(46), 252 (43), 239 (10.7), 238 (13.4), 210 (10.4), 181 (16.3), 147 (46), 146 (36.5), 145 (12.7, P^{2+}?), 136 (82.3), 135 (79), 132 (20), 122 (53), 121 (56), 119 (38), 108 (18.7), 107 (37), 106 (14.5), 105 (23), 104 (17.6), 94 (16.3), 93 (31), 92 (41), 78 (16.3), 77 (41), 76 (19.5), 65 (34), 42 (26.8), 39 (21.4), 28 (31), and 18 (18.7).

The pmr spectrum (CF_3CO_2H) follows: τ 2.05–3.55 (m, 8H), 6.92 (s, 6H); two doublets can be discerned within the multiplet, at τ 2.55 and 3.30 ($J \approx 9$ Hz).

Method B (in the Dark).—The previous reaction was performed with the flask wrapped in aluminum foil. An ir spectrum of the crude product mixture showed no azide absorption in the 4.0–5.0 μ region. The same work-up procedure was performed, giving **17** (54.5%), unknown **20** (96 mg), and acid **15** (7.5%), amide **18** (4%), and **13** (3.5%). The higher yield of **17** is obtainable if **17** is not left in solution for prolonged periods.[39] The aniline **19** was not detected in this run.

Photolysis of 13.—Azimine **13** (0.5866 g, 2.2 mmol) in 250 ml of N_2-saturated dichloromethane was photolyzed for 3 hr. During this time the solution was allowed to reflux. No appreciable gas evolution was observed through the N_2 bubbler. The solution showed no visible color change. Evaporation of the solvent gave back **13** (0.585 g, >99%).

Synthesis of 17.[37] **A. *N'*-Anthranilyl-*N*,*N*-dimethyl-*p*-phenylenediamine.**—Isatoic anhydride (Aldrich, 1.35 g, 8.30 mmol) and *N*,*N*-dimethyl-*p*-phenylenediamine (Eastman, 1.15 g, 8.50 mmol) were heated together on a steam bath until gas evolution ceased (15 min). This left a black solid mass (2.10 g, 99%), mp 134–138°. Two recrystallizations from ethanol gave a gray solid (0.94 g, 45%): mp 147–148° (lit.[37] mp 146–148°); ir (KBr disc) 2.85 and 2.96 μ (m, NH_2), 3.30 (w, NH), 3.40 and 3.49 (w, CH), 6.06 (vs, C=O), 12.22 and 12.39 (s, para), and 13.35 (s, ortho); pmr ($CDCl_3$) τ 2.3 (br, s, 1 H), 2.7 (m, 4 H), 3.3 (m, 4 H), 4.7 (broad s, 2 H), 7.10 (1 s, 6 H).

B.—The amide (0.724 g, 2.84 mmol) was dissolved in 30 ml of 1 *M* H_2SO_4, cooled to 0°, and treated with 0.20 g (2.84 mmol) of $NaNO_2$. After 10 min, the solution was neutralized with $NaHCO_3$ and filtered. The precipitate was washed with water and air dried, leaving 0.762 g (100%) of yellow powder, mp 235–238° dec. Recrystallization from acetone gave **17**, mp *ca.* 245° dec (lit.[37] mp 249–250°). The mixture melting point with **17** from nitrosation of **16** was 244–245° dec. The ir spectra were identical.

Registry No.—**3**, 33986-91-3; **13**, 33986-92-4; **16**, 33986-93-5; **18**, 33986-94-6; methyl 2-(4'-dimethylaminophenylazo)benzoate, 20412-23-1; methyl red, 493-52-7.

Acknowledgment.—We gratefully acknowledge support from Rohm and Haas Co. and from the Research Foundation of State University of New York.

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[39] Benzotriazinones are unstable to light: E. M. Burgess and G. Milne, *Tetrahedron Lett.*, 93 (1966).

