J. Org. Chem., Vol. 38, No. 9, 1973

Reactions of the Nitrosonium Ion. V. Nitrosative Cleavage of the Carbon–Nitrogen Double Bond. The Attempted Exchange of Oxygen for Nitrogen[1a]

Michael P. Doyle,* Mary A. Zaleta,[1b] James E. DeBoer, and Wendell Wierenga[1c]

Department of Chemistry, Hope College, Holland, Michigan 49423

Received October 20, 1972

N-Benzylidenetriphenylmethylamine reacts with $NO^+BF_4^-$ to give benzaldehyde, nitrogen, and the triphenylmethyl cation. When *N*-benzylidenebenzhydrylamine is similarly treated with $NO^+BF_4^-$ in acetonitrile, nitrogen, nitric oxide, and nitrous oxide are formed; and when the reaction solution is quenched with water, benzaldehyde, benzophenone, protonated imine, and *N*-(diphenylmethyl)acetamide are observed. With *N*-benzylidenebenzylamine, silane quenching of the reaction products gives dibenzyl ether; using *N*-benzylidenebenzylamine-α-d_2, the dibenzyl ether formed contains only two deuterium atoms per molecule. Similar reactions with other imines, pyridines, and various unsaturated heterocyclic compounds are presented. Results are discussed in terms of competitive nitrosative cleavage of the carbon–nitrogen double bond and hydrogen transfer to the nitrosyl group.

We have previously reported that *N*-benzylideneanilines react with nitrosonium salts under mild conditions in anhydrous media to produce benzaldehydes and benzenediazonium salts (eq 1).[2] Yields were generally greater than 90%, and no major competing side reactions were observed. Similar results had been reported for the reactions of benzylideneaniline with nitrosyl chloride, dinitrogen tetroxide, and nitrosylsulfuric acid.[3]

$$ArCH{=}NAr' + NO^+X^- \longrightarrow ArCHO + Ar'N_2^+X^- \quad (1)$$

Although no previous study has been reported, we expected that *N*-alkylimines would also undergo nitrosative cleavage of the carbon–nitrogen double bond to form a carbonyl compound and, following the loss of nitrogen, an alkyl cation (Scheme I). If the carbonyl compound produced is the most basic species in solution, O-alkylation by the carbenium ion would provide the net result of an oxygen exchange for the imine nitrogen (eq 5). For this purpose nitrosonium salts, such as $NO^+BF_4^-$, are most suitable since the nonbasic anion is not expected to undergo reactions with carbenium ion products.[4]

Scheme I

$$R_2C{=}NR' + NO^+ \longrightarrow R_2C{=}O + R'N_2^+ \quad (2)$$

$$R'N_2^+ \longrightarrow R'^+ + N_2 \quad (3)$$

$$R'^+ + R_2C{=}O \longrightarrow R_2C{=}\overset{+}{O}{-}R' \quad (4)$$

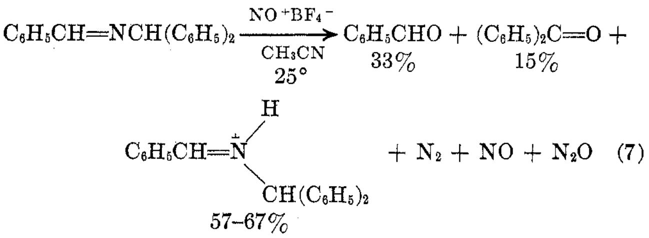
$$R_2C{=}NR' + NO^+ \longrightarrow R_2C{=}\overset{+}{O}R' + N_2 \quad (5)$$

Results

N-Benzylidenetriphenylmethylamine.—To determine if nitrosative cleavage would occur with *N*-alkylimines to produce carbonyl compounds, nitrogen, and alkyl cations, *N*-benzylidenetriphenylmethylamine was treated with an equivalent amount of nitrosonium tetrafluoroborate in acetonitrile to give the results shown in eq 6. The benzylideneimines were chosen because side reactions with the benzylidene moiety do not occur and because benzaldehyde is stable toward $NO^+BF_4^-$ under the reaction conditions studied.[2] A nearly quantitative yield of nitrogen was observed. The pmr spectrum of the reaction solution after complete nitrogen evolution was identical with that produced when an equimolar amount of benzaldehyde and trityl salt were added to acetonitrile. Benzaldehyde, produced in greater than 95% yield, was confirmed prior to quenching and work-up by glpc analysis. Addition of triethylsilane, an effective trapping agent for carbenium ions,[5] yielded triphenylmethane quantitatively; quenching with water gave triphenylmethanol. The protonated imine was produced when small amounts of water were present in the reaction medium.

