Reactions of the Nitrosonium Ion. VIII. Reactions of Nitrosonium Tetrafluoroborate and Benzhydryl Tetrafluoroborate with Benzhydryl Azides. The Mechanism of Aldehyde and Ketone Formation[1]

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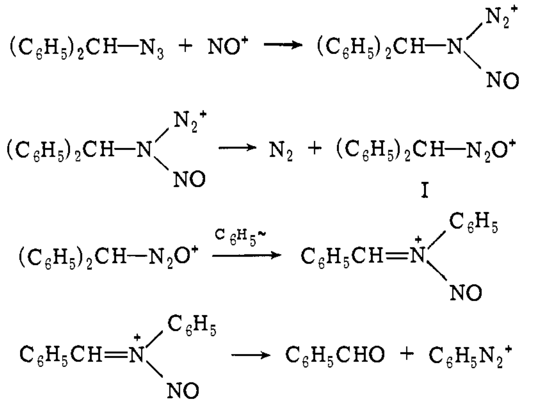
Abstract: Substituted benzhydryl azides react with $NO^+BF_4^-$ in anhydrous acetonitrile to give benzaldehydes, benzophenones, and products emanating from the benzhydryl cation. The migratory aptitudes for aryl migration to nitrogen that results in aldehyde formation are identical with those found in reactions of substituted benzhydryl azides with the corresponding benzhydryl tetrafluoroborates; a good correlation with σ^+ values is observed with $\rho = -0.64$. Hydrogen migration resulting in benzophenone production competes with aryl migration; the ratio of benzophenone to benzaldehyde products is 1.41 ± 0.10 for a series of meta and para substituted benzhydryl compounds. These results, which differ markedly from those of the analogous Curtius rearrangement in protic acids, are consistent with steric interference by the benzhydryl group in aryl migration. The extent of hydride abstraction by the nitrosonium ion in reactions with benzhydryl azides has also been determined. The effect of substitution on the ratio of substituted benzhydrols to the corresponding *N*-(diphenylmethyl)acetamides, which is a measure of the responsiveness of the equilibrium between the benzhydryl cation and the *N*-benzhydryl acetonitrilium ion to substituents, has been measured; correlation with σ^+ gives a ρ value of -1.47.

Alkyl azides react with stable nitrosonium salts such as $NO^+BF_4^-$ to yield carbenium ions through the loss of nitrogen and nitrous oxide (eq 1).[3]

$$R{-}N_3 + NO^+ \longrightarrow R^+ + N_2 + N_2O \qquad (1)$$

The reaction is rapid even at temperatures less than 0° and, because carbenium ions are cleanly produced, has proved useful in mechanistic studies of the Ritter reaction[4] and in the synthesis of heterocyclic compounds.[1] Unlike other alkyl azides that we have investigated, nitrosation of benzhydryl azide is complicated by the formation, after water quenching, of benzaldehyde, benzenediazonium tetrafluoroborate, and benzophenone in addition to those products emanating from the benzhydryl cation. The source of the benzaldehyde from this reaction was originally believed to be a reaction intermediate (I) formed through nitrosation at the substituted azide nitrogen followed by the loss of nitrogen (Scheme I);[3] phenyl migration to nitrogen with subsequent nitrosative cleavage of the carbon-nitrogen double bond[5] could account for the observed production of benzaldehyde and the benzenediazonium salt.

Scheme I



$$(C_6H_5)_2CH{-}N_3 + NO^+ \longrightarrow (C_6H_5)_2CH{-}N{<}^{N_2^+}_{NO} \qquad (2)$$

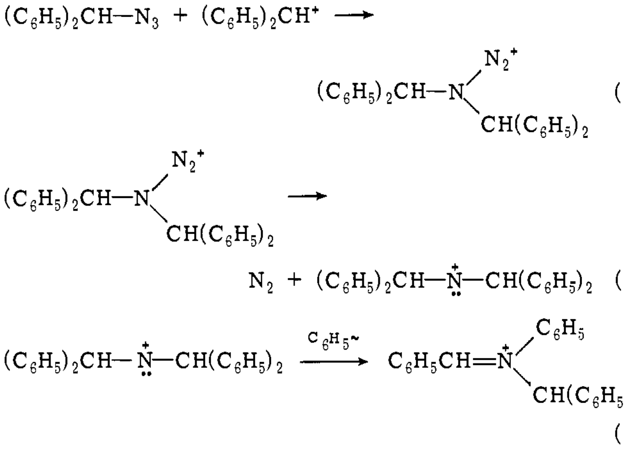
$$(C_6H_5)_2CH{-}N{<}^{N_2^+}_{NO} \longrightarrow N_2 + \underset{\text{I}}{(C_6H_5)_2CH{-}N_2O^+} \qquad (3)$$

