a reflux condensor 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 spectra[24] as well as by its melting point. The products from the reaction of benzhydryl azide with $NO^+BF_4^-$ were separated 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. Benzhydrol 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.

---

[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).

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, benzhydrol, benzophenone, and benzaldehyde. With benzonitrile or phenylacetonitrile 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 benzhydrol 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*-benzhydrylacetonitrilium ion in equilibrium with the benzhydryl cation. Addition of various nucleophiles, including water, alcohols, and carboxylic acid, affects the relative yield of benzhydrol, 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 paper[2] 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-

$$RN_3 + NO^+ \longrightarrow R^+ + N_2 + N_2O \qquad (1)$$

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 temperature; (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).

Table I. Products from the Reaction of Benzhydryl Azide with $NO^+BF_4^-$ in Various Solvents[a]

Solvent	Reaction temp, °C	Yield, %[b]				
		$(C_6H_5)_2CHNHCOR$, R =		$(C_6H_5)_2CHOH$	$(C_6H_5)_2CO$	C_6H_5CHO
Acetonitrile	30	CH_3	38	30	20	12
	−30	CH_3	65	27	5	3
Phenylacetonitrile	30	$CH_2C_6H_5$	82	0	4	14
Benzonitrile	30	C_6H_5	84	0	6	10
Nitromethane[c]	30			12	21	27
	−30			25	21	17
Chloroform[d]	30			2	22	76
Chloroform + 1 equiv of acetonitrile[e]	30	CH_3	37	11	13	39

[a] Benzhydryl azide in 15 ml of the anhydrous solvent was added to an equivalent amount of $NO^+BF_4^-$ in 15 ml of the same solvent. Water was added at the same temperature 5 min after gas evolution had ceased. [b] Unless indicated otherwise, relative yields of products after work-up based on pmr analysis using an internal standard. Absolute yields were 90 ± 2%. [c] Absolute yields of products are given. [d] Unreacted benzhydryl azide (41%) was present after a reaction time of 6 hr. [e] Chloroform-d_1 was used as the solvent. A reaction time of 18 hr was allowed for complete reaction; after 1 hr only 25% of the azide had reacted.

water, both benzhydrol and *N*-(diphenylmethyl)acetamide are formed.[2] The benzhydryl cation in acetonitrile is in equilibrium with the *N*-benzhydrylacetonitrilium ion. Production of amide is essentially a Ritter process usually written, however, as involving irreversible formation of an *N*-alkylnitrilium ion from the corresponding nitrile and carbenium ion.[4] Since alcohols are used to form amides in the Ritter reaction, the benzhydryl azide–$NO^+BF_4^-$ system is rather unique in that amide is not formed exclusively after water quenching, and appears to be well suited to a study of the mechanism of competitive formation of alcohol and amide.

Results and Discussion

Effect of Solvent. Results from the reaction of benzhydryl azide with $NO^+BF_4^-$ in several solvents are presented in Table I. The effect of increasing basicity of the solvent is clearly shown in the data for reactions in acetonitrile, phenylacetonitrile, and benzonitrile; both benzonitrile and phenylacetonitrile are more basic than acetonitrile.[5] In acetonitrile the benzhydryl cation is in equilibrium with the *N*-benzhydrylacetonitrilium ion, a process that is rapid on the pmr time scale.[2] The reaction in acetonitrile provides both amide and alcohol when water is added, but use of either benzonitrile or phenylacetonitrile gives amide and no benzhydrol after addition of the same amount of water. In addition, the change in nitrile solvents does not affect benzaldehyde production, but the yield of benzophenone is greatly reduced in benzonitrile and phenylacetonitrile. Since these nitriles are better proton acceptors than acetonitrile, the process leading to benzophenone[2] does not seem to involve hydrogen abstraction by solvent.

In nitromethane, with the exception of the benzenediazonium ion, only those products listed in Table I were identified. The benzenediazonium ion was identified from its characteristic ir spectrum prior to the addition of water and work-up. Product(s) resulting from the reaction of nitromethane with the benzhydryl cation[6] were not observed after work-up of the reaction solution. Compared to the nitrile solvents, an unexpectedly high yield of benzaldehyde and benzophenone is encountered from the reactions in nitromethane. The yield of benzaldehyde is increased relative to benzophenone, and even at −30° nearly 40% of the reaction proceeds with phenyl migration and hydrogen abstraction.