$$C_6H_5CH{=}NC(C_6H_5)_3 + NO^+BF_4^- \xrightarrow[25^\circ]{CH_3CN} C_6H_5CHO + N_2 + (C_6H_5)_3C^+BF_4^- \quad (6)$$

N-Benzylidenebenzhydrylamine was similarly treated with $NO^+BF_4^-$ (1.1 equiv) in anhydrous acetonitrile at room temperature (eq 7). In addition to nitrogen, nitric oxide and a small amount of nitrous oxide were produced; the total yield of gaseous products, based on the expected production of 1 mol of gas per mole of imine, was greater than 70%. Benzaldehyde and benzophenone were observed by pmr spectroscopy and from glpc analysis prior to quenching; protonated *N*-benzylidenebenzhydrylamine accounted for approximately 60% of the reaction products. Quenching the reaction mixture with 1 equiv of water produced *N*-(diphenylmethyl)acetamide (16–26%); the same yields of benzaldehyde, benzophenone, and protonated imine were observed before and after quenching. The *N*-benzhydrylacetonitrilium ion could not be detected in the reaction solution prior to



$$C_6H_5CH{=}NCH(C_6H_5)_2 \xrightarrow[CH_3CN,\ 25^\circ]{NO^+BF_4^-} \underset{33\%}{C_6H_5CHO} + \underset{15\%}{(C_6H_5)_2C{=}O} + \underset{57\text{–}67\%}{C_6H_5CH{=}\overset{+}{N}(H)CH(C_6H_5)_2} + N_2 + NO + N_2O \quad (7)$$

---

[1] (a) These results were presented in part at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 28 to April 2, 1971, Abstracts, ORGN 15; (b) National Science Foundation Undergraduate Research Participant, summer, 1971; (c) National Science Foundation Undergraduate Research Participant, summer, 1969.

[2] M. P. Doyle, W. Wierenga, and M. A. Zaleta, *J. Org. Chem.*, **37**, 1597 (1972).

[3] (a) J. Turcan, *Bull. Soc. Chim. Fr.*, **2**, 627 (1935); (b) R. M. Scribner, *J. Org. Chem.*, **29**, 3429 (1964).

[4] M. P. Doyle and W. Wierenga, *J. Amer. Chem. Soc.*, **94**, 3901 (1972).

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

quenching.[6] Quenching with triethylsilane yielded diphenylmethane, presumably produced from both the benzhydryl cation and benzophenone.[4,7]

When the nitrosation of *N*-benzylidenebenzhydrylamine by $NO^+BF_4^-$ was run in chloroform-d_1 at 25°, a 54% yield of gaseous products was obtained in addition to benzaldehyde (42%) and the protonated imine (44%). After quenching with water (1.2 equiv), benzaldehyde (44%), benzophenone (15%), and protonated imine (47%) were the only components of the mixture that could be identified; no benzhydrol was detected. In a separate experiment, triethylsilane quenching (2 equiv) yielded diphenylmethane in 52% yield along with 40% of protonated *N*-benzylidenebenzhydrylamine and 15% of dibenzyl ether. When the imine–$NO^+BF_4^-$ reaction was carried out in chloroform-d_1 at 65°, the products and per cent yields were similar to those obtained at 25° with the exception that diphenylmethane (5%) was produced prior to quenching.

Although *N*-benzylidenebenzhydrylamine undergoes nitrosative cleavage with nitrosonium salts, competing reactions that lead to benzophenone, diphenylmethane, nitric oxide, and nitrous oxide are also evident. No evidence was obtained for the production of O-alkylated benzaldehyde using this imine.

***N*-Benzylidenebenzylamine.**—The addition of *N*-benzylidenebenzylamine to an equivalent amount of $NO^+BF_4^-$ in anhydrous acetonitrile at 25° yielded gaseous products (54%), benzaldehyde, and the corresponding N-protonated imine (54%). The protonated imine showed no tendency to react with $NO^+BF_4^-$ even when the salt was used in large excess or when the reaction was run at temperatures as high as 60°.

The yield of benzaldehyde from the reaction in acetonitrile was 28% by pmr spectroscopy, based on integration of the characteristic signal at δ 10.0 and compared to an internal standard. This yield, however, would not reflect the total yield of benzaldehyde from nitrosative cleavage if the process given in eq 4 had occurred. In separate experiments between 0.5 and 1.0 equiv of benzaldehyde was added to an acetonitrile solution of the *N*-benzylacetonitrilium ion, prepared from the reaction between benzyl azide and nitrosonium tetrafluoroborate.[6] The pmr signals of both benzaldehyde (δ 10.0) and the *N*-benzylacetonitrilium ion (δ 5.37 and 2.85) were diminished; as the amount of benzaldehyde was increased, the integrated signal of benzaldehyde also increased while those for the nitrilium ion decreased. However, both species could be observed even at 0.5 and 1.0 equiv of added benzaldehyde; only when an excess of benzaldehyde (1.5 equiv) was added were the nitrilium ion signals absent. No absorptions other than those of benzaldehyde and the *N*-benzylacetonitrilium ion were evident under our pmr conditions (37°, 0.4 *M* nitrilium ion).

