equiv of urea to the reaction solution at 30° immediately after gas evolution had ceased, followed by water quenching and work-up, gave the results shown in eq 6. The



amine products were isolated separately and identified from their spectra as well as by gas chromatography.

(9) G. A. Olah and T. E. Kiovsky, *J. Amer. Chem. Soc.*, **90**, 4666 (1968).

(10) (a) G. A. Olah, *ibid.*, **86**, 932 (1964); (b) D. G. Farnum, *ibid.*, **86**, 934 (1964).

(11) Upon quenching with water at 25° the benzhydryl chloride-silver tetrafluoroborate system yielded 35% of benzhydryl and 65% of *N*-(diphenylmethyl)acetamide.

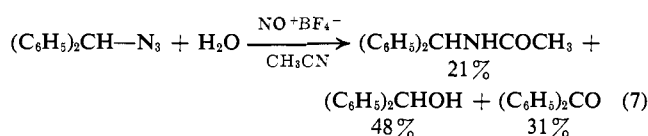
(12) P. A. S. Smith, "The Chemistry of Open-Chain Organic Nitrogen Compounds," Vol. I, W. A. Benjamin, New York, N. Y., 1965.

Table I. Variation of the Relative Yields of Products with Changes in Reaction Temperature^a

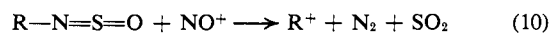
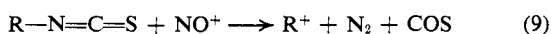
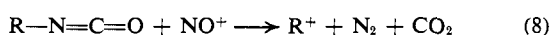
| Temp, °C ^c | Yield, % ^b | | | | | |
|-----------------------|--|--|--|-----------------------------------|---|-------------------|
| | (C ₆ H ₅) ₂ CHOH | (C ₆ H ₅) ₂ - CHNHC ₂ H ₅ | (C ₆ H ₅) ₂ CO | C ₆ H ₅ CHO | (C ₆ H ₅) ₂ CO + C ₆ H ₅ CHO | % alcohol/% amide |
| 55 | 35 | 30 | 18 | 17 | 35 | 1.17 |
| 30 | 30 | 38 | 20 | 12 | 32 | 0.79 |
| 10 ^{d,e} | 23 | 52 | 15 | 10 | 25 | 0.44 |
| 0 | 23 | 50 | 16 | 11 | 27 | 0.46 |
| -10 | 21 | 51 | 17 | 11 | 28 | 0.41 |
| -20 | 30 | 54 | 7 | 9 | 16 | 0.55 |
| -30 | 27 | 65 | 5 | 3 | 8 | 0.42 |

^a Benzhydryl azide (5.0 mmol) in 15 ml of acetonitrile was added to NO⁺BF₄⁻ (5.0 mmol) in 15 ml of acetonitrile. Water (50 mmol) was added at the same temperature 5 min after gas evolution had ceased. ^b Relative yields of products after work-up based on pmr analysis using an internal standard. Duplicate runs show precision of ±2%. Absolute yields were greater than 90%. Gas evolution was that expected from the production of 2 equiv of gaseous products from 1 equiv of azide. ^c Temperature control was ±2° for all runs. ^d Involved addition of NO⁺BF₄⁻ to the azide in acetonitrile. ^e Relative yields based on actual isolation of products.

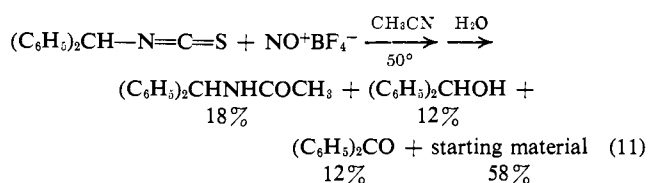
The presence of water in the reaction solution changes the reaction products considerably. When benzhydryl azide and 5 equiv of water are added simultaneously to the nitrosonium salt in acetonitrile, no benzaldehyde is produced and the yield of benzophenone is increased over that of the comparable reaction in Table I (eq 7).