Upon addition of benzhydryl azide to $NO^+BF_4^-$ in chloroform no gas evolution was noted. The azide was unchanged until approximately 45 min after addition, whereupon a vigorous evolution of gas occurred over a period of 15 min. Slow gas evolution continued and water was added. Benzaldehyde and benzophenone were the only major isolated reaction products; benzhydrol was only a minor product. However, when 1 equiv of acetonitrile was added to the chloroform solvent, the reaction between azide and nitrosonium salt proceeded smoothly to give the results shown in Table I. Although reaction times were long, there was no apparent induction period prior to gas evolution, and the *N*-benzhydrylacetonitrilium ion was easily distinguished by pmr spectroscopy prior to the addition of water.

Although nitrosonium salts are insoluble in chloroform, we had expected reaction with benzhydryl azide to produce the benzhydryl cation. The reaction of triphenylmethyl azide with $NO^+BF_4^-$ proceeds nearly as well in chloroform as in acetonitrile, in which solvent $NO^+BF_4^-$ is soluble.[8] The expected amount of gas evolved over a period of 30 min, nearly twice as long as for the comparable reaction in acetonitrile, and upon quenching with water triphenylmethanol was quantitatively produced. However, with benzhydryl azide observation of the induction period prior to gas evolution, the long reaction times, and the production of essentially only benzophenone and benzaldehyde indicate that product formation in this reaction need not be explained entirely by nitrosonium ion processes and may involve protonic decomposition of the azide, resulting in benzaldehyde.[9] When only 1 equiv of acetonitrile is added to the chloroform solvent, the course of the reac-

---

(4) (a) L. I. Krimen and D. J. Cota, *Org. Reactions*, 17, 213 (1969); (b) J. J. Ritter and J. Kalish, *J. Amer. Chem. Soc.*, 70, 4048 (1948); (c) H. Christol, A. Laurent, and G. Solladie, *Bull. Soc. Chim. Fr.*, 877 (1963), and references therein.

(5) J. F. Coetzee and D. K. McGuire, *J. Phys. Chem.*, 67, 1810 (1963); N. C. Deno, R. W. Gaugler, and M. J. Wisotsky, *J. Org. Chem.*, **31**, 1967 (1966); N. C. Deno and M. J. Wisotsky, *J. Amer. Chem. Soc.*, **85**, 1735 (1963).

(6) O-Alkylation of nitromethane by the benzhydryl cation leading to formation of the corresponding nitronate ester is a probable process in this solvent.[7]

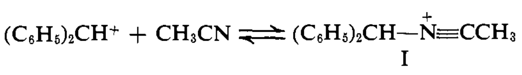
(7) (a) P. A. S. Smith, "The Chemistry of Open-Chain Organic Nitrogen Compounds," Vol. II, W. A. Benjamin, New York, N. Y., 1966; (b) G. A. Olah and T. E. Kiovsky, *J. Amer. Chem. Soc.*, **90**, 6461 (1968); (c) G. A. Olah and J. R. DeMember, *ibid.*, **92**, 2562 (1970).

(8) G. A. Olah and J. A. Olah, *J. Org. Chem.*, **30**, 2386 (1965).

(9) The acid catalyst may be produced in the hydrogen abstraction reaction which yields benzophenone.

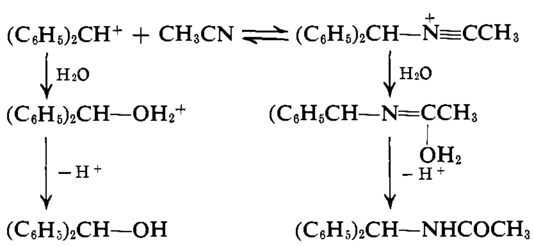
tion is markedly affected. The normal reaction of benzhydryl azide with $NO^+BF_4^-$ was observed even though reaction times are long. Similar observations were made with carbon tetrachloride as the solvent.

Effect of Quenching Agent. The production of both benzhydrol and *N*-(diphenylmethyl)acetamide after addition of water to the products formed from the reaction of benzhydryl azide with $NO^+BF_4^-$ indicates that the benzhydryl cation in acetonitrile at room temperature is in equilibrium with the *N*-benzhydrylacetonitrilium ion, I (eq 2). The pmr spectrum of the reaction solution[2] is consistent with this interpretation. We expected that addition of a sufficient amount of water to the reaction solution might irreversibly quench the benzhydryl cation and I (Scheme I) and allow an estimation of the equilibrium constant for the reaction in eq 2.[10] In addition, observation that benzhydrol is formed directly from the benzhydryl cation would provide additional evidence that carbenium ions are indeed produced from alkyl azides by reaction with nitrosonium salts. If the production of alcohol and amide corresponds to Scheme I, variation of the amount of water used to react with the benzhydryl cation and I should have no effect on the ratio of amide to alcohol. In addition, changing the amount of acetonitrile should directly affect the production of amide. However, benzhydrol production may occur by direct displacement of acetonitrile from I by water, along with addition of water to I leading to amide (eq 3); the ratio of amide to alcohol in this case should be independent of both the amount of water added and the concentration of I in acetonitrile. Alternatively, benzhydrol may be formed by alkyl–nitrogen fission of amide or its tautomer, as in eq 4; examples of this type of heterolysis of amides have been reported.[11] In this case increasing the amount of water will increase the amount of benzhydrol produced, but acetamide should also be formed.