Reactions of the Nitrosonium Ion. IV. Nitrosative Cleavage of the Carbon–Nitrogen Double Bond. The Reaction of *N*-Arylimines and Ketimines with Nitrosonium Salts[1a]

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Received November 9, 1971

N-Benzylideneanilines react with nitrosonium salts at or below room temperature to produce benzaldehydes and benzenediazonium salts. These reactions proceed with initial N-nitrosation and are proposed to involve the intermediacy of N-substituted oxadiazetine compounds. Competing reactions are observed only with *p*-methoxy substituents. When a proton is produced in these reactions, as when benzophenonimine undergoes nitrosative cleavage, protonation of the imine occurs to the exclusion of further reaction with the nitrosonium ion.

Reactions of nitrosonium compounds with compounds containing the carbon–carbon double bond have been well characterized.[2] Similar reactions with other functional groups, however, have received less attention. Although imines represent the simplest class of organic compounds for use in a study of the reactions of nitrosonium compounds with the carbon–nitrogen double bond, few examples of such reactions have been reported.[3–5] Turcan in 1935 reported that nitrosyl chloride, dinitrogen tetroxide, and nitrosyl sulfuric acid react with *N*-benzylideneaniline under mild conditions to produce benzaldehyde and the corresponding benzenediazonium salt (eq 1).[3] Since these reactions were run under anhydrous conditions in benzene or ether, the production of benzaldehyde and the benzenediazonium salt could not have involved prior hydrolysis of the imine followed by diazotization of aniline. Similar results were obtained when *N*-heptylideneaniline, *N*-benzylidene-*p*-bromoaniline, and *N*-benzylidene-α-naphthylamine were treated with nitrosyl chloride under mild conditions, although no yields were given.[3] The reaction of *N*-benzylideneaniline with dinitrogen tetroxide was recently shown, however, to proceed in high yield to benzaldehyde and benzenediazonium nitrate.[4]

$$C_6H_5CH{=}NC_6H_5 + XNO \longrightarrow C_6H_5CHO + C_6H_5N_2^+X^- \quad (1)$$
$$X = Cl, NO_3, HSO_4$$

Unlike the carbon–carbon double bond, which undergoes initial electrophilic addition with nitrosyl halides and related compounds,[2] aldimines react with nitrosonium compounds with cleavage to form carbonyl and diazonium compounds.[6] Since aldimines are formed from aldehydes and amines and the parent aldehyde re-formed, the net effect of the reaction of aldimines with nitrosonium compounds is an efficient diazotization of the amine. The mechanism of carbon–nitrogen double bond cleavage may be represented as involving the intermediacy of an N-substituted oxa-

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[1] (a) For part III, see M. P. Doyle and W. Wierenga, *J. Amer. Chem. Soc.*, in press; (b) National Science Foundation Undergraduate Research Participant, summer 1969.

[2] (a) L. J. Beckham, W. A. Fessler, and M. A. Kise, *Chem. Rev.*, **48**, 319 (1951); (b) J. Meinwald, Y. D. Meinwald, and T. N. Baker, *J. Amer. Chem. Soc.*, **86**, 4074 (1964); (c) H. C. Hamann and D. Swern, *ibid.*, **90**, 6481 (1968); (d) E. F. Schoenbrunn and J. H. Gardner, *ibid.*, **82**, 4905 (1960).

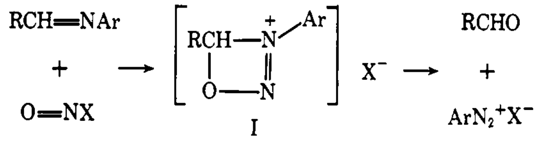
[3] J. Turcan, *Bull. Soc. Chim. Fr.*, **2**, 627 (1935).

[4] R. M. Scribner, *J. Org. Chem.*, **29**, 3429 (1964).

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

[6] Only one example of an apparent addition reaction has been reported: E. P. Goldberg and H. R. Nace, *J. Amer. Chem. Soc.*, **75**, 6260 (1953).

SCHEME I



diazetine compound (I), as shown in Scheme I, although no such intermediate has been directly observed.