$$(C_6H_5)_2CH{-}N_2O^+ \xrightarrow{C_6H_5\sim} C_6H_5CH{=}\overset{+}{N}{<}^{C_6H_5}_{NO} \qquad (4)$$

$$C_6H_5CH{=}\overset{+}{N}{<}^{C_6H_5}_{NO} \longrightarrow C_6H_5CHO + C_6H_5N_2^+ \qquad (5)$$

Recently, however, McGirk and White[6] have suggested that the benzaldehyde formed in the reaction between benzhydryl azide and nitrosonium salts is produced from the reaction between the benzhydryl cation and benzhydryl azide (Scheme II), a reaction formally analogous to the Curtius rearrangement.[7,8] They found that benzaldehyde is produced from benzhydryl azide when the benzhydryl cation is formed from benzhydryl chloride and silver tetrafluoroborate and the imine product is hydrolyzed with water. The nitrosation reaction of benzhydryl azide using a limited amount of $NO^+BF_4^-$ also yielded benzaldehyde in amounts suggesting the validity of Scheme II.

Scheme II



$$(C_6H_5)_2CH{-}N_3 + (C_6H_5)_2CH^+ \longrightarrow (C_6H_5)_2CH{-}N{<}^{N_2^+}_{CH(C_6H_5)_2} \qquad (6)$$

$$(C_6H_5)_2CH{-}N{<}^{N_2^+}_{CH(C_6H_5)_2} \longrightarrow N_2 + (C_6H_5)_2CH{-}\overset{+}{\underset{\cdot\cdot}{N}}{-}CH(C_6H_5)_2 \qquad (7)$$

$$(C_6H_5)_2CH{-}\overset{+}{\underset{\cdot\cdot}{N}}{-}CH(C_6H_5)_2 \xrightarrow{C_6H_5\sim} C_6H_5CH{=}\overset{+}{N}{<}^{C_6H_5}_{CH(C_6H_5)_2} \qquad (8)$$

Interestingly, Scheme I predicts that benzaldehyde would be observed prior to water quenching, whereas Scheme II requires the addition of water before benzaldehyde can be observed. Although we have observed both benzaldehyde and the benzenediazonium ion prior to water quenching, their presence does not demonstrate that Scheme I is operative since the *N*-benzhydrylbenzylidenanilinium ion produced in eq 8 could have reacted with the nitrosonium ion to yield the benzhydryl cation and the *N*-nitrosobenzylidenanilinium ion or have been hydrolyzed by water present in the reaction medium. A conclusive determination of the source of benzaldehyde and the mechanism of its formation, however, can be made by comparing the migratory aptitudes of substituted benzhydryl azides in reactions with the

Table I. Product Yields from the Reactions of Substituted Benzhydryl Azides with $NO^+BF_4^-$ in Acetonitrile[a]

$ArPhCHN_3$ Ar =	Product yield, %[b]					PhCHO/ArCHO	Total product yield, %
	ArPhCHOH	$(ArPhCH)_2O$	$ArPhCHNHCOCH_3$	ArPhC=O	Aldehyde		
p-$CH_3OC_6H_4$–[c]					5	14.8	
p-$CH_3C_6H_4$–	26	5	12	34	17	1.66	94
m-$CH_3C_6H_4$–	17	6	18	32	16	1.26	89
p-FC_6H_4–	10	5	11	29	17	1.06	72
C_6H_5–	17	6	30	27	14		94
p-ClC_6H_4–	14	3	27	42	9	0.85	95
p-BrC_6H_4–	8	3	25	50	11	0.76	97
p-$NO_2C_6H_4$–[d]	6	0	89	2	0		97

[a] Reactions were run at 25 ± 1°. [b] Actual yields of individual products determined by GLC and/or ^1H NMR analysis. Duplicate runs were performed for each azide. Precision of analysis was ±0.5% for alcohol, amide, and ether products. [c] Only benzaldehyde and p-anisaldehyde were detected; the presence of alcohol, amide, and ether was not apparent in the ^1H NMR spectrum of the reaction solution. [d] Gas evolution continued over a 1.5-hr period.