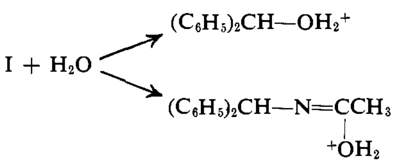


$$(C_6H_5)_2CH^+ + CH_3CN \rightleftharpoons \underset{\text{I}}{(C_6H_5)_2CH{-}\overset{+}{N}{\equiv}CCH_3} \qquad (2)$$

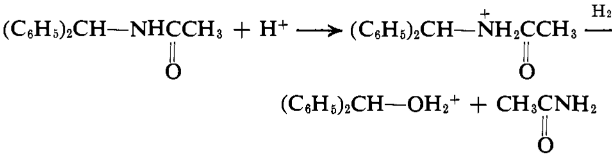
Scheme I



$$\begin{array}{ccc} (C_6H_5)_2CH^+ + CH_3CN & \rightleftharpoons & (C_6H_5)_2CH{-}\overset{+}{N}{\equiv}CCH_3 \\ \downarrow{\scriptstyle H_2O} & & \downarrow{\scriptstyle H_2O} \\ (C_6H_5)_2CH{-}OH_2^+ & & (C_6H_5CH{-}N{=}\underset{OH_2}{C}CH_3 \\ \downarrow{\scriptstyle -H^+} & & \downarrow{\scriptstyle -H^+} \\ (C_6H_5)_2CH{-}OH & & (C_6H_5)_2CH{-}NHCOCH_3 \end{array}$$



$$I + H_2O \begin{array}{l} \nearrow (C_6H_5)_2CH{-}OH_2^+ \\ \searrow (C_6H_5)_2CH{-}N{=}\underset{^+OH_2}{C}CH_3 \end{array} \qquad (3)$$



$$(C_6H_5)_2CH{-}NH\underset{O}{\underset{\|}{C}}CH_3 + H^+ \longrightarrow (C_6H_5)_2CH{-}\overset{+}{N}H_2\underset{O}{\underset{\|}{C}}CH_3 \xrightarrow{H_2O} (C_6H_5)_2CH{-}OH_2^+ + CH_3\underset{O}{\underset{\|}{C}}NH_2 \qquad (4)$$

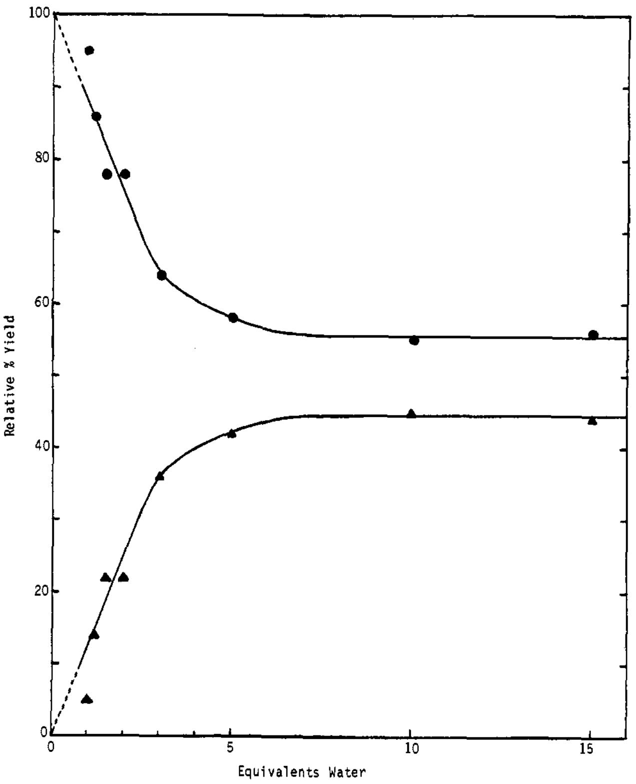


Figure 1. Effect of added water on the yields of benzhydrol (▲) and *N*-(diphenylmethyl)acetamide (●) at 30°.