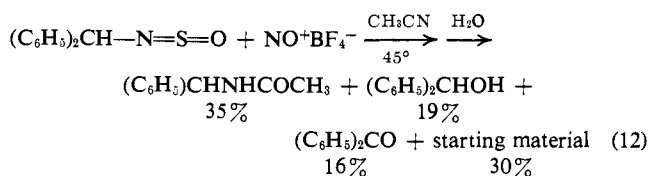
The reactions of some representative alkyl isocyanates, isothiocyanates, and alkylsulfanylamines with nitrosonium salts have been reported.¹³ These compounds react with the nitrosonium ion to form carbenium ions with the loss of nitrogen and an equivalent amount of carbon dioxide, carbonyl sulfide, or sulfur dioxide, respectively (eq 8–10). To compare



these methods with the corresponding azide reaction we prepared benzhydryl isothiocyanate and benzhydryl-sulfanylamine and treated each with NO⁺BF₄⁻ in acetonitrile. Addition of the isothiocyanate to NO⁺BF₄⁻ at room temperature gives no noticeable reaction after 30 min, as detected by gas evolution. Upon heating at 50° for 1 hr followed by addition of water, results were obtained as shown in eq 11. Similarly



benzhydrylsulfanylamine reacted very slowly at room temperature. Heating at 45° for 6 hr, followed by the addition of water, gave the results shown in eq 12.

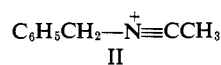


(13) G. A. Olah, N. Friedman, J. M. Bollinger, and J. Lukas, *J. Amer. Chem. Soc.*, **88**, 5328 (1966).

When compared to the corresponding azide reaction which gives similar results, except for the production of benzaldehyde, it is apparent that in at least this one case the azide is a more efficient source of carbenium ions in acetonitrile.

Treatment of benzhydrylamine with 1.1 equiv of NO⁺BF₄⁻ in acetonitrile at 10° produces immediate gas evolution and, upon addition of water, 9% *N*-(diphenylmethyl)acetamide, 25% benzhydryl, 4% benzophenone, and 58% starting material. The large excess of alcohol over amide is due to the production of water in this reaction. No benzaldehyde is observed by glpc or pmr analysis either in this reaction or in the reactions of benzhydryl isothiocyanate or benzhydrylsulfanylamine with NO⁺BF₄⁻.

Benzyl Azide. The reaction between benzyl azide and nitrosonium salts was qualitatively as rapid as the corresponding reactions with triphenylmethyl and benzhydryl azides. After the addition at 20° of benzyl azide in acetonitrile to an equivalent amount of NO⁺BF₄⁻, also in acetonitrile, the expected yield of 2 equiv of gaseous products was realized, and the pmr spectrum of the solution consisted of three separate absorptions attributable to the *N*-benzylacetanilium ion (II).