Although we were not able to detect O-alkylated benzaldehyde, similar compounds have been observed in other media.[8] The observation of benzaldehyde and the nitrilium ion, even when equivalent amounts of both compounds were present in solution, suggests an equilibrium process (eq 8). Addition of triethylsilane

$$C_6H_5CH_2\overset{+}{N}{\equiv}CCH_3 + C_6H_5CHO \rightleftharpoons \underset{\text{I}}{[C_6H_5CH{=}\overset{+}{O}CH_2C_6H_5]} + CH_3CN \quad (8)$$

produced dibenzyl ether, the expected reduction product from I.[7]

Addition of 10 equiv of water to the acetonitrile solution from the reaction of *N*-benzylidenebenzylamine with $NO^+BF_4^-$ gave benzaldehyde (95%), benzylamine (55%), *N*-benzylacetamide (25%), and benzyl alcohol (10%). No significant differences in the identities or yields of products were observed when the reaction was performed at −13° or when $NO^+BF_4^-$ was added *to N*-benzylidenebenzylamine.

The addition of triethylsilane (1.2 equiv) to the acetonitrile reaction solution after complete gas evolution gave dibenzyl ether (6%). No benzaldehyde was observed by pmr spectroscopy immediately following the addition of triethylsilane. The yield of protonated imine was not noticeably affected by silane quenching.

In acidic media benzaldehyde is reduced by trialkylsilanes to dibenzyl ether in high yield.[9] This explains the formation of dibenzyl ether from silane quenching of the products from the reaction between *N*-benzylidenebenzhydrylamine and NO^+BF_4 in chloroform-d_1, noted earlier. Thus, the presence of dibenzyl ether from silane quenching in the nitrosative cleavage reactions of *N*-benzylidenebenzylamine does not unambiguously suggest the process described in Scheme I. We, therefore, treated *N*-benzylidenebenzylamine-α-d_2 with $NO^+BF_4^-$ in anhydrous acetonitrile at 25°. The yields of gaseous products, protonated imine, and observed benzaldehyde were identical with those from the same reaction with the undeuterated compound. Quenching with triethylsilane followed by addition of water and work-up yielded dibenzyl ether-α-d_2 (II), strongly suggesting the process shown in eq 9. A 5% yield of II was obtained.

$$C_6H_5CH{=}NCD_2C_6H_5 \xrightarrow[CH_3CN]{NO^+BF_4^-} C_6H_5CH{=}\overset{+}{O}CD_2C_6H_5 \xrightarrow{Et_3SiH} \underset{\text{II}}{C_6H_5CH_2OCD_2C_6H_5} \quad (9)$$

Treatment of *N*-benzylidenebenzylamine with NO^+-BF_4^- in chloroform at 55° gave gaseous products (65%), benzaldehyde (30%), and the protonated imine (30%) as the only products definable by pmr spectroscopy. The pmr spectrum did, however, exhibit a distinct signal at δ 3.95, characteristic of a ring-substituted diphenylmethane (>5%); no attempt was made to characterize this product. Under similar reaction conditions the benzyl cation, produced from the reaction between benzyl azide and $NO^+BF_4^-$, undergoes Friedel-Crafts alkylation of benzene.[10] The addition of 2 equiv of triethylsilane followed by addition of water and work-up gave an 18% yield of dibenzyl ether with 55 mol % of recovered benzaldehyde. In separate experiments the addition of tri-*n*-butylsilane and triphenylsilane gave dibenzyl ether in 10 and 11% yield,

---

[6] The *N*-alkylacetonitrilium ions, produced in high yields from alkyl azides and nitrosonium salts, have been detected under similar reaction conditions: M. P. Doyle and W. Wierenga, *J. Amer. Chem. Soc.*, **94**, 3869 (1972).

[7] M. P. Doyle, D. J. DeBruyn, and D. A. Kooistra, *ibid.*, **94**, 3896 (1972).

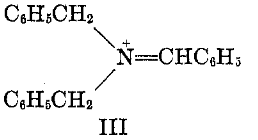
[8] G. A. Olah and J. M. Bollinger, *ibid.*, **89**, 2993 (1967).