The effect of added water on the production of both benzhydrol and *N*-(diphenylmethyl)acetamide in the reaction of benzhydryl azide with $NO^+BF_4^-$ in acetonitrile at 30° is shown graphically in Figure 1. The yields of benzaldehyde (11 ± 1%) and benzophenone (17 ± 2%) were not included for convenience and clarity. The amounts of benzhydryl azide, $NO^+BF_4^-$, and acetonitrile were constant for all reported reactions. Water was added directly and all at once by syringe to the reaction solution within 15 min after gas evolution was complete. Clearly, the relative amount of alcohol produced is dependent on the amount of water added, but only up to approximately 5 equiv. Addition of more than 5 equiv of water had no effect on the relative yield of either amide or alcohol products; even when greater than 40 equiv of water was added, no change was observed. In addition, no acetamide was detected, and *N*-(diphenylmethyl)acetamide was shown to be stable under the reaction conditions employed.

Increasing the concentration of benzhydryl azide and $NO^+BF_4^-$ in acetonitrile effects an increase in the relative yield of alcohol produced. These results are given in Table II. Although the change in yield with change in concentration is small, a trend is clear, and the variation is outside of experimental error.

Neither Scheme I, as written, nor eq 3 or 4 adequately explain the data in Figure 1 and Table II. Production of benzhydrol according to eq 4, although showing dependence on water added, demands that acetamide also be formed in equal amounts. Since production of benzhydrol is dependent on both the concentration of reactants and the amount of water added, eq 3 cannot be the sole pathway for alcohol formation. Irreversible formation of alcohol and amide (Scheme I) would be independent of the amount of water added.

---

[10] This is true, of course, only if water shows no selectivity in reactions with the benzhydryl cation and I.

[11] R. N. Lacey, *J. Chem. Soc.*, 1633 (1960).

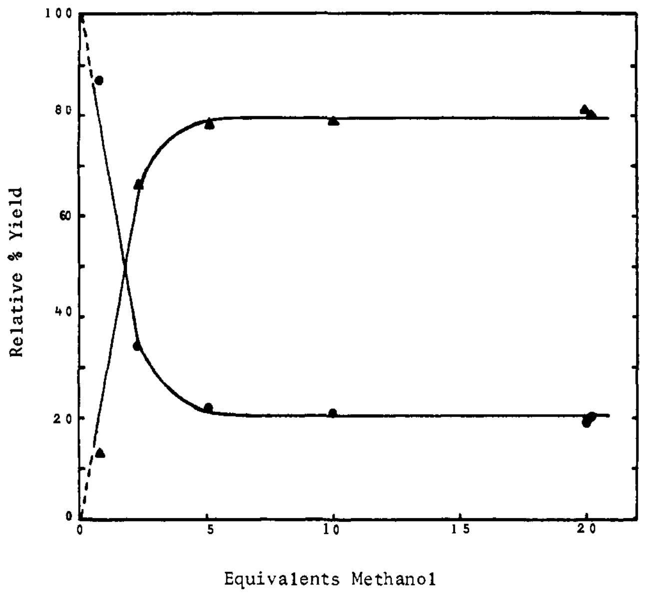


Figure 2. Effect of added methanol on the yields of benzhydryl methyl ether (▲) and *N*-(diphenylmethyl)acetamide (●) at 25°.

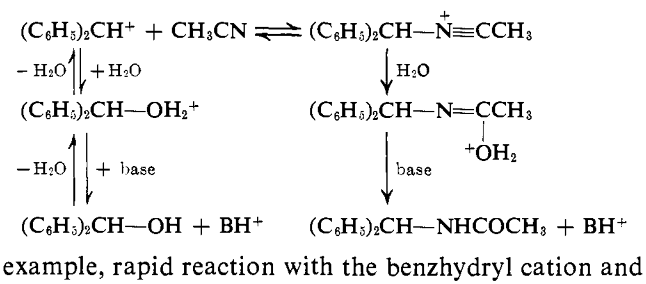
However, these data can be explained by irreversible formation of amide from I in competition with reversible reaction of the benzhydryl cation with water (Scheme II). When only 1 equiv of water is added, for example, rapid reaction with the benzhydryl cation and I occurs, and although protonated benzhydrol may be formed, re-formation of the benzhydryl cation occurs at a more rapid rate than does benzhydrol formation. The result is that the amide is almost exclusively formed. As more water is added, re-formation of the benzhydryl cation becomes less pronounced until, with greater than 5 equiv of added water, alcohol formation is essentially irreversible (Scheme I).