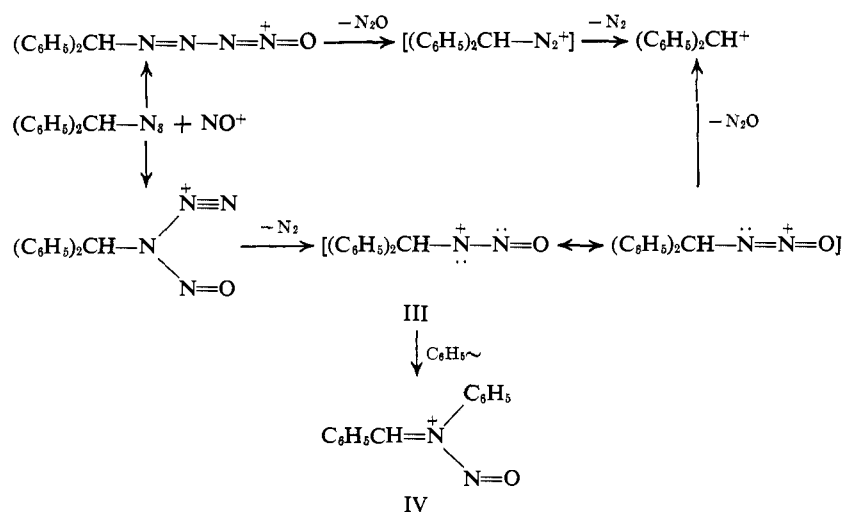


The phenyl hydrogens were seen as a singlet at δ 7.55, while the *N*-methylene group consisted of six lines centered at δ 5.37 and the *C*-methyl group showed a five-line pattern centered at δ 2.85. The chemical shifts as well as H–H and ¹⁴N–H coupling constants corresponded to those reported by Olah and Kiovsky for related *N*-alkylacetanilium ions.⁹ Upon addition of water *N*-benzylacetamide was produced in 99% yield with benzaldehyde accounting for the remaining 1%. No other products were observed. Benzyl alcohol was not produced even when large excesses of water were added after completion of the reaction.

The necessity of keeping the reaction solution free from water and other nucleophilic contaminants is evident in reactions of benzyl azide with nitrosonium salts. Small amounts of water, for example, add to II to form the corresponding acetamide which coexists with II and can be readily observed by pmr spectroscopy. Under anhydrous conditions II is stable in solution for more than a day at room temperature.

No difference in products or product yields was observed when the reaction was run at -5°. When 1

Scheme I



equiv of water was added with the azide to NO^+BF_4^- at 25° , only *N*-benzylacetamide was produced. Only when 5 equiv of water was added with azide to NO^+BF_4^- was there a substantial increase in the yield of benzaldehyde (11%).

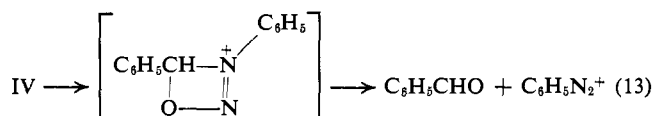
By comparison to benzyl isothiocyanate, benzyl azide reacts rapidly and efficiently with nitrosonium salts in acetonitrile. No gas evolution was observed even after 1 hr at room temperature when benzyl isothiocyanate was added to NO^+BF_4^- in acetonitrile. The pmr spectrum of the reaction solution showed only unchanged isothiocyanate. Only after heating for 1 hr at 60° was one-half of the expected yield of gas evolved and II detected by pmr spectroscopy. Upon addition of water both *N*-benzylacetamide and benzaldehyde were observed as was unreacted starting material.

Discussion

The use of the reactions of transition metal azides, especially azidopentaaminocobalt(III), with nitrous acid to study the characteristics of unimolecular substitution reactions for transition metal complexes is well known.^{6,7} When carried out in nonaqueous solvents, $\text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$ reacts with $\text{NO}^+\text{ClO}_4^-$ to produce labile solvent complexes which have proven useful as synthetic intermediates.¹⁴ Similar reactions between azide and nitrosoruthenium complexes^{15a} and between the nitrosonium ion and azidoruthenium complexes^{15b} have also been recently reported. However, until publication of our earlier communication^{1a} no examples of the reaction of aliphatic azides with nitrosonium compounds had been reported. The results reported here demonstrate that aliphatic azides react rapidly and efficiently with nitrosonium salts to produce carbenium ions or the corresponding solvent complex. In acetonitrile carbenium ion stability is reflected in the products from the reaction of alkyl azide with NO^+BF_4^- and in the water quenching reactions.

Products resulting from the intermediacy of carbenium ions do not represent the only pathway for alkyl azide reactions with nitrosonium salts. Benzhydryl azide yields benzophenone, benzaldehyde, and benzene-

diazonium tetrafluoroborate, in addition to carbenium ion products. With the exception of benzophenone, the mechanism written in Scheme I will account for the products from the benzhydryl azide- NO^+BF_4^- reaction. Phenyl migration to the electron-deficient nitrogen of III produces *N*-nitrosobenzylideneaniline (IV) which undergoes rearrangement to the observed products, benzaldehyde and the benzenediazonium ion (eq 13).^{1a}



The observation of aniline, produced after urea quenching (eq 6), strongly suggests the formation of IV as an intermediate.