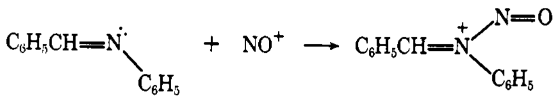
The cleavage reaction is not unique to *N*-aryl aldimines, however. When ketimines are treated with nitrosyl chloride, *N*-nitrosoketimines are formed and may be isolated.[5] On standing at room temperature these compounds decompose to nitrogen and the parent ketone in a manner consistent with formation of an intermediate similar to I.[5a]

Since only a limited number of imines have been examined in their reactions with nitrosonium compounds and no attempt has been made to study the scope of the reaction, we undertook our present investigation of imines. Nitrosonium salts, including $NO^+BF_4^-$ and $NO^+SbF_6^-$, were chosen for this study since the nitrosonium ion represents the apparent reactive species in the cleavage of the carbon–nitrogen double bond. In addition, the counterion is sufficiently nonnucleophilic so as to minimize side reactions.

Results

Treatment of *N*-benzylideneaniline with 1 equiv of $NO^+BF_4^-$ or $NO^+SbF_6^-$ in anhydrous acetonitrile or nitromethane at room temperature or below produced benzaldehyde and benzenediazonium tetrafluoroborate or hexafluoroantimonate nearly quantitatively. Benzaldehyde was identified in the reaction mixture by pmr, ir, and glpc analysis. The benzenediazonium ion was confirmed by both pmr and ir spectroscopy and by *in situ* conversion to fluorobenzene (Schiemann reaction)[7] and chlorobenzene (Sandmeyer reaction).[8] Yields of products were determined of aliquots removed from the reaction mixture by integration of specific pmr absorptions.[9] Isolated yields of benzaldehyde averaged 95%.

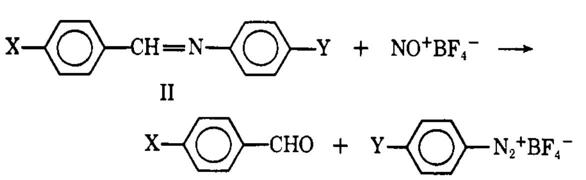
N-Benzylideneaniline reacts rapidly with $NO^+BF_4^-$ even at temperatures below 25°. At 25° the production of benzaldehyde and benzenediazonium tetrafluoroborate is complete within 10 min. The pmr spectrum of *N*-benzylideneaniline in acetonitrile before addition of the nitrosonium salt shows the C hydrogen as a singlet at δ 8.65 relative to internal TMS. Upon addition of $NO^+BF_4^-$ the C hydrogen is shifted to δ 9.18, and a new proton resonance due to benzaldehyde appears at δ 10.0. The benzaldehyde signal increases in intensity with time at the expense of the δ 9.18 absorption. Protonated *N*-benzylideneaniline, produced by adding *N*-benzylideneaniline to 1 equiv of FSO_3H–SbF_5 in acetonitrile, shows a doublet for the C hydrogen, centered at δ 9.30 (J = 17.5 Hz).[10] These data



$$C_6H_5CH{=}\ddot{N}\!-\!C_6H_5 + NO^+ \longrightarrow C_6H_5CH{=}\overset{+}{N}(N{=}O)\!-\!C_6H_5 \qquad (2)$$

indicate that nitrosation of the imine (eq 2) occurs as a discrete step prior to cleavage of the carbon–nitrogen double bond, a conclusion reasonable in terms of the strong Lewis acidity of the nitrosonium ion and the observation by Olah and coworkers that *N*-nitrosopyridinium salts are readily prepared from nitrosonium salts and pyridines.[11]

Treatment of a series of substituted *N*-benzylideneanilines (IIa–j) at room temperature with 1 equiv of $NO^+BF_4^-$ in anhydrous acetonitrile produced the corresponding aldehyde and diazonium compound in yields usually greater than 90% (eq 3). The amounts



(3)

a, X = H; Y = H
b, X = H; Y = NO_2
c, X = H; Y = Cl
d, X = H; Y = CH_3
e, X = H; Y = OCH_3
f, X = NO_2; Y = H
g, X = Cl; Y = H
h, X = CH_3; Y = H
i, X = OCH_3; Y = H
j, X = OCH_3; Y = OCH_3

of aldehyde and diazonium compound were identical within experimental error. Only with the methoxy-substituted compounds (IIe,i,j) were product yields less than 90%: with IIe and IIi the yield of aldehyde and diazonium ion was 83%, and with IIj only a 75% yield of products was obtained. With methoxy-substituted imines processes such as nitrosation of the aromatic ring[12] and hydrogen abstraction[13] may compete with nitrosative cleavage. When, for example, *p*-anisaldehyde was treated with 1 equiv of $NO^+BF_4^-$ under the same reaction conditions used for nitrosative cleavage, only 58% of the aldehyde remained intact after 40 min. Benzaldehyde was unaffected by $NO^+BF_4^-$ in acetonitrile at room temperature over the same period of time.