Table II. Effect of Variation of the Concentration of Benzhydryl Azide and $NO^+BF_4^-$ in Acetonitrile on the Yields of Amide and Alcohol[a]

$[(C_6H_5)_2CHN_3]$, mol/l.[c]	Temp, °C	Yield, %[b]	
		$(C_6H_5)_2CHOH$	$(C_6H_5)_2CH$-$NHCOCH_3$
0.64	10	40	60
0.32	10	33	67
0.16	10	30	70

[a] $NO^+BF_4^-$ in 15 ml of anhydrous acetonitrile was added to an equivalent amount of benzhydryl azide in the same solvent. Reaction temperature was 10°. Greater than 25 equiv of water was added to the reaction solution. [b] See footnote *b*, Table I. Yields of benzaldehyde and benzophenone were approximately 9 and 14%, respectively. [c] An equivalent amount of $NO^+BF_4^-$ was used.

Scheme II



Since diffusion of water through the solution is not instantaneous under our reaction conditions, even when greater than 5 equiv of water is added, we cannot expect the ratio of alcohol to amide to reflect the equilibrium ratio of their respective precursors. Additionally, water may be selective in the competitive reaction with benzhydryl cation and I. Because of the complicated nature of the quenching reaction no attempt was made to calculate equilibrium constants or to attempt numerical fitting of the observed results with the processes in Schemes I and II. Even the elegant study by Brauman and Archie[12] of the reaction of the trityl cation with water was sufficiently complicated to prevent calculation of equilibrium constants. However, our data do show that the success of production of N-substituted amides from alcohols and other compounds capable of forming carbenium ions in the presence of nitriles[4] depends on the irreversible quenching of *N*-alkylnitrilium intermediates, similar to I.

Results similar to those for water quenching are observed when methanol is the quenching agent, as shown in Figure 2. Again irreversible formation of amide explains the results when approximately 1 equiv of methanol is used. With more than 2 equiv of methanol added, however, the predominant product is benzhydryl methyl ether. Selectivity in quenching is evident by comparison of these results with those for water quenching (Figure 1).

Table III gives the yields of products from the addition of a variety of nucleophiles to the benzhydryl azide–$NO^+BF_4^-$ reaction products in acetonitrile. Except for the data given for reaction with water, all reactions were run at −20° until gas evolution had ceased to minimize the production of benzaldehyde and benzophenone. The solutions were then warmed to room temperature and the appropriate nucleophile added. When reaction with the various alcohols was performed at −20°, the pmr spectrum of the solution indicated the presence of the imino ester, $(C_6H_5)_2CH—N=C(CH_3)OR$;[13] complete conversion to the amide occurred only slowly upon standing at room temperature.

Addition of methanol, 2-propanol, and 2-methyl-2-propanol quenching agents produces the corresponding benzhydryl ethers predominantly. Changes in the ratio of ether to amide for these alcohols reflect the variation in the relative nucleophilic reactivity of the alcohols with the benzhydryl cation. Similar results have been obtained in the reaction of diaryldiazomethanes with acids in alcoholic media.[14] In addition, when the results for acetic acid, water, and the alcohols are compared, it is evident that the greater the acidity of the quenching agent, the greater the amount of amide formed. This further substantiates the mechanism written in Scheme II, since acetic acid and water are also better leaving groups than the alcohols[15] and would favor production of amide, which is irreversible. These results also indicate substantial selectivity in quenching the benzhydryl cation over the *N*-benzyhydrylacetonitrilium ion.

---

(12) J. I. Brauman and W. C. Archie, Jr., *J. Amer. Chem. Soc.*, **92**, 5981 (1970).

(13) This situation was observed both for quenching by methanol and 2-propanol.

(14) D. Bethell and R. D. Howard, *Chem. Commun.*, 94 (1966); D. Bethell and J. D. McCallister, *J. Chem. Soc.*, 3801, 3808 (1963).

(15) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962.

Table III. Reaction of the Benzhydryl Azide–$NO^+BF_4^-$ Reaction Products in Acetonitrile with Various Quenching Agents[a]

Quenching agent	Equiv added	Temp, °C[c]	Yield, %[b]					% $(C_6H_5)_2CHX$/% amide
			$(C_6H_5)_2CH$-$NHCOCH_3$	$(C_6H_5)_2CH$-X, X =		$(C_6H_5)_2CO$	C_6H_5CHO	
H_2O[d]	15	30	38	OH	30	21	11	0.79
CH_3OH	20	25	16	OCH_3	64	10	10	4.0
$(CH_3)_2CHOH$	20	25	17	$OCH(CH_3)_2$	67	8	8	3.9
$(CH_3)_3COH$	20	25	24	$OC(CH_3)_3$	58[e]	12	6	2.4
CH_3CO_2H	20	25	70	O_2CCH_3	16	8	6	0.23
CH_3CO_2Na[f]	10	25	25	O_2CCH_3	61	8	6	2.4
Bu_3SiH[g]	20	25		H	81			
$(C_6H_5)_3CBr$[f,g]	3	−20		Br	48	*h*	*h*	
$(C_6H_5)_3CCl$[f,g]	3	−20		Cl	52	*h*	*h*	

[a] Benzhydryl azide in acetonitrile was added to an equivalent amount of $NO^+BF_4^-$ in anhydrous acetonitrile at −20°. After gas evolution had ceased, the reaction solution was warmed to 25° and the appropriate reagent added. [b] See footnote *b*, Table I. [c] Temperature at which quenching agent was added. [d] Azide reaction with $NO^+BF_4^-$ was run at 30°. [e] Includes 8% of benzhydrol. [f] Added as a solid. [g] Absolute yield of the indicated product. [h] Not determined.