The fact that no observable difference in reactivity is found when triphenylmethyl, benzhydryl, and benzyl azides are treated with NO^+BF_4^- and the observation of phenyl migration argues against a mechanism in which NO^+ attack is followed by formation of the carbenium ion and nitrosyl azide. Although the duality of the reaction site for NO^+ attack on substituted azides has been recognized,^{6b,c} our results are the first indication that part or all of the reaction proceeds through attack at the substituted nitrogen.

The production of benzophenone in the nitrosonium ion decomposition of benzhydryl azide could be explained by hydrogen migration. However, in reactions where water is added to the nitrosonium salt no benzaldehyde is observed and benzophenone production is increased (Table I). In addition, when benzhydryl isothiocyanate or benzhydrylsulfonylamine is added to NO^+BF_4^- , benzophenone is produced in a reaction where the intermediacy of electron-deficient nitrogen species is unlikely.¹³ Similarly, benzophenone is also produced from benzhydrylamine under similar reaction conditions. Because of these observations and the lack of hydrogen migration in the Curtius rearrangement of benzhydryl azide,¹⁶ the production of benzophenone (and of benzaldehyde from benzyl azide) can be reasonably explained by an α -hydrogen abstraction either by the nitrosonium ion¹⁷ or by the solvent. Since

(14) (a) J. K. Hurst and H. Taube, *J. Amer. Chem. Soc.*, **90**, 1174 (1968); (b) J. L. Burmeister and N. J. De Stefano, *Inorg. Chem.*, **9**, 962 (1970).

(15) (a) F. J. Miller and T. J. Meyer, *J. Amer. Chem. Soc.*, **93**, 1294 (1971); (b) P. G. Douglas, R. D. Feltham, and H. G. Metzger, *ibid.*, **93**, 84 (1971).

(16) C. H. Gudmundsen and W. E. McEwen, *ibid.*, **79**, 329 (1957); see also P. A. S. Smith in "Molecular Rearrangements," P. deMayo, Ed., Interscience, New York, N. Y., 1963, Chapter 8.

(17) Hydride abstraction from cumene by nitrosonium salts has been

Table II. Comparison of Reactions of Benzhydryl Derivatives with NO^+BF_4^- or Ag^+BF_4^- in Acetonitrile

| $(\text{C}_6\text{H}_5)_2\text{CH-X}$ X = | Temp, °C | Time, hr | % completion | Relative yield, % | | | |
|--|-------------|-------------|-----------------|---|---|-------------------------------------|----------------------------------|
| | | | | $(\text{C}_6\text{H}_5)_2\text{-}$ CHNHCOCH_3 | $(\text{C}_6\text{H}_5)_2\text{-}$ CHOH | $(\text{C}_6\text{H}_5)_2\text{CO}$ | $\text{C}_6\text{H}_5\text{CHO}$ |
| NNN ^a | 10 | 0.5 | 100 | 52 | 23 | 15 | 10 |
| NCS ^a | 50 | 1.0 | 42 | 43 | 29 | 28 | 0 |
| NSO ^a | 45 | 6 | 70 | 50 | 27 | 23 | 0 |
| NH ₂ ^a | 10 | 0.5 | 42 | 24 | 66 | 10 | 0 |
| Cl ^b | 10 | 0.5 | 100 | 65 | 35 | 0 | 0 |

^a Reaction with 1.1 equiv of NO^+BF_4^- . ^b Reaction with excess AgBF_4 .

no significant difference in benzophenone production is noted when benzhydryl azide is added to NO^+BF_4^- (where an excess of NO^+BF_4^- is always present) or when NO^+BF_4^- is added to the azide, hydrogen abstraction must occur in competition with phenyl migration and carbenium ion formation. Of the three alkyl azides reported in this study, only benzhydryl azide shows all three processes in competition.

Numerous methods for the production of carbenium ions either as reaction intermediates or products have been reported. In Table II five such methods are directly compared. For the reactions of benzhydryl derivatives with NO^+BF_4^- the azide is the most versatile, direct, and rapid. The amine requires more than 2 equiv of the nitrosonium ion for complete diazotization; water, produced as a side product in amine demininations, reacts with the nitrosonium ion to form dinitrogen trioxide which escapes from the reaction solution. The reaction of benzhydryl chloride with silver ion, although producing no side products, required a large excess (>2 equiv) of AgBF_4 before I could be observed by pmr spectroscopy.