At 25° or below the diazonium salts produced from II in acetonitrile are stable for prolonged periods of time. However, heating above 35° effects the loss of nitrogen accompanying decomposition of the diazonium compound. For example, within 20 min at 40° the amount of benzenediazonium tetrafluoroborate, produced from IIa,f–i, was reduced by 20%. In addition to fluorobenzene, mentioned earlier, decomposition of benzenediazonium tetrafluoroborate yielded 23% of acetanilide, isolated after work-up and identified from its pmr and ir spectrum and by glpc analysis.

When water is present in trace amounts in the reaction mixture, the yield of products from reaction 3 is

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[7] A. Roe in "Organic Reactions," Vol. V. R. Adams, Ed., Wiley, New York, N. Y., 1949, Chapter 4.

[8] S. C. Dickerman, D. J. DeSouza, and N. Jacobson, *J. Org. Chem.*, **34**, 710 (1969), and references cited therein.

[9] Reactants and products are soluble in the solvents used. The aldehydic proton resonance signal of benzaldehyde (δ 10.0) and the signals for the ortho hydrogens of the benzenediazonium ion (δ 8.2–8.5) were used with reference to a standard to calculate absolute yields.

[10] This observation is in accord with the spectra of protonated *N*-benzylideneaniline reported in different solvents: G. A. Olah and P. Kreienbuhl, *J. Amer. Chem. Soc.*, **89**, 4756 (1967).

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

[12] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 531.

[13] Hydrogen abstraction reactions by the nitrosonium ion have been observed with aliphatic ethers[14] and are inferred in the nitric acid oxidation of 2-methoxyethanol.[15] Evidence for hydride abstraction from cumene by nitrosonium salts has also been given.[16]

[14] Unpublished results of M. P. Doyle.

[15] E. J. Stojny, R. I. Iwamasa, and L. K. Frevel, *J. Amer. Chem. Soc.*, **93**, 1171 (1971).

[16] G. A. Olah and N. Friedman, *ibid.*, **88**, 5330 (1966).

decreased due to formation of the corresponding protonated imine, observed by pmr spectroscopy by the characteristic doublet[9] at δ 8.9–9.4 (J = 17–18 Hz).[17] The protonated imine does not undergo nitrosative cleavage. In a separate experiment 1 equiv of $NO^+BF_4^-$ was added to protonated benzylideneaniline, formed when IIa was treated with 1 equiv of FSO_3H–SbF_5 in anhydrous acetonitrile. Production of either benzaldehyde or benzenediazonium tetrafluoroborate was not observed over a 90-min period. These results show that the nitrosonium ion is a weaker Lewis acid than a proton and that, for reactions of the nitrosonium ion with basic compounds in which a proton is produced in the course of the reaction, protonation of the substrate will serve to quench further reaction with the nitrosonium ion.