[9] D. N. Kursanov, A. N. Parnes, N. M. Loim, and G. V. Bakalova, *Proc. Acad. Sci. USSR*, **179**, 328 (1968).

[10] Unreported results from our laboratory.

respectively. Quenching with sodium borohydride gave only a small amount (<2%) of dibenzyl ether.

An attempt was made to trap reaction products, such as I, by the addition of cyanide salts following complete gas evolution from the reaction between *N*-benzylidenebenzylamine and $NO^+BF_4^-$ in acetonitrile. The same procedure was used that had been successful in trapping compound III in experiments described by Smith and Loeppky.[11] Under our reaction conditions no evidence for cyanide products derived from I, III, or IV was obtained, and no phenylacetonitrile was produced.



III

$$C_6H_5CH{=}\overset{+}{N}{=}CHC_6H_5$$

IV

Since the major competing processes in the nitrosative cleavage of imines are those leading to protonated imines, we attempted to treat the imine with $NO^+BF_4^-$ in the presence of a base that was stable toward $NO^+BF_4^-$, yet sufficiently strong to accept the protons produced in these reactions. Pyridine was chosen because Olah has reported that nitrosonium salts react with pyridine to form stable N-nitrosated pyridinium salts.[12] Addition of equimolar amounts of *N*-benzylidenebenzylamine and pyridine to $NO^+BF_4^-$ in acetonitrile at 29° gave, however, only 18% of gaseous products and no improvement in the yields of products from the nitrosative cleavage reaction.

Other Imines.—When *N*-benzylidene-*tert*-butylamine was added to an equivalent amount of $NO^+BF_4^-$ in anhydrous acetonitrile at 29°, a 76% yield of gaseous products, 73% of the corresponding protonated imine, and 17% of benzaldehyde were obtained; after quenching with water and work-up a minor amount (<5%) of *N*-*tert*-butylacetamide was observed. *N*-Benzylidenemethylamine was similarly treated with $NO^+BF_4^-$ to give gaseous products (45%), protonated imine (49%), and benzaldehyde (23%); addition of triethylsilane to the reaction solution after complete gas evolution did not produce benzyl methyl ether.

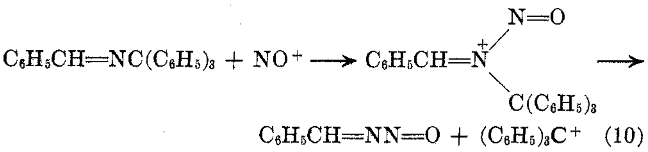
Pyridines.—Results from the reaction of *N*-benzylidenebenzylamine with $NO^+BF_4^-$ which indicated the production of I prompted us to consider the possibility that pyridine could also undergo nitrosative cleavage with an exchange of oxygen for nitrogen. Although pyrylium salts can be converted to pyridines, no method exists for the direct preparation of pyrylium compounds from pyridines.[13] Since both 2,4,6-trimethyl- and 2,4,6-triphenylpyrylium tetrafluoroborates are stable compounds and easily characterized, the corresponding trisubstituted pyridines were chosen for study.

Results similar to those reported by Olah[12] were obtained when pyridine was added to an excess of $NO^+BF_4^-$. When 2,4,6-trimethylpyridine was added to a slight molar excess of $NO^+BF_4^-$ in anhydrous acetonitrile, approximately 16 mol % of gaseous products, identified as mainly nitrous oxide and nitrogen dioxide, was produced. Only 2,4,6-trimethylpyridinium tetrafluoroborate (>90%) was observed by pmr and ir analyses. Similarly, 2,4,6-triphenylpyridine produced only the corresponding pyridinium salt when added to $NO^+BF_4^-$ in acetonitrile; again, a low yield (<20%) of gaseous products was obtained. Under the same reaction conditions, 2,4,6-trimethylpyrylium tetrafluoroborate was unaffected by $NO^+BF_4^-$. When 2,4,6-trimethylpyridine was added to 0.5 equiv of $NO^+BF_4^-$ in acetonitrile at room temperature, the same yield of gaseous products was obtained (16% based on the pyridine, 32% based on $NO^+BF_4^-$) and only the pyridinium salt (50%) and unreacted pyridine (50%) were observed; addition of another 0.5 equiv of $NO^+BF_4^-$ to the reaction solution increased the yield of pyridinium salt to 100%. Neither changing the rate of addition of the pyridine, nor increasing the reaction temperature to 60°, nor using as much as a tenfold excess of $NO^+BF_4^-$, nor changing the reaction solvent from acetonitrile to nitromethane or to using no solvent, nor performing the reaction under a dry nitrogen atmosphere, changed the course of the reaction. No evidence was obtained for the production of pyrylium salts.