Table II. Product Yields from the Reactions of Substituted Benzhydryl Azides with $ArPhCH^+BF_4^-$ in Acetonitrile[a]

$ArPhCHN_3$ Ar =	$ArPhCH^+BF_4^-$[b] Ar =	Product yield, %[c]		PhCHO/ArCHO
		ArPhC=O	Aldehyde	
p-$CH_3OC_6H_4$–	p-$CH_3OC_6H_4$–[d]		4	16.1
p-$CH_3C_6H_4$–	p-$CH_3C_6H_4$–	48	32	1.65
p-$CH_3C_6H_4$–	C_6H_5–	*e*	35	3.33
C_6H_5–	p-$CH_3C_6H_4$–	*e*	31	3.45
m-$CH_3C_6H_4$–	m-$CH_3C_6H_4$–	50	33	1.45
p-FC_6H_4–	p-FC_6H_4–	46	33	1.05
C_6H_5–	C_6H_5–	45	36	
p-ClC_6H_4–	p-ClC_6H_4–	52	40	0.92
p-BrC_6H_4–	p-BrC_6H_4–	42	28	0.90
p-$NO_2C_6H_4$–[f]	p-$NO_2C_6H_4$–	*e*	23	0.33

[a] Reactions were run at 25 ± 1°. [b] ArPhCHCl was added to $AgBF_4$ and $ArPhCHN_3$ in acetonitrile. [c] Actual yields of products determined by GLC and ^1H NMR analyses. The yield of ArPhC=O is the combined yield of ArPhC=O and ArPhC=NCHPhAr. Precision of analysis was ±2% for aldehyde and ketone products as determined from duplicate runs. [d] Only benzaldehyde and p-anisaldehyde were detected. [e] Yield not determined. [f] Only one run was made. Reaction was terminated after 5 hr; gas evolution was low (41%) and unreacted azide was observed.

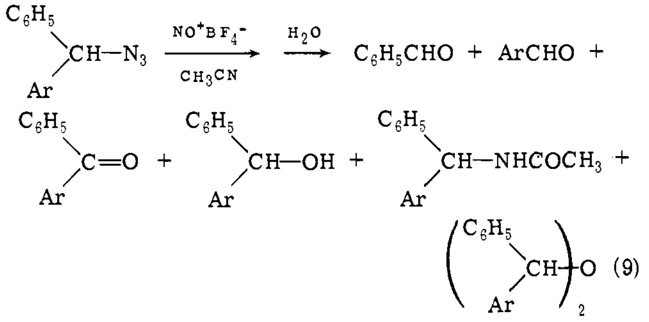
nitrosonium ion and with the benzhydryl cation. The migratory aptitudes in such a comparative study would be expected to be significantly different if Scheme I is operative.

McGirk and White have also observed that hydrogen migration competes with phenyl migration in the reaction of the benzhydryl cation with benzhydryl azide.[6] This process has not been previously detected in the Curtius rearrangements of benzhydryl azides.[7,9] However, benzophenone, the product resulting from hydride migration after hydrolysis, could also be formed by hydride abstraction from benzhydryl azide by the nitrosonium ion.[3]

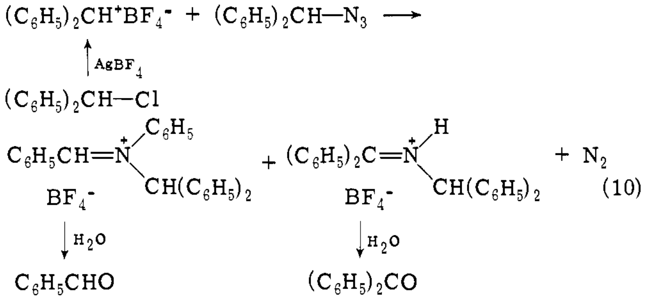
We report the results of the reactions in acetonitrile of a series of substituted benzhydryl azides with both the nitrosonium ion and appropriately substituted benzhydryl cations and their relationship to the mechanism of benzaldehyde formation, the production of benzophenone, and the effect of substitution on the ratio of N-(diphenylmethyl)acetamide to benzhydrol.