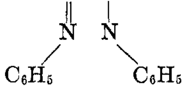
Protonic quenching of nitrosative cleavage of imines was readily observed in the reaction of benzophenonimine with $NO^+BF_4^-$. Dropwise addition of benzophenonimine to 1 equiv of $NO^+BF_4^-$ in anhydrous acetonitrile at 20° produced a deep blue-purple colored solution. The dark color, characteristic of *N*-nitrosobenzophenonimine,[5a] changed rapidly to give a yellow reaction solution with evolution of approximately 0.5 equiv of a gaseous product, assumed to be nitrogen. The pmr spectrum was characteristic of benzophenone with the exception that a sharp singlet was observed at δ 7.75 in an integral ratio of approximately 1:1 with the benzophenone multiplet at δ 7.3–8.0.[18] Glpc analysis confirmed the identity of benzophenone and showed the presence of another product having the same retention time as benzophenonimine, formed in an amount equal to benzophenone. Neither addition of an additional 1 equiv of $NO^+BF_4^-$, heating at 80° for 30 min, nor standing at room temperature for over 20 hr had any effect on the glpc product ratio or the pmr spectrum. The ir spectrum of the products isolated after evaporation of the solvent exhibited strong, broad absorptions at 3400–3100 cm^{-1} (N–H stretching) and 1100–1020 cm^{-1} (BF_4^-) and a sharp absorption at 1605 cm^{-1} (C=N stretching), characteristic of benzophenoniminium tetrafluoroborate, $(C_6H_5)_2C{=}NH_2^+BF_4^-$.[19] The addition of methanol did not change the product composition. However, benzophenone was the only product observed when water was added to the reaction solution. These results are consistent with the stoichiometry and products given in eq 4.

$$2(C_6H_5)_2C{=}NH + NO^+BF_4^- \longrightarrow (C_6H_5)_2C{=}O + N_2 + (C_6H_5)_2C{=}NH_2^+BF_4^- \quad (4)$$

N-Arylketimines also undergo nitrosative cleavage with nitrosonium salts. *N*-Benzhydrylideneaniline (III) gave both benzophenone and benzenediazonium tetrafluoroborate when treated with 1 equiv of $NO^+BF_4^-$, and benzil dianil (IV) produced benzil quantitatively when treated with 2 equiv of $NO^+BF_4^-$ at room temperature.

$(C_6H_5)_2C{=}NC_6H_5$

III



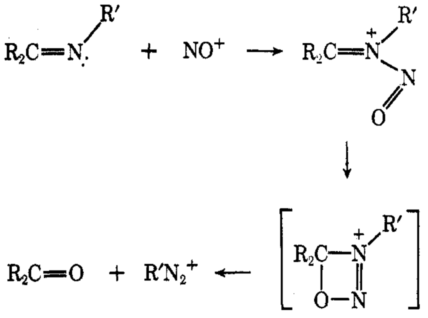
$C_6H_5C(=NC_6H_5)-C(=NC_6H_5)C_6H_5$

IV

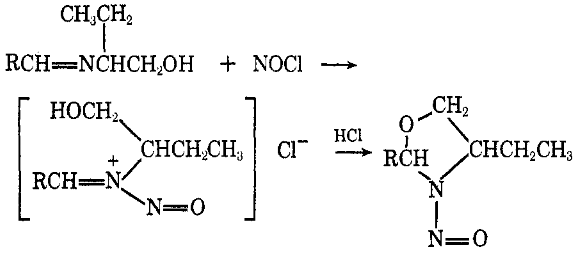
Discussion

The reaction of imines with nitrosonium compounds may be represented by the sequence of steps given in Scheme II. Our observation of N-nitrosated *N*-benzylideneaniline and the previously reported isolation of *N*-nitrosoketimines[5] suggests that nitrosation of the imine occurs as a rapid step prior to rate-limiting product formation. In addition, the conversion of substituted 2-imino-1-butanols to oxazolidines with nitrosyl chloride[6] indicates the intermediacy of an N-nitrosated imine that is prevented from undergoing cleavage by intramolecular trapping (eq 5). We speculate that the production of carbonyl and diazonium compounds is preceded by rate-limiting formation of an N-substituted oxadiazetine compound (V), although we have no evidence to support the independent existence of such an unusual compound.

SCHEME II



V



(5)

Although we have given evidence here for the reactions of only a select class of organic compounds, a mechanism similar to that given in Scheme II may be used to explain a larger number of previously observed reactions of compounds containing the carbon–nitrogen double bond with nitrosonium salts. The production of alkyl cations and acylium ions in the reactions of nitrosonium salts with isocyanates, thioisocyanates, and sulfinylamines (eq 6–8), first observed by Olah and coworkers,[20] are prime examples of nitrosative cleavage of the carbon–nitrogen and sulfur–nitrogen double bond. Bott had previously found that aryl sulfinylamines produce the corresponding aryldiazonium compounds and sulfur dioxide when treated with nitrosonium perchlorate and hexachloroantimonate (eq 9).[21] We have also found evidence which suggests

$$RN{=}C{=}O + NO^+ \longrightarrow R^+ + N_2 + CO_2 \quad (6)$$

$$RN{=}C{=}S + NO^+ \longrightarrow R^+ + N_2 + COS \quad (7)$$

$$RN{=}S{=}O + NO^+ \longrightarrow R^+ + N_2 + SO_2 \quad (8)$$

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[17] Chemical shift varies with the individual compound.