Other Heterocyclic Compounds.—Similar attempts were made to exchange oxygen for nitrogen in imidazole, *N*-methyl-, and *N*-benzylimidazole, 2,5-diphenyloxazole, benzoxazole, benzothiazole, phenazine, and 1*H*-1,2,4-triazole. Gaseous products, mainly nitrogen dioxide, and the protonated substrate were produced. Again, no evidence for an exchange of oxygen for nitrogen was obtained.

Discussion

Results from the reaction of *N*-benzylidenetriphenylmethylamine with $NO^+BF_4^-$ demonstrate that nitrosative cleavage of *N*-alkylimines does occur with formation of a carbonyl compound, nitrogen, and a carbenium ion. In this case, however, an alternate mechanism to that given in Scheme I, involving N-nitrosation followed by dissociation to the trityl cation and *N*-nitrosobenzylideneimine (eq 10), cannot be excluded; *N*-nitrosobenzylideneimine would be expected to yield nitrogen and benzaldehyde in a manner analogous to that of *N*-nitrosoketimines.[2,14] With *N*-alkylimines able to provide less stable carbenium ions, nitrosative cleavage is also observed; and the occurrence of a similar dissociation of an initially formed N-nitrosated *N*-alkylimine is less likely.



$$C_6H_5CH{=}NC(C_6H_5)_3 + NO^+ \longrightarrow C_6H_5CH{=}\overset{+}{N}(N{=}O)C(C_6H_5)_3 \longrightarrow C_6H_5CH{=}NN{=}O + (C_6H_5)_3C^+ \quad (10)$$

With *N*-benzylidenebenzylamine, nitrosative cleavage with loss of nitrogen results in the production of the O-alkylated benzaldehyde, I. The existence of this species, which represents a net exchange of oxygen for nitrogen in the nitrosative cleavage reaction, rests mainly on the results of silane quenching of the products from the reaction of *N*-benzylidenebenzylamine-α-d_2 with $NO^+BF_4^-$. The observation of dibenzyl

---

[11] P. A. S. Smith and R. N. Loeppky, *J. Amer. Chem. Soc.*, **89**, 1147 (1967).

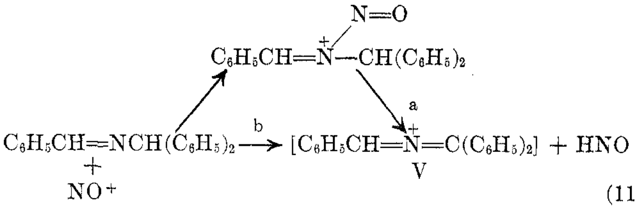
[12] G. A. Olah, J. A. Olah, and N. A. Overchuk, *J. Org. Chem.*, **30**, 3373 (1965).

[13] A. T. Balaban, W. Schroth, and G. Fischer, *Advan. Heterocycl. Chem.*, **10**, 241 (1969).

[14] (a) C. J. Thoman and I. M. Hunsberger, *J. Org. Chem.*, **33**, 2852 (1968); (b) J. Jappy and P. N. Preston, *Tetrahedron Lett.*, 1157 (1970).

ether having two deuterium atoms per molecule can only be explained by reduction of an O-alkylated benzaldehyde; the reduction of benzaldehyde alone would have resulted in dibenzyl ether with no deuterium per molecule. The yield of dibenzyl ether from reactions in acetonitrile is low, accounting for less than 15% of the reacted *N*-benzylidenebenzylamine. Since benzaldehyde is observed in relatively high yield (>50% of reacted imine) and not observed following triethylsilane quenching, reduction products other than dibenzyl ether, which were not identified in this present study, must account for the difference. Neither the protonated imine nor the *N*-benzylacetonitrilium ion lead to dibenzyl ether; the protonated imine is unaffected by silane quenching, and the *N*-benzylacetonitrilium ion is reduced to the corresponding imine.