Results

Product yields from the reactions of a series of substituted benzhydryl azides with $NO^+BF_4^-$ in anhydrous acetonitrile followed by water quenching (eq 9) are given in Table I. In all reactions, the azide was added to an excess of the nitrosonium salt. Except for the nitrosation of p-nitrobenzhydryl azide, reaction times were short; gas evolution was complete within 30 min after the addition of the azide. Following complete gas evolution, 10 equiv of water (based on azide) was added, the reaction solution was neutralized by the addition of solid sodium bicarbonate, and the reaction products were analyzed directly by GLC and/or ^1H NMR techniques. Excellent accountability was obtained for the reaction products obtained from these reactions.



Benzhydryl azide reacts with benzhydryl tetrafluoroborate to yield nitrogen and imine products resulting from hydrogen and phenyl migration to nitrogen (eq 10).[6] Quenching the reaction solution with water produces benzaldehyde rapidly; benzophenone is formed slowly by hydrolysis of N-benzhydrylidenebenzhydrylamine. Treatment of a series of substituted benzhydryl azides in acetonitrile with the corresponding benzhydryl chlorides and silver tetrafluoroborate also yields aldehyde and ketone products after quenching with water. The yields of these products are given in Table II.



For reactions of benzhydryl azides with benzhydryl chlorides and silver tetrafluoroborate, the chloride in acetonitrile was added to a mixture of the azide and silver tetrafluoroborate also in acetonitrile. Altering this mode of addition by adding the azide after the chloride and silver tetrafluoroborate were mixed produced no noticeable change in product yields. The benzhydryl azides were stable toward silver tetrafluoroborate under the reaction conditions employed in this study.

Reaction times for the benzhydryl chloride–$AgBF_4$–benzhydryl azide reactions were noticeably sensitive to substitution, unlike those for the benzhydryl azide-$NO^+BF_4^-$ reactions. When the yield of nitrogen from the reactions listed in Table II was followed with time, the time at which one-half of the nitrogen was evolved (given in parentheses) occurred in the order: *p*-CH_3O- (1 min), *p*-CH_3- (8 min), *m*-CH_3- (12 min), H- (15 min), *p*-Cl- (50 min), *p*-Br- (60 min). In one series of reactions, induction periods during which no nitrogen was evolved were noticed. The induction period was also sensitive to the substituent, lasting between 5 and 15 sec for reactions between reactants with *p*-methyl substituents and as long as 90 sec for reactions between *p*-bromo substituted compounds. This early lag in nitrogen evolution was due to the presence of water in the silver tetrafluoroborate used and was not observed when the rigorously dried silver salt was used. However, the benzaldehyde to substituted benzaldehyde ratios and the relative yields of aldehyde and ketone products were the same for reactions without and with an induction period for nitrogen evolution.

The low yield of products identified from the reaction of *p*-methoxybenzhydryl azide with either nitrosonium tetrafluoroborate or *p*-methoxybenzhydryl chloride–silver tetrafluoroborate and the similarity of the ^1H NMR spectra obtained of the products from these reactions is understandable if Friedel-Crafts alkylation of the activated *p*-methoxyphenyl group was predominant. The triarylmethane thus formed would be subject to hydride transfer to the *p*-methoxybenzhydryl cation, a reaction process well documented for comparable substrates under similar conditions.[10] Spectral evidence suggests a multitude of products from reactions of *p*-methoxybenzhydryl azide with $NO^+BF_4^-$ and with the corresponding benzhydryl chloride-$AgBF_4$ and that $ArCH_2Ph$ products account for between 20 and 40% of the total.

In a separate experiment, benzhydryl chloride was added in portions to a mixture of benzhydryl azide and silver tetrafluoroborate in acetonitrile to determine if the benzhydryl cation could exhibit any catalytic activity in the rearrangement process represented by eq 10. However, the yield of nitrogen corresponded directly to the amount of benzhydryl chloride added, even when time periods as long as 24 hr were allowed between partial additions of benzhydryl chloride. Equal amounts of benzhydryl azide and benzhydryl chloride–$AgBF_4$ were required for complete reaction.