Organosilicon hydrides have been shown to reduce relatively stable carbenium ions, generated from alcohols or olefins in acidic media, to the corresponding hydrocarbons.[16] Selectivity in the reduction of the benzhydryl cation in acetonitrile was examined to determine if diphenylmethane would be the exclusive product of hydride transfer from silane. When 1 equiv of triethylsilane was added to the benzhydryl azide–$NO^+BF_4^-$ reaction solution at 35° in acetonitrile after complete gas evolution and followed within 15 min by the addition of water, a 50% yield of diphenylmethane was realized in addition to 13% (*N*-diphenylmethyl)-acetamide, 9% benzaldehyde, and 12% benzophenone. By increasing the amount of trialkylsilane[17] to 20 equiv the yield of diphenylmethane was increased to 75% with approximately 6% of the amide produced by water addition. Increasing the reaction time for silane reduction to 45 min gives the result shown in Table III. No benzaldehyde or benzophenone was observed in this latter reaction.[18] Trialkylsilanes reacted selectively with the benzhydryl cation since no imine or amine was observed, as would be expected if silane reacted with I. Addition of 1 molar equiv of sodium borohydride effected the production of 38% diphenylmethane within 15 min with 42% of the amide recovered after the addition of water.

Addition of triphenylmethyl halides gives the products expected from intermolecular halogen exchange (eq 5). After the addition of triphenylmethyl bromide

$$(C_6H_5)_2CH^+ + (C_6H_5)_3C{-}X \longrightarrow (C_6H_5)_2CH{-}X + (C_6H_5)_3C^+ \quad (5)$$

to the benzhydryl azide–$NO^+BF_4^-$ reaction solution, the pmr spectrum showed the disappearance of the δ 6.94 absorption attributed to the methine hydrogen of I,[2] and the appearance of a singlet at δ 6.30, due to benzhydryl bromide. Likewise, after the addition of triphenylmethyl chloride, a new signal at δ 6.13, due to benzhydryl chloride, was observed. These results are given in Table III. Subsequent addition of triethylsilane did not produce diphenylmethane, and neither benzhydrol nor the corresponding amide were produced after water addition. No attempt was made to improve the yields of benzhydryl chloride or bromide. Similar results have been observed under different reaction conditions.[20] Intermolecular halogen exchange, although well documented in strongly acidic solutions,[21] is not commonly observed in weakly ionizing solvents such as acetonitrile.[22]

Effect of Nitrosonium Compound. With regard to reaction conditions, alkyl azides appear to be much like amines in their reactions with nitrosonium salts.[2,23] Amines, however, react with many different nitrosonium compounds and under a wide variety of experimental conditions.[3a,24] It was, therefore, of interest to examine several reactions with azides under conditions similar to those for amine diazotization.

Triphenylmethyl azide did not react with excess nitrosyl chloride in carbon tetrachloride. Only unreacted starting material was recovered after reaction times exceeding 10 hr at room temperature or above. Attempts were made to react benzhydryl azide with nitrous acid in acidic media and with isoamyl nitrite under conditions similar to those employed in amine diazotizations.[25] Only unreacted starting material was recovered after the attempted reactions in acetic acid or dioxane solutions containing sodium nitrite, water, and sulfuric acid, even after heating at elevated temperatures. No reaction was observed when benzhydryl azide was treated with isoamyl nitrite in refluxing benzene for 3 hr. However, when azide and water were added simultaneously to the nitrosonium salt in acetonitrile, or when azide was added to $NO^+BF_4^-$ in acetonitrile after water had been added, reaction conditions under which protonated nitrous acid or dinitrogen trioxide predominate over the unsubstituted nitrosonium ion,[26] benzhydryl azide easily reacted to

---

(16) F. A. Carey and H. S. Tremper, *J. Org. Chem.*, **36**, 758 (1971), and references therein.

(17) Both triethyl- and tri-*n*-butylsilanes were used. Silanes were observed to reduce $NO^+BF_4^-$ quantitatively and rapidly under our reaction conditions.