Experimental Section

Instrumentation. Analytical glpc analyses were performed on either an Aerograph Model 90P3 or Varian Aerograph Models 1864 and 2720 gas chromatographs using thermal conductivity detectors. Use was made of 5-ft columns of 20% Carbowax 20M, 20% SE-30 and 20% diisodecyl phthalate, all on Chromosorb P. Infrared spectra were obtained on either a Perkin-Elmer Model 137 Infracord or Model 621 grating spectrophotometer. A Cary 14 recording spectrophotometer was used to obtain uv spectra. Proton magnetic resonance spectra were obtained with a Varian Model A-60A spectrometer. Chemical shifts are reported in δ units using tetramethylsilane as internal reference; no difference was obtained using an internal or external reference for cation spectra in acetonitrile. Thin layer chromatographic analyses were performed on 19×19 cm plates using silica gel G; preparative tlc was performed using siliclar TLC-7GF. Melting points, obtained on a Thomas-Hoover apparatus, and boiling points were uncorrected.

Materials. The nitrosonium salts and silver tetrafluoroborate were obtained from Ozark-Mahoning Co. and were dried over phosphorus pentoxide in a vacuum desiccator at 1.0 Torr for several hours prior to use. Acetonitrile of spectral grade quality was distilled from calcium hydride and stored over molecular sieves. *N*-(Diphenylmethyl)acetamide was prepared by the Ritter reaction from benzhydrol,¹⁸ and *N*-benzylacetamide was produced in the reaction of benzylamine with acetyl chloride.¹⁹ Benzhydryl isothiocyanate was prepared from benzhydryl chloride and potassium isothiocyanate in acetonitrile,²⁰ and *N*-diphenylmethylsulfanylamine was prepared from benzhydrylamine and thionyl chloride.²¹ Other reactants were commercially available and used without further purification.

observed: G. A. Olah and N. Friedman, *J. Amer. Chem. Soc.*, **88**, 5330 (1966).

(18) P. Bronislaw, *Chem. Anal. (Warsaw)*, **8**, 255 (1963).

(19) M. J. Schlatter, *J. Amer. Chem. Soc.*, **63**, 1735 (1941).

(20) J. J. Donleavy and J. English, Jr., *ibid.*, **62**, 218 (1940).

(21) H. Ulrich, B. Tucker, and A. A. R. Sayigh, *J. Org. Chem.*, **34**, 3200 (1969).

Azide Syntheses. Triphenyl and benzhydryl azides were prepared by a procedure modified from that of Gudmundsen and McEwen.¹⁶ To a three-necked flask fitted with a reflux condenser, thermometer, and addition funnel were added 0.15 mol of potassium azide and 0.050 mol of the appropriate alcohol in 75 ml of anhydrous benzene. To this well-stirred solution was added dropwise 0.20 mol of trifluoroacetic acid in 25 ml of benzene. The reaction temperature was maintained at 35–36° for 28 hr, after which time the benzene solution was decanted from the solid trifluoroacetate salt and washed with water until the washings were nonacidic. The benzene solution was dried over anhydrous magnesium sulfate and the solvent removed under reduced pressure. Benzhydryl azide¹⁶ and triphenylmethyl azide²² were prepared in greater than 90% yield. Benzyl azide could not be obtained by this method and was prepared by the procedure of Boyer²³ in 91% yield.

General Procedure for Nitrosation of Azides. To 5.0 mmol of azide in 20 ml of anhydrous acetonitrile, placed in a three-necked flask fitted with dropping funnel, thermometer, and gas outlet tube, was added dropwise 5.5 mmol of nitrosonium salt, usually as a slurry, in 10 ml of acetonitrile. A more convenient procedure involved addition of the azide to the nitrosonium salt. The addition was at such a rate (15–30 min) as to cause no significant rise in reaction temperature. Prior to addition the entire system was flushed with dry nitrogen and, except for those runs where gas evolution was measured, the reaction was run under a nitrogen atmosphere. Temperature control was effected by using an appropriate heating or cooling bath.