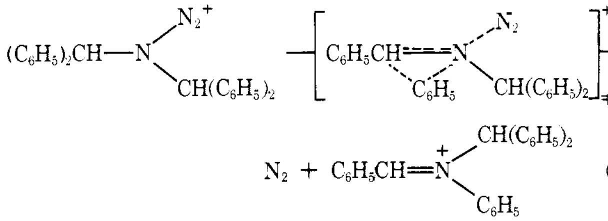
To determine if aryl migration was occurring after the formation of a symmetrical intermediate, *p*-methylbenzhydryl azide was reacted with benzhydryl tetrafluoroborate, and benzhydryl azide was treated with *p*-methylbenzhydryl tetrafluoroborate in separate experiments under identical reaction conditions (Table II). The ratio of benzaldehyde to *p*-tolualdehyde was, within experimental limitations, exactly twice that observed in the reaction between *p*-methylbenzhydryl azide and *p*-methylbenzhydryl tetrafluoroborate, demonstrating that aryl migration does occur through a reaction intermediate in which both of the benzhydryl groups are bonded to nitrogen.

Discussion

The ratios of benzaldehyde to substituted benzaldehyde from the reactions of substituted benzhydryl azides with $NO^+BF_4^-$ (Table I) and with substituted benzhydryl tetrafluoroborates (Table II) are identical within experimental error. These results further demonstrate that, as pointed out by McGirk and White,[6] aldehyde products are formed from benzhydryl azide by a Curtius rearrangement process with the benzhydryl cation rather than by the process represented by Scheme I. Although not evident from a comparison of reaction times for gas evolution in the two reactions, the nitrosation reaction being at least five times faster than the corresponding reaction with benzhydryl chloride–silver tetrafluoroborate, benzhydryl azide reacts with the nitrosonium ion and with the benzhydryl cation competitively. The relative yield of aldehyde products from the nitrosation reaction reflects the relative rates for these two reactions.

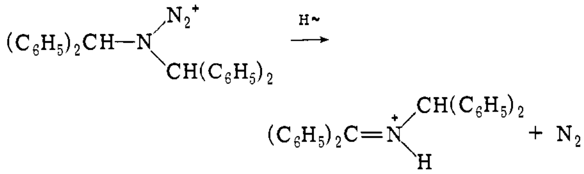
Since the ratio of benzaldehyde to substituted benzaldehyde is equal to the ratio of the specific rate constants for aryl to phenyl migration, the relatively small range in the aldehyde ratio (a factor of 5 between substitution of *p*-nitro and *p*-methyl)[11] reflects a relative insensitivity in the rate of migration to substituents. A good correlation in a Hammett plot with σ^+ [12] is observed, and the ρ value obtained is -0.64 (correlation coefficient $-$ 0.992).[13] The correlation with σ^+ indicates that there is charge development at carbon during migration. However, compared with the rearrangement of substituted benzhydryl azides[9,14] and α-methylbenzhydryl azides[9,15] with protic acids, the corresponding reactions with benzhydryl cations in acetonitrile are markedly different. The reactions with protic acids are characterized by ρ values less than -2 when determined with σ^+ constants.

In the rearrangement of benzhydryl azides, the loss of nitrogen and aryl migration may occur in two steps with the intermediate formation of a highly reactive nitrenium ion intermediate (eq 7 and 8)[16] or take place as a synchronous process (eq 11). In protic acids, the concerted rearrangement of alkyl azides appears to be most probable.[7] Synchronous loss of nitrogen and aryl migration is similarly likely for the rearrangement of benzhydryl azides in acetonitrile, a solvent whose ionizing properties are significantly less than those of aqueous mineral acids. The low ρ value for the rearrangement of substituted benzhydryl azides in acetonitrile reflects the charge distribution in the transition state for rearrangement and indicates that the extent of aryl migration is not great compared with similar rearrangements in protic acids.



$$(C_6H_5)_2CH{-}\overset{+}{N}(N_2)CH(C_6H_5)_2 \longrightarrow \left[C_6H_5CH{\cdots}N(N_2)(C_6H_5)CH(C_6H_5)_2\right]^{+}_{\ddagger} \longrightarrow N_2 + C_6H_5CH{=}\overset{+}{N}(CH(C_6H_5)_2)C_6H_5 \qquad (11)$$