[18] The NH absorption of benzophenonimine, observed at δ 9.61, was not found in the pmr spectrum of the reaction solution.

[19] Characteristic absorptions for benzophenone were also observed.

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

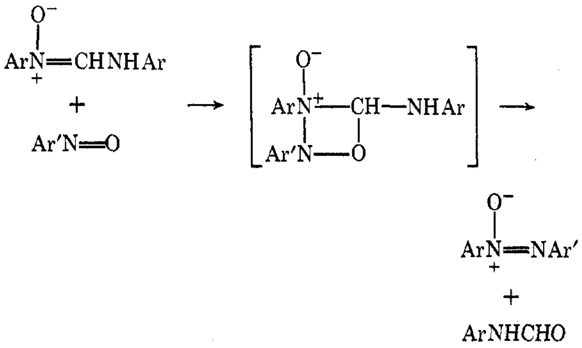
[21] K. Bott, *Angew. Chem.*, **77**, 132 (1965).

$$\mathrm{ArN{=}S{=}O + NO^+ \longrightarrow ArN_2^+ + SO_2} \qquad (9)$$

that carbodiimides lead to isocyanates and alkyl cations according to eq 10.[14] Nitrosyl chloride similarly effects nitrosative cleavage of phosphineimines[22] and sulfinylamines.[23] These reactions point to the generality of nitrosative cleavage of the carbon–nitrogen double bond and suggest that compounds containing the S=N and P=N bonds react in a similar manner.

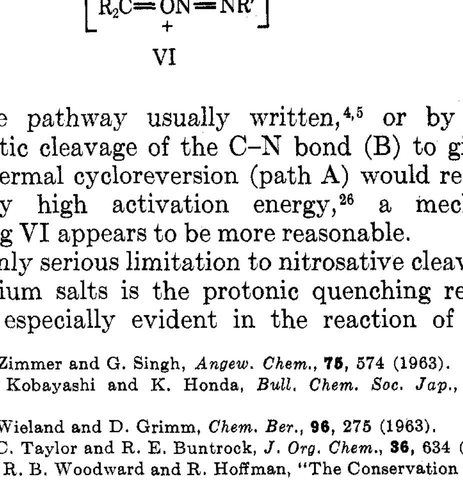
$$\mathrm{RN{=}C{=}NR + NO^+ \longrightarrow RN{=}C{=}O + R^+ + N_2} \qquad (10)$$

The formation of carbonyl and diazonium compounds from N-nitrosated imine appears to involve an oxadiazetine intermediate.[4,5a] A similar compound may be used to explain the production of carbonyl compounds and nitrous oxide from oximes and nitrous acid,[24] and Taylor has recently proposed that a discrete 1,2,3-oxadiazetidine intermediate may be involved in the reaction of nitrosobenzenes with α-arylamino-*N*-arylnitrones (eq 11).[25] Ring opening of V may be written as producing the observed products by either of two extremes (Scheme III): directly in a concerted process (A), the pathway usually written,[4,5] or by initial heterolytic cleavage of the C–N bond (B) to give VI. Since thermal cycloreversion (path A) would require a relatively high activation energy,[26] a mechanism involving VI appears to be more reasonable.



(11)

SCHEME III



The only serious limitation to nitrosative cleavage by nitrosonium salts is the protonic quenching reaction. This is especially evident in the reaction of benzophenonimine with $NO^+BF_4^-$. Competing reactions of the nitrosonium ion with aldehyde, ketone, or methyl substituents on benzene do not occur under our reaction conditions, and even a methoxy group provides for only a limited loss of products.