The production of benzophenone from *N*-benzylidenebenzhydrylamine can be explained by hydrogen transfer to the nitrosyl group (eq 11a) in an elimination



$$C_6H_5CH{=}NCH(C_6H_5)_2 + NO^+ \rightarrow C_6H_5CH{=}\overset{+}{N}(N{=}O){-}CH(C_6H_5)_2 \xrightarrow{a} [C_6H_5CH{=}\overset{+}{N}{=}C(C_6H_5)_2] + HNO$$

$$C_6H_5CH{=}NCH(C_6H_5)_2 + NO^+ \xrightarrow{b} \underset{V}{[C_6H_5CH{=}\overset{+}{N}{=}C(C_6H_5)_2]} + HNO \quad (11)$$

reaction similar to that observed by Smith and Loeppky in the nitrosative cleavage of tertiary amines.[11] Alternatively, hydride abstraction from the imine by the nitrosonium ion (eq 11b), analogous to that observed by Olah and Friedman with cumene,[15] would also explain the observed results. Nitrosyl hydride is known to form nitrous oxide and water (eq 12)[11,16] and, when

$$2HNO \longrightarrow N_2O + H_2O \quad (12)$$

produced in the presence of the nitrosonium ion, nitric oxide and a proton (eq 13);[11,17] both nitrous and nitric

$$HNO + NO^+ \longrightarrow 2NO + H^+ \quad (13)$$

oxides were observed as gaseous products from the reaction of *N*-benzylidenebenzhydrylamine with $NO^+BF_4^-$. Although no evidence for the independent existence of V was obtained, the production of benzophenone, nitrous oxide, and nitric oxide requires that hydrogen transfer must have occurred. Under the same reaction conditions the solvent does not react with $NO^+BF_4^-$, and no evidence for isomerization of *N*-benzylidenebenzhydrylamine to *N*-benzhydrylidenebenzylamine was obtained. The production of diphenylmethane when the nitrosative cleavage reaction was run in chloroform at elevated temperatures indicated that hydride abstraction by the benzhydryl cation might also yield V; however, attempts to generate V using trityl salts in acetonitrile at 65° were unsuccessful.

The decomposition of nitrosyl hydride also partially explains the formation of protonated imines in these reactions. However, if the protonated imine is produced only through the hydrogen transfer reaction that leads to benzophenone (eq 11), only a 15% yield of protonated imine would have been expected. The high yields of protonated imine, produced under reaction conditions where water contamination was carefully avoided, require other reaction processes. Since we are able to account for greater than 90% of the reaction products in most reactions, only a small proportion of *N*-alkylimine must be involved in other proton-producing processes. This latter explanation also accounts for the sole production of pyridinium salts in the reactions of trisubstituted pyridines with $NO^+BF_4^-$; if nitrosative cleavage of the carbon–nitrogen bond is involved, the unsaturated ring-opened product might be expected to be quite susceptible to electrophilic attack by the nitrosonium ion, followed by elimination of a proton.

The results obtained in this study can be explained by nitrosative cleavage of the carbon–nitrogen double bond in competition with hydrogen transfer to the nitrosyl group. Alternate processes that lead to protonation of the substrate utilize only a small fraction of the total amount of substrate; however, protonation of the substrate quenches further reaction with nitrosonium salts.

Experimental Section

General.—Instrumentation has been described.[6] Gaseous products were identified by mass spectroscopy using a Finnigan Model 1015 mass spectrometer at 70 eV, as well as by infrared analyses with a Perkin-Elmer Model 621 spectrometer. Use was made of 5-ft columns of 20% SE-30 on Chromosorb P and 3% SE-30 on Varaport 30 and of 3-ft columns of 20% Carbowax 20M on Chromosorb P. Nitrosonium salts were obtained from Ozark Mahoning Co. and were dried over phosphorus pentoxide in a vacuum desiccator at 1.0 Torr prior to use. Analytical grade acetonitrile and nitromethane were distilled twice from calcium hydride and stored over molecular sieves. The water content of the acetonitrile was determined by measuring the amount of *N*-benzylacetamide formed in the reaction between benzyl azide and $NO^+BF_4^-$;[6] analysis of the reaction products by pmr spectroscopy shows *N*-benzylacetamide when water is present. The amide is formed quantitatively from the reaction of water with an equivalent amount of the *N*-benzylacetonitrilium ion, and coexists in acetonitrile solutions with the acetonitrilium ion; the acetonitrile generally contained less than 0.02 mmol of water per ml. Chloroform was purified by standard procedures; chloroform-d_1 was obtained from Merck Sharpe and Dohme and used without further purification.

***N*-Benzylidenealkylamines.**—*N*-Benzylidenetriphenylmethylamine was prepared from benzaldehyde and triphenylmethylamine in refluxing benzene by removal of water with a Dean–Stark trap. The crude product was recrystallized from chloroform–ether, yielding white crystals in 83% yield: mp 152.0–152.5°; pmr (CDCl$_3$) δ 7.87 (s, 1, CH=N), 7.9–7.7 (m, 2, *o*-H), 7.6–7.1 (m, 18, Ph).

Anal. Calcd for $C_{26}H_{21}N$: C, 89.88; H, 6.09. Found: C, 89.90; H, 6.16.