(18) Benzophenone is reduced to diphenylmethane and benzaldehyde to dibenzyl ether as was observed by Kursanov.[19]

(19) D. N. Kursanov, Z. N. Parnes, G. I. Bassova, N. M. Loim, and V. I. Zdanovich, *Tetrahedron*, **23**, 2235 (1967).

(20) H. Volz and W. D. Mayer, *Tetrahedron Lett.*, 5249 (1966).

(21) G. A. Olah and J. R. DeMember, *J. Amer. Chem. Soc.*, **92**, 2562 (1970), and previous articles in this series.

(22) Since triphenylmethyl chloride does not ionize in acetonitrile (V. Gutmann, M. Baaz, and O. Kunze, *Monatsh. Chem.*, **93**, 1142 (1962)), formation of benzhydryl chloride would not be expected to occur by donation of a chloride ion from a trityl chloride ion pair.

(23) G. A. Olah, N. A. Overchuk, and J. C. Labierre, *J. Amer. Chem. Soc.*, **87**, 5785 (1965).

(24) For a review of deamination reactions see (a) R. J. Baumgarten, *J. Chem. Educ.*, **43**, 398 (1966); (b) E. H. White and D. J. Woodcock in "The Chemistry of the Amino Group," S. Patai, Ed., Interscience, New York, N. Y., 1968, pp 407–497.

(25) J. H. Ridd, *Quart. Rev., Chem. Soc.*, **15**, 418 (1961).

(26) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience, New York, N. Y., 1966; H. Schmid and

Table IV. Reactions of Benzhydryl Azide with NO^+ in the Presence of Added Water

Temp, °C	H_2O added, equiv	Yield, %[a] $(C_6H_5)_2$-$CHNHCOCH_3$	Yield, %[a] $(C_6H_5)_2$-CHOH	Yield, %[a] $(C_6H_5)_2$-CO
50	5.0[b]	45	16	39
25	5.0[b]	21	48	31
−10	5.0[b]	21	44	35
25	1.0[b]	72		28
25	1.0[c]	55		45

[a] Absolute yield of products based on direct pmr analysis. [b] Benzhydryl azide and water in acetonitrile were added to $NO^+BF_4^-$ in acetonitrile. [c] Benzhydryl azide in acetonitrile was added to the acetonitrile solution of $NO^+BF_4^-$ after the water had been added.

give the results shown in Table IV. Reaction times, as measured by gas evolution, were noticeably longer with water addition; the reaction at −10°, for example, required more than 3 hr for completion. Direct pmr and glpc analysis showed that benzaldehyde had not been produced under any of the reaction conditions given in Table IV. Benzyl azide behaved similarly; with 1 equiv of water added with azide only *N*-benzylacetamide was produced, and upon addition of 5 equiv of water with azide at room temperature 89% amide and 11% benzaldehyde were observed.

Except when water is added to $NO^+BF_4^-$ prior to benzhydryl azide, the amount of benzophenone produced is approximately equal to the total yield of benzaldehyde and benzophenone under anhydrous conditions (see Table I). The absence of phenyl migration in these reactions, however, is surprising in view of the interpretation that phenyl migration in the analogous Curtius rearrangement of benzhydryl azide is a concerted process.[27] If benzophenone and benzaldehyde both result from attack by NO^+ on the substituted nitrogen of benzhydryl azide, as is indicated by our previous results,[2] both products would be expected even when water is present. Further work is in progress to determine whether loss of nitrogen and phenyl migration are synchronous or occur in two steps.

Experimental Section

General. Instrumentation has been described.[2] Nitrosonium salts were obtained from Ozark Mahoning Co. and were dried over phosphorus pentoxide in a vacuum dessicator at 1.0 Torr for several hours prior to use. Spectral grade acetonitrile and nitromethane were distilled from calcium hydride and stored over molecular sieves. Benzonitrile and phenylacetonitrile were successively dried over anhydrous magnesium sulfate and anhydrous calcium sulfate. Reagent grade chloroform was washed with aqueous sulfuric acid to remove the added stabilizer, dried, and distilled prior to use. Reactants and products were prepared by standard techniques or as previously described.[2] The quenching agents were commercially available.

Solvent Studies. Reactions were run according to procedures previously given.[2] The $NO^+BF_4^-$ was only slightly soluble in benzonitrile and phenylacetonitrile; reaction times for reactions with benzhydryl azide were greater than 90 min at 30°. Benzaldehyde was analyzed by pmr and ir spectroscopy after quenching and prior to work-up in benzene. Distillation of benzonitrile and phenylacetonitrile under reduced pressure followed by pmr spectral analysis afforded yields of benzophenone and amide products. These products were confirmed by glpc which also showed the absence of benzhydrol (<0.1%).