Total gas evolution was measured on the closed system by water displacement from a calibrated gas buret. In all cases total gas evolution was within $\pm 5\%$ of the expected amount. In those runs where nitrogen and nitrous oxide were measured separately, a trap utilizing a liquid nitrogen-isopentane slush at -155° allowed nitrogen to pass through while nitrous oxide solidified quantitatively. The ir spectrum of the respective gases was used to detect and identify the nitrous oxide.

Prior to the addition of quenching agent to the reaction solution the pmr spectrum was taken in several runs. Glpc and ir analyses were also used at this point to detect products prior to quenching. Usually, however, 10 equiv of water was added within 15 min after gas evolution was complete. The quenching procedure involved injection of the water from a syringe directly into the reaction solution. In several runs a pmr spectrum of the solution was taken directly after quenching. Methylene chloride was then added followed by water and the mixture separated after thorough shaking. The water layer was washed twice with methylene chloride, and the combined methylene chloride extracts were washed twice with water and passed through anhydrous magnesium sulfate; the solvent was removed under reduced pressure. For those runs where organic bases were isolated the reaction solution was made basic using sodium carbonate prior to work-up, or the combined water washings were made basic and washed with methylene chloride.

Reaction products were analyzed after identification of each component by integration of the individual and characteristic absorption signals of each compound by pmr spectroscopy in carbon tetrachloride or chloroform-*d*₁. Integrations were maximized and averaged over several integrations of the same signal. Absolute yields were obtained by weighing the product mixture or the individual components after separation, or by using an internal standard, 1,2-dibromoethane, added to the reaction mixture after work-up.

The same procedure was employed for the reactions of amine, isothiocyanate, and sulfanylamine with nitrosonium salt except that

(22) W. H. Saunders and J. C. Ware, *J. Amer. Chem. Soc.*, **80**, 3328 (1958).

(23) J. H. Boyer, *ibid.*, **77**, 951 (1955); **78**, 325 (1956).

a reflux condenser was added to the reaction flask for reactions above room temperature. Benzhydryl chloride was added to AgBF_4 in acetonitrile at 10° under a dry nitrogen atmosphere.

Product Separation and Identification. Triphenylmethyl tetrafluoroborate was isolated from the reaction solution by distillation of acetonitrile under reduced pressure and identified from its pmr, ir, and uv spectra²⁴ as well as by its melting point. The products from the reaction of benzhydryl azide with NO^+BF_4^- were separated

(24) Pmr and uv spectra were taken in acetonitrile. The ir spectrum was taken of the salt in a Nujol mull. All spectra corresponded with those reported: J. I. Brauman and W. C. Archie, Jr., *J. Amer. Chem. Soc.*, **92**, 5981 (1970); D. W. A. Sharp and N. Sheppard, *J. Chem. Soc.*, 674 (1957); M. S. Newman and N. C. Deno, *J. Amer. Chem. Soc.*, **73**, 3644 (1951); G. Branch and H. Walba, *ibid.*, **76**, 1564 (1954).

by preparative tlc using benzene as the eluent. Benzaldehyde was identified from its pmr and ir spectra as well as by glpc analysis. The identity of isolated benzophenone was determined by comparison of its ir and pmr spectra with those of an authentic sample and by formation of its 2,4-dinitrophenylhydrazone derivative. Benzhydryl and *N*-(diphenylmethyl)acetamide were characterized by their pmr and ir spectra and by melting point. Products from other reactions were characterized by at least two separate methods.

Acknowledgment. We gratefully acknowledge the support of the Research Corporation and the National Science Foundation for this work. We wish to thank Dr. G. A. Olah for his encouragement and helpful discussions.