N-Benzylidenebenzhydrylamine,[18] *N*-benzylidenebenzylamine,[19] and *N*-benzylidene-*tert*-butylamine[20] were prepared by the same method and purified by recrystallization or distillation. *N*-Benzylidenemethylamine was commercially available.

General Procedure for Nitrosation of Imines.—The *N*-alkylimine (5.0 mmol) in 7 ml of anhydrous acetonitrile or chloroform was added dropwise to a constantly stirred solution of $NO^+BF_4^-$ (5.5 mmol) in 3 ml of the same solvent. Reactions were run in a three-necked flask fitted with a dropping funnel, thermometer, and gas outlet tube. *N*-Benzylidenetriphenylmethylamine was added as a solid in portions from an erlenmeyer flask fitted to the reaction flask with tygon tubing. Except when mass spectral identification of the gaseous products was made, the entire system was flushed with dry nitrogen prior to addition. The imine was added at such a rate (15–30 min) as to cause no sig-

---

[15] G. A. Olah and N. Friedman, *J. Amer. Chem. Soc.*, **88**, 5330 (1966).

[16] F. Q. Kohant and F. W. Lamps, *ibid.*, **87**, 5795 (1965).

[17] E. J. Strojny, R. T. Iwamasa, and L. K. Frevel, *ibid.*, **93**, 1171 (1971).

[18] A. Lespagnol, S. Dicop, and J. Vanlerenberghe, *Bull. Soc. Pharm. Lille*, 49 (1945).

[19] G. Mignonac, *Ann. Chim. (Paris)*, [11], **2**, 225 (1934).

[20] E. Cordes and W. Jencks, *J. Amer. Chem. Soc.*, **85**, 2843 (1963).

nificant rise in the reaction temperature. Temperature control was effected by using an appropriate heating or cooling bath. For reactions run with pyridine, an equimolar amount of pyridine was added to $NO^+BF_4^-$ prior to the imine.

Total gas evolution was measured on the closed system by water displacement from a calibrated gas buret. Gas evolution was usually complete within 1 hr after addition at room temperature. The yield of gaseous products was calculated on the basis of 1 mol of gas per mole of imine. Gaseous products from the reactions of $NO^+BF_4^-$ with *N*-benzylidenetriphenylmethylamine and -benzhydrylamine were identified by mass spectroscopy using representative gas samples.

A pmr spectrum of the reaction products was usually obtained prior to quenching. Glpc analyses were also used at this point to detect products prior to quenching. Following analysis between 2 and 10 equiv of water or deuterium oxide was added, usually within 30 min after gas evolution was complete; and a pmr spectrum of the reaction solution was again obtained. For reactions in which silanes were used as the quenching agent, between 1 and 2 equiv of the appropriate silane was added instead of water. Methylene chloride (25 ml) was added along with water (20 ml) and the resulting layers were separated after thorough mixing. The aqueous layer was washed once with methylene chloride (25 ml) and made basic with sodium carbonate, and the basic solution was washed twice with 25-ml portions of methylene chloride. The combined methylene chloride extracts were passed through anhydrous magnesium sulfate and the solvent was removed under reduced pressure.

Reaction products were analyzed by integration of the individual and characteristic absorptions 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. A measured amount of an internal standard, usually 1,2-dibromoethane or nitromethane, was used for each analysis. Individual products were identified either from the pmr spectrum of the reaction solution and from glpc retention times and peak enhancement, or after isolation by glpc using appropriate spectral methods. Protonated imines were identified prior to work-up by comparison to authentic samples prepared in acetonitrile by adding an equivalent amount of FSO_3H–SbF_5 to the imine. Pmr spectra in acetonitrile at 37° were similar to those previously reported:[21] $C_6H_5CH{=}NHC(C_6H_5)_3^+$, δ 8.85 (d, CH=N, $J_{CH=NH} = 18$ Hz); $C_6H_5CH{=}NHCH(C_6H_5)_2^+$, δ 12.0 (broad, NH), 8.94 (d, CH=N, $J_{CH=NH} = 17$ Hz), 6.62 (d, CHN, $J_{CHNH} = 6$ Hz); $C_6H_5CH{=}NHCH_2C_6H_5^+$, δ 12.7 (broad, NH), 9.01 (CH=N, $J_{CH=NH} = 18.5$ Hz, $J_{CHCH_2} = 1.0$ Hz), 5.12 (CH_2N, $J_{CH_2NH} = 6.0$ Hz); $C_6H_5CH{=}NHC(CH_3)_3^+$, δ 8.80 (d, CH=N, $J_{CH=NH} = 18.3$ Hz); $C_6H_5CH{=}NHCH_3^+$, δ 8.85 (CH=N, $J_{CH=NH} = 18$, $J_{CHCH_3} = 1$ Hz), 3.63 (CH_3N, $J_{CH_3NH} = 5$ Hz).