The facile reaction of nitrosonium salts with *N*-arylimines and ketimines suggests that alkyl cations would be produced from *N*-alkylimines. In this regard, we have found that the trityl cation is quantitatively formed from *N*-benzylidenetriphenylmethylamine and $NO^+BF_4^-$. The reactions of *N*-alkylimines and those of other unsaturated compounds with nitrosonium compounds will be presented in subsequent publications.

Experimental Section

General.—Instrumentation has been described.[27] Use was made of 5 ft columns of 10% Carbowax 20M and 20% SE-30 on Chromosorb P and of 3% SE-30 on Varaport 30. Nitrosonium salts 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. Spectral grade acetonitrile and nitromethane were distilled twice from calcium hydride and stored over molecular sieves. Substituted *N*-benzylideneanilines were prepared from the corresponding benzaldehydes and anilines in refluxing benzene by removal of water with a Dean-Stark trap and purified by recrystallization or distillation. Benzhydrylideneaniline was commercially available. Benzophenonimine was prepared by the method of Pickard and Tolbert.[28]

Benzil Dianil (IV).—A mixture of 10.5 g (0.05 mol) of benzil, 7.0 g (0.075 mol) of aniline, and 0.3 ml of 10% hydrochloric acid was heated to 140–150° for 3 hr under a constant flowing nitrogen atmosphere. Water vapor was allowed to escape through an unstoppered opening in the reaction flask. After cooling the solution to 50° ethanol was added and the crude monoanil was allowed to crystallize. Recrystallization from ethanol afforded the yellow monoanil in 79% yield, mp 103–104° (lit.[29] mp 103–106°). Repeating the above procedure using benzil monoanil gave the dianil in 63% yield, mp 142.5–143.5° (lit.[29] mp 143–145°).

General Procedure for Nitrosation of Imines.—To 5.5 mmol of nitrosonium salt in 3 ml of anhydrous acetonitrile or nitromethane was added 5.0 mmol of imine in 7 ml of the same solvent, usually over a 15-min period. Prior to addition of imine the entire system was flushed with dry nitrogen, and, except for those runs where gas evolution was measured, the reaction was run under a nitrogen atmosphere. The solution was constantly stirred and temperature control was effected using an appropriate cooling bath. Reactions were usually run at 25°. No difference in yields or composition of products was observed when the nitrosonium salt was added to the imine (reverse addition), when the reaction was run at 0°, or when a greater volume of solvent was used. For benzophenonimine total gas evolution (0.52 equiv) was measured on the closed system by water displacement from a calibrated gas buret.

Reaction of *N*-Benzylideneaniline (IIa) with $NO^+BF_4^-$ and $NO^+SbF_6^-$.—After treatment of IIa with $NO^+BF_4^-$ in acetonitrile, benzaldehyde was identified by pmr, ir, and glpc analysis of the reaction solution. The benzenediazonium ion was detected by comparison of the pmr spectrum of the reaction solution with a comparable mixture of benzaldehyde and benzenediazonium tetrafluoroborate in acetonitrile. When the same reaction was run in nitromethane, the absorption band in the ir for the diazonium group at 2300 cm^{-1} was clearly visible. Heating the acetonitrile solution of products from IIa and $NO^+BF_4^-$ or $NO^+SbF_6^-$ to 70° for 15 min produced fluorobenzene in 40% yield. Fluorobenzene was confirmed by glpc, ir, and pmr comparison to an authentic sample as well as by its boiling point. In a separate experiment heating to 50° for 2 hr produced, after work-up, acetanilide in 23% yield. Production of chloro-

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[22] H. Zimmer and G. Singh, *Angew. Chem.*, **75**, 574 (1963).

[23] M. Kobayashi and K. Honda, *Bull. Chem. Soc. Jap.*, **39**, 1778 (1966).

[24] T. Wieland and D. Grimm, *Chem. Ber.*, **96**, 275 (1963).

[25] E. C. Taylor and R. E. Buntrock, *J. Org. Chem.*, **36**, 634 (1971).

[26] See R. B. Woodward and R. Hoffman, "The Conservation of Orbital Symmetry," Springer-Verlag, New York, N. Y., 1970, for a discussion of 2+2 cycloaddition reactions.