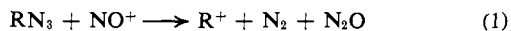
Reactions of the Nitrosonium Ion. III. Reaction of Alkyl Azides with Nitrosonium Compounds. The Effect of Solvent, Quenching Agent, and Nitrosonium Compound^{1a}

Michael P. Doyle* and Wendell Wierenga^{1b}

Contribution from the Department of Chemistry, Hope College, Holland, Michigan 49423. Received August 9, 1971

Abstract: Benzhydryl azide reacts with NO^+BF_4^- in anhydrous acetonitrile at room temperature to yield, after quenching with water, *N*-(diphenylmethyl)acetamide, benzhydryl, benzophenone, and benzaldehyde. With acetonitrile or phenylacetone solvents only amide, benzaldehyde, and benzophenone are produced, and the yield of benzophenone is reduced from that found in acetonitrile. With nitromethane the process leading to benzaldehyde is enhanced. In chloroform, however, production of products from the benzhydryl cation is only a minor process; products resulting from phenyl migration and hydrogen abstraction, benzaldehyde and benzophenone, account for 98% of the reaction products. The effect of addition of various amounts of water and of changes in concentration of azide on the production of benzhydryl and *N*-(diphenylmethyl)acetamide are presented, and these results are interpreted by irreversible formation of amide and reversible production of alcohol from reaction of water with the *N*-benzhydrylacetoneitrilium ion in equilibrium with the benzhydryl cation. Addition of various nucleophiles, including water, alcohols, and carboxylic acid, affects the relative yield of benzhydryl, or the corresponding ether or ester, compared to amide. Reduction by silanes and halogen transfer from triphenylmethyl halides have also been observed. Unsuccessful attempts to react alkyl azides with nitrosyl chloride, isoamyl nitrite, and nitrous acid under the usual conditions for deamination are presented. When benzhydryl azide reacts with the nitrosonium ion in the presence of water the products of phenyl migration, benzaldehyde and the benzenediazonium ion, are not observed while that of hydrogen abstraction, benzophenone, is increased in yield.

In the previous paper² the reactions of alkyl azides with the nitrosonium ion were shown to proceed predominantly with loss of nitrogen and nitrous oxide to the corresponding alkyl cation (eq 1). Two com-



peting reactions resulting from attack of the nitrosonium ion on the substituted nitrogen were also identified: migration to electron-deficient nitrogen and hydrogen abstraction. The extent of these competing reactions was, however, found to be temperature dependent and could be nearly eliminated at low temperatures when acetonitrile was used as the solvent.

The formation of carbenium ions from alkyl azides is unique in that (1) alkyl azides are very reactive toward nitrosonium salts in acetonitrile, even below room tem-

perature; (2) the leaving groups, nitrogen and nitrous oxide, are gases and pass out of the reaction solution; (3) no nucleophile is produced in the reaction, as is the case with amine deamination reactions;³ and (4) when nitrosonium salts such as NO^+BF_4^- are used, the counter ion does not usually interfere with the primary product. Carbenium ions produced in this way are free from reactions with external nucleophiles, except when the solvent is the nucleophile. The choice of solvent, then, would be expected to dictate the type and extent of solvent-carbenium ion interactions and should enable the study of these cations under a wide variety of conditions.

When benzhydryl azide is treated with NO^+BF_4^- in acetonitrile and the resulting cations quenched with

(1) (a) These results were presented in part at the 2nd Midwest Regional Meeting of the American Chemical Society, Ohio State University, Columbus, Ohio, June 3-5, 1970; (b) National Science Foundation Undergraduate Research Participant, summer 1969.

(2) Part II: M. P. Doyle and W. Wierenga, *J. Amer. Chem. Soc.*, **94**, 3896 (1972).

(3) (a) R. A. Moss and M. J. Landon, *Tetrahedron Lett.*, 3897 (1969), and previous papers in this series; (b) L. Friedman and J. H. Bayless, *J. Amer. Chem. Soc.*, **91**, 1790, 1795 (1969); (c) W. Kirmse and H. Schütte, *ibid.*, **89**, 1284 (1967); E. H. White, M. J. Todd, M. Ribi, T. J. Ryan, and A. A. F. Sieber, *Tetrahedron Lett.*, 4476 (1970); T. Koenig, T. Fithian, M. Tolela, S. Markwell, and D. Rogers, *J. Org. Chem.*, **34**, 953 (1969).