The substituted benzophenones from reactions of benzhydryl azides with benzhydryl chlorides and silver tetrafluoroborate are formed by hydride migration to nitrogen (eq 12), a process that has not been observed in rearrangements of benzhydryl azides in protic acids. Surprisingly, the yield of substituted benzophenones in these reactions is greater than that of the aldehyde products (see Table III), and the ketone to aldehyde ratio is constant (1.41 ± 0.10). Generally in protic acids, the smallest groups are observed to migrate the least, whereas the opposite is observed here. This difference between rearrangements in protic acids and those effected by the benzhydryl cation can be attributed either to energy differences between the conformations from which



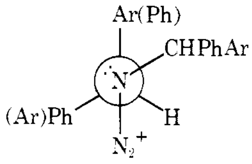
$$(C_6H_5)_2CH{-}N(N_2^+)CH(C_6H_5)_2 \xrightarrow{H\sim} (C_6H_5)_2C{=}\overset{+}{N}(CH(C_6H_5)_2)H + N_2 \qquad (12)$$

Table III. Ketone–Aldehyde Ratios from the Reactions of Substituted Benzhydryl Azides with $NO^+BF_4^-$ and with $ArPhCH^+BF_4^-$ and Yields of Benzophenones from Hydride Abstraction by the Nitrosonium Ion

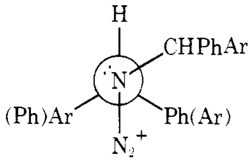
$ArPHCH{-}N_3$ Ar =	ArPhCO–Aldehyde[a] Reaction with $NO^+BF_4^-$	 Reaction with $ArPhCH^+BF_4^-$	% hydride abstraction
p-$CH_3C_6H_4$–	2.00	1.50	8
m-$CH_3C_6H_4$–	2.00	1.52	8
p-FC_6H_4–	1.71	1.39	6
C_6H_5–	1.93	1.25	10
p-ClC_6H_4–	4.67	1.30	30
p-BrC_6H_4–	4.55	1.50	34
p-$NO_2C_6H_4$–	*b*	*c*	2

[a] Data taken from Tables I and II. [b] No aldehyde products were observed in the nitrosation reaction. [c] Yield of p-nitrobenzophenone was not determined.

nitrogen loss and migration occur (II and III)[17] or to steric interference by the benzhydryl group in aryl migration.



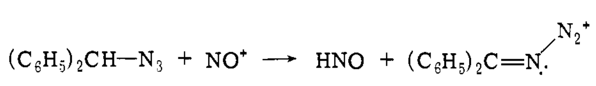
II



III

If conformational factors are of primary importance, the relative stability of the conformers from which migration occurs should influence relative migratory aptitudes.[7] Inspection of conformers II and III leads to the prediction that conformer II should be of lower energy than conformer III and that aryl migration should be predominant. The opposite is observed, however, and suggests that aryl migration is hindered relative to hydrogen migration by steric interference with the bulky benzhydryl group. Molecular models of conformers II and III clearly show that the nonrearranging benzhydryl group can interfere with aryl migration to nitrogen. The constancy of the substituted benzophenone to benzaldehyde ratio, the low ρ value for aryl migration and the absence of hydride transfer for reactions in protic acids are consistent with this suggestion.

A comparison of the substituted benzophenone to benzaldehyde ratios for reactions of benzhydryl azides with $NO^+BF_4^-$ and with $ArPhCH^+BF_4^-$ (Table III) shows that, in reactions with the nitrosonium ion, the yield of substituted benzophenone is consistently greater than would be predicted solely on the basis of hydride migration as described in eq 12. With the exception of p-nitrobenzhydryl azide, the percent difference between observed benzophenone and that expected in the Curtius reaction increases with decreasing reactivity of the azide toward the corresponding benzhydryl cation and toward the nitrosonium ion. Since the nitrosonium ion is capable of hydride abstraction and has been observed to oxidize such diverse compounds as hydrocarbons,[18] ethers,[19] amines,[3,20] and imines,[5b] hydride abstraction from benzhydryl azides leading to benzophenone (eq 13) is not an unlikely process.[21] The iminodiazonium ion that would be generated by hydride abstraction can react with water to form benzophenone.[22] Nitrosyl hydride is known to form nitrous oxide and water.[20,24] Hydrolysis, by water produced from nitrosyl hydride in the reaction medium, of imine products formed in reactions 11 and 12 and of the iminodiazonium ion formed in reaction 13 explains our ability to detect benzaldehyde, benzophenone, and benzenediazonium tetrafluoroborate prior to quenching by an external source of water.[3]