Nitrosonium tetrafluoroborate was partially soluble in nitromethane.[8] Reaction times for $NO^+BF_4^-$ and benzhydryl azide in nitromethane were similar to those in acetonitrile. Products were analyzed by pmr spectroscopy and confirmed by ir and glpc methods.

Addition of benzhydryl azide (5.0 mmol) in 15 ml of chloroform to the constantly stirred solid $NO^+BF_4^-$ (5.0 mmol) in 15 ml of chloroform at 30° under a nitrogen atmosphere afforded no reaction. Gas evolution was insignificant until between 30 and 45 min after initiation of addition, at which time a rapid flow of gas was observed. After 75 min a slow reaction continued until the solution was quenched with 5 equiv of water approximately 6 hr after initial addition.

Addition of benzhydryl azide and 1 equiv of acetonitrile in chloroform-d_1 to $NO^+BF_4^-$ in the same solvent at 30° afforded a slow but constant evolution of gas. The progress of the reaction was monitored by removal of aliquots that were subjected to pmr analysis. The pmr spectrum after 18 hr showed broad singlet absorptions at δ 2.48 and 6.96 in an integral ratio of 3:1 $[(C_6H_5)_2C\mathit{H}NCC\mathit{H}_3]^+$, phenyl absorptions at δ 7.1–7.9, a broadened singlet at δ 9.0, a singlet at δ 9.98 ($C_6H_5C\mathit{H}O$), and the acetonitrile signal at δ 1.92.

Quenching Studies. Reactions were run according to standard procedures.[2] Water quenching studies were performed at 30°. Five minutes after the quenching agent was introduced, a large excess of water was added along with methylene chloride and the products isolated in the usual manner.

Reactions of benzhydryl azide with $NO^+BF_4^-$ in the methanol quenching study were run at −20° in a carbon tetrachloride–Dry Ice slush bath to minimize production of benzaldehyde (8 ± 2%) and benzophenone (8 ± 2%). After gas evolution was complete (3 hr), the solution was warmed to 25° and methanol added directly by syringe. A similar procedure was used for quenching reactions with 2-propanol, 2-methyl-2-propanol, acetic acid, sodium acetate, and tri-*n*-butylsilane.

Triphenylmethyl halide was added directly as a solid to the reaction solution at −20° and the solution analyzed by pmr spectroscopy. Triethylsilane (10 equiv) was added 20 min later followed by water (20 equiv). Under the reaction conditions the triphenylmethyl halides were converted to triphenylmethane by triethylsilane. The benzhydryl halides were converted to the corresponding alcohol and acetamide by water within 30 min after water was added.

Reactions with Various Nitrosonium Compounds. Triphenylmethyl azide was treated with nitrosyl chloride by a procedure similar to that of Clark and Helmkamp.[28] Only unreacted starting material was isolated with reaction times in excess of 10 hr. Benzhydryl azide did not react with isoamyl nitrite after refluxing in benzene for 3 hr.[28,29] No reaction was observed when benzhydryl azide was treated with sodium nitrite in acetic acid according to the procedure of Berson, McRowe, and Bergman.[30] Using aqueous dioxane or acetic acid as the solvent, benzhydryl azide was recovered after treatment with sodium nitrite even though the reaction solution contained approximately 10% sulfuric acid by volume and was heated at 90° for more than 2 hr.

In reactions of benzhydryl azide with $NO^+BF_4^-$ in the presence of water the reaction products were confirmed by glpc analysis. The absence of benzaldehyde (<0.1%) was also shown by glpc.

Acknowledgment. This work was supported by a Frederick Cottrell Grant from the Research Corporation and by Grant No. GP-27587 from the National Science Foundation. We are grateful to Miss Martha Patrie for preliminary results in the quenching studies.

C. Essler, *Monatsh. Chem.*, **91**, 484 (1960); F. Seel and R. Schwaebel, *Z. Anorg. Allg. Chem.*, **274**, 169 (1953).

(27) C. H. Gudmundsen and W. E. McEwen, *J. Amer. Chem. Soc.*, **79**, 329 (1957); P. A. S. Smith in "Molecular Rearrangements," P. deMayo, Ed., Interscience, New York, N. Y., 1963, Chapter 8.

(28) R. D. Clark and G. K. Helmkamp, *J. Org. Chem.*, **29**, 1316 (1964).

(29) R. M. Carlson and S. Y. Lee, *Tetrahedron Lett.*, 4001 (1969).

(30) J. A. Berson, A. W. McRowe, and R. G. Bergman, *J. Amer. Chem. Soc.*, **89**, 2573 (1967).