***N*-Benzylidenebenzylamine-*α*-d_2.**—Benzylamine-*α*-d_2 was synthesized from benzonitrile and lithium aluminum deuteride (Ventron) in 32% yield using the procedure of Amundsen and Nelson,[22] bp 29° (0.15 Torr). No signal for the *α* hydrogens was observed by pmr spectroscopy. Benzaldehyde was condensed with benzylamine-*α*-d_2, using the procedure previously described, to give *N*-benzylidenebenzylamine-*α*-d_2 in 73% yield: bp 107–109° (0.15 Torr); pmr (CCl_4) δ 8.38 (s, 1, CH=N), 8.0–7.1 (m, 10, Ph). The ir spectrum was consistent with the structure.

Treatment of the deuterated imine with $NO^+BF_4^-$ in anhydrous acetonitrile according to the general procedure gave, by pmr analysis prior to quenching, a 42% yield of "protonated" imine (pmr δ 8.92 for $CH{=}N^+$, $J = 18$ Hz; no signal was observed between δ 7.0 and 4.0) and 26% of benzaldehyde (pmr δ 10.0 for CH=O). An absorption for the $C{=}NH^+$ of the protonated imine was observed as a broad signal (δ 11.5–10.8) and integrated to only one-half the value for the $CH{=}N^+$ signal; with undeuterated imine these signals have the same area. After quenching with water and after work-up no signal between δ 7.0 and 4.0 was detected by pmr spectroscopy; *N*-benzylacetamide-*α*-d_2 was detected by glpc analysis and confirmed by pmr spectroscopy. With triethylsilane quenching (5 equiv) the product corresponding to dibenzyl ether was collected by glpc and identified by pmr spectroscopy, δ 7.27 (s, 10.0) and 4.53 (s, 2.0).

Nitrosation of Pyridines and Other Heterocyclic Compounds.—Compounds were commercially available. The same general procedure as that given for the imines was used. With 2,4,6-trimethylpyridine, reactions were run at 25° and at 60° for between 1 and 3 hr, in acetonitrile, nitromethane, or without solvent, and with 1, 2, and 10 equiv of $NO^+BF_4^-$; only the pyridinium salt was detected prior to quenching by pmr and ir spectroscopy. The corresponding pyrylium salt would have been detected by these methods. 2,4,6-Trimethylpyrylium tetrafluoroborate was commercially available. 2,4,6-Trimethylpyridinium tetrafluoroborate was isolated from several reactions and characterized by comparison to the authentic sample by pmr and ir spectroscopy and from its melting point (233–235°). Similar reactions were attempted with 2,4,6-triphenylpyridine and gave identical results.

The reactions of $NO^+BF_4^-$ with imidazole, *N*-methyl- and *N*-benzylimidazole, 2,5-diphenyloxazole, benzoxazole, benzothiazole, phenazine, and 1*H*-1,2,4-triazole were carried out in a manner analogous to that for the pyridines. *N*-Methylimidazole and 2,5-diphenyloxazole were studied under the greatest variety of reaction conditions. Only the corresponding protonated compound could be detected.

Protonated substrates were prepared by adding the nitrogen heterocycle to a slight molar excess of fluoroboric acid in benzene. The water from the 40% aqueous fluoroboric acid was removed using a Dean-Stark trap, and the benzene was distilled under reduced pressure.

Registry No.—*N*-Benzylidenetriphenylmethylamine, 38662-28-1; *N*-benzylidenebenzhydrylamine, 36728-52-6; *N*-benzylidenebenzylamine, 780-25-6; *N*-benzylidene-*tert*-butylamine, 6852-58-0; *N*-benzylidenebenzhydrylamine, 622-29-7; nitrosonium tetrafluoroborate, 14635-75-7; 2,4,6-trimethylpyridine, 108-75-8; 2,4,6-triphenylpyridine, 580-35-8; *N*-benzylidenebenzylamine-*α*-d_2, 38662-32-7.

Acknowledgment.—We gratefully acknowledge the support of the National Science Foundation (Grant No. GP-27587) and of the Research Corporation for this work. We wish to thank Mr. J. Gregory Kalmbacher for preliminary studies with pyridines.

---

(21) G. A. Olah and P. Kreienbühl, *J. Amer. Chem. Soc.*, **89**, 4756 (1967).

(22) L. H. Amundsen and L. S. Nelson, *ibid.*, **73**, 242 (1951).