$$(C_6H_5)_2CH{-}N_3 + NO^+ \longrightarrow HNO + (C_6H_5)_2C{=}\overset{N_2^+}{N} \qquad (13)$$

The absence of phenyl migration observed in reactions of benzhydryl azide with nitrosonium tetrafluoroborate in the presence of added water[4] can now be explained by the results from this study. The added water decreases the rate of reaction of the benzhydryl cation with benzhydryl azide relative to that of the nitrosonium ion with benzhydryl azide (eq 1 and 13) by reacting with the benzhydryl cation or the corresponding acetonitrilium ion as they are formed. The observation that benzyl azide and p-nitrobenzhydryl azide yield respectively N-benzyl-[3] and N-p-nitrobenzhydrylacetonitrilium tetrafluoroborate nearly exclusively in reactions with $NO^+BF_4^-$ without competition from a Curtius reaction reflects the unreactivity of nitrilium ions toward alkyl azides. The results from these reactions also set a limitation on this competing rearrangement process in nitrosation reactions with other alkyl azides.

In a previous study, we showed that, in acetonitrile, the benzhydryl cation exists in equilibrium with the corresponding N-benzhydrylacetonitrilium ion (eq 14).[3] Water quenching resulted in formation of both benzhydrol and N-(diphenylmethyl)acetamide.[3,4] From reactions in which

$$(C_6H_5)_2CH^+ + CH_3C{\equiv}N\colon \rightleftharpoons (C_6H_5)_2CH{-}\overset{+}{N}{\equiv}CCH_3 \qquad (14)$$

substituted benzhydryl cations are generated in acetonitrile, the ratio of alcohol to amide products should indicate the relative influence of substituents on the benzhydryl cation–acetonitrilium ion equilibrium. Using the ratio of alcohol products (alcohol + ether) to amide, a good correlation is observed with σ^+, and the calculated ρ value is -1.47 (correlation coefficient -0.993). If, as expected, the same factors influence water quenching for each of the benzhydryl cations generated in this study, the ρ value of -1.47 is a measure of the responsiveness of the equilibrium process of eq 14 to substituents and an indicator of the effectiveness of acetonitrile as a leaving group.

Experimental Section

General. Instrumentation has been previously described.[3b] A Varian Model 485 digital integrator was used to determine peak areas in GLC analyses. Use was made of 5- and 6-ft columns of 20% Carbowax 20M on Chromosorb P. Nitrosonium tetrafluoroborate 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. Acetronitrile was twice distilled from calcium hydride and stored over molecular sieves. Substituted benzaldehydes and benzophenones were commercially available. Substituted benzhydryl azides and chlorides were prepared by standard procedures; their physical constants corresponded to those reported in the literature.[9,25]

Reactions of Benzhydryl Azides with Nitrosonium Tetrafluoroborate. To 6.3 mmol of nitrosonium tetrafluoroborate in 8.0 ml of anhydrous acetonitrile, placed in a three-necked flask fitted with a dropping funnel, gas inlet tube, and gas outlet tube, was added dropwise the azide (5.0 mmol) dissolved in 7.0 ml of acetonitrile. (p-Nitrobenzhydryl azide, which was only partially soluble in acetonitrile, was added as a solid to the nitrosonium salt in 15 ml of acetonitrile.) The addition to the rapidly stirred solution was at such a rate (10–15 min) as to cause no significant rise in reaction temperature, kept at 25° by means of a water bath. Prior to addition of the azide, the entire system was flushed with dry nitrogen.

Total gas evolution was measured on the closed system by water displacement from a calibrated gas buret. Total gas evolution prior to quenching with water was within ±5% of that expected from the combination of reactions 1, 11, 12, and 13. With p-methoxybenzhydryl azide, exactly 1.95 equiv of gas was produced, indicating that reaction 1 is, by far, the dominant reaction process. With p-bromobenzhydryl azide, only 1.10 equiv of gas was produced, indicating the importance of the reaction described by eq 13. The total yield of gaseous products from other substrates fell between these two limits; *p*-fluorobenzhydryl azide was the only exception, yielding 2.5 equiv of gaseous products (based on azide) whose composition was not established.

After gas evolution was complete, 10 equiv of deuterium oxide (1.0 ml) was added rapidly through a syringe directly into the reaction mixture. A small amount of gas that included nitrogen dioxide was usually evolved at this time. The acidic solution was then neutralized by the addition of 0.5–1.0 g of sodium bicarbonate, and the resulting mixture was reduced to approximately one-half of its original volume by distillation of the solvent under reduced pressure. An aliquot was removed from the reaction solution and subjected to ^{1}H NMR analysis. Reaction products were analyzed by integration of the individual and characteristic absorption signals of each compound through reference to the internal standards, benzaldehyde, and substituted benzaldehyde. The average values of at least three integrations were utilized in the calculation of relative percent yields.

Benzaldehyde, benzophenone, benzhydrol, *N*-(diphenylmethyl)acetamide, and benzhydryl ether products were the only compounds indicated in analyses after water quenching. Benzylidenaniline products[6] were not observed after quenching with water and were presumed to be rapidly hydrolyzed to benzaldehyde and aniline products. Similarly, benzophenone imine products were not detected except in one case, that of the nitrosation of *p*-fluorobenzhydryl azide.[26] When an excess of nitrosonium tetrafluoroborate is used, the hydrolysis of imines is an irreversible process; the amines produced are nitrosated under these reaction conditions, accounting for the observation of gas evolution during the quenching step.

After ^{1}H NMR analysis, an internal standard, anisole, was added to the reaction solution, and the actual yields of benzaldehyde and benzophenone products were determined by GLC analysis. The average of at least two GLC traces was employed. Yields were calculated through the use of experimentally determined thermoconductivity ratios. Aldehyde ratios from GLC analysis were identical with those found through ^{1}H NMR analysis. The yields of benzhydryl products were determined from the known yields of aldehyde products.

Reactions of Benzhydryl Azides with Benzhydryl Tetrafluoroborate. To a three-necked flask, covered with aluminum foil and fitted with a dropping funnel, gas inlet tube, and gas outlet tube, was added 6.0 mmol of silver tetrafluoroborate. This addition took place in a drybox under subdued light and was followed by the addition of 5.0 mmol of the benzhydryl azide dissolved in 9.0 ml of anhydrous acetonitrile. To this well-stirred mixture was added all at once 5.1 mmol of the appropriate benzhydryl chloride in 7.0 ml of acetonitrile. Prior to the addition of the benzhydryl chloride, the entire system was flushed with dry nitrogen.

Upon addition of the benzhydryl chloride, immediate precipitation of silver chloride was observed, and gas evolution commenced within 20 sec. Total gas evolution was measured as previously described and amounted to a volume corresponding closely to the sum of the yields of benzaldehyde and benzophenone products given in Table II. Quenching and neutralization were effected as previously described with the exception that 0.5 g of sodium chloride was added to ensure precipitation of any excess silver ion. Product yields were determined as previously described.

In these reactions, water quenching converted benzylidenaniline products to benzaldehyde and substituted benzaldehydes. Precautions were taken to ensure that complete hydrolysis of aldimine products had occurred and that reformation of imine products did not occur during analysis. *N*-Benzhydrylbenzophenone imine products, however, hydrolyzed slowly, and the yield of benzophenone products listed in Table II is the sum of benzophenone and *N*-benzhydrylbenzophenone imine. Yields of products were obtained as previously described; the yield of *N*-benzhydrylbenzophenone imine was determined by ^{1}H NMR analyses of the characteristic absorptions for the *N*-benzhydryl group. Reaction products other than those resulting in benzaldehydes and benzophenones, specifically benzhydrol, *N*-(diphenylmethyl)acetamide, and *N*-benzhydrylaniline products, were also observed, but their yields were not determined.

Acknowledgment. We gratefully acknowledge the support of the National Science Foundation for this work.

References and Notes

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