[27] M. P. Doyle and W. Wierenga, *J. Amer. Chem. Soc.*, in press.

[28] T. L. Tolbert and P. L. Pickard, *J. Org. Chem.*, **26**, 4886 (1961).

[29] P. L. Julian, E. W. Meyer, A. Magnani, and W. Cole, *J. Amer. Chem. Soc.*, **67**, 1203 (1945).

benzene in 40% yield from benzenediazonium tetrafluoroborate was effected by adding cuprous chloride to the reaction mixture.

Product Analyses.—After complete addition of $NO^+BF_4^-$ or $NO^+SbF_6^-$ to the imine in acetonitrile a measured amount of a standard, usually nitromethane, was added to the reaction solution and an aliquot was removed for pmr analysis. Analyses were usually performed within 1 hr after initiation of reaction, although no change in product composition was observed over longer periods of time. A pmr spectrum was taken and integrated within 10 min after the sample was placed in the probe at 41° so as to minimize decomposition of diazonium salt. For spectra taken within 10 min no noticeable decomposition was observed. Another spectrum was recorded after 20 min in the nmr probe; only when the unsubstituted benzenediazonium ion was produced was there a noticeable change in the spectrum. Products were identified by spectral comparison to the authentic materials under comparable conditions. Yields were determined by averaging several integrations of the absorption signals for products. Reproducibility was ±2% when averaged over several reactions of the same components. Comparison was made both to the added standard and to the total phenyl region with no noticeable difference. Except for III and IV, absorptions for both the carbonyl compound and benzenediazonium ion were clearly distinguishable by pmr spectroscopy. Product per cent yields determined by this method follow: IIa, 95; IIb, 95; IIc, 95; IId, 90; IIe, 83; IIf, 90; IIg, 95; IIh, 90; IIi, 83; IIj, 75. Products from the reaction of III with $NO^+BF_4^-$ were detected by glpc and ir analyses. Benzil was recovered in good yield after treatment of IV with $NO^+BF_4^-$ in acetonitrile and work-up in dichloromethane under conditions where both monoanil and dianil could have been detected.

Registry No.—Nitrosonium ion, 33904-18-6.

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The Novel Reaction of 1,3-Dimethyl-6-amino-5-nitrosouracil with Lead Tetraacetate[1]

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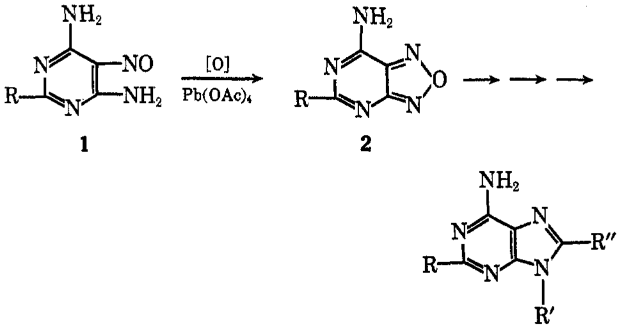
Lead tetraacetate oxidation of 1,3-dimethyl-6-amino-5-nitrosouracil (**4**) in glacial acetic acid solution results in rapid discharge of the purple color of **4**, evolution of nitrogen, and the formation of 1,3,6,8-tetramethyl-2,4,5,7-(1*H*,3*H*,6*H*,8*H*)-pyrimido[5,4-*g*]pteridinetetrone 10-oxide (**6**), along with a minor amount of 4,6-dimethyl-5,7-(4*H*,6*H*)-furazano[3,4-*d*]pyrimidinedione (**5**). The structure of **6** was established by reductive and hydrolytic studies.

We have described in a recent paper[4] the lead tetraacetate oxidation of a series of 4,6-diamino-5-nitrosopyrimidines (**1**) to 7-aminofurazano[3,4-*d*]pyrimidines (**2**), and the subsequent utilization of the latter as versatile intermediates for the unequivocal synthesis of 9-substituted adenines (**3**). The present paper describes the novel and unexpected result of lead tetraacetate oxidation, under identical conditions, of 1,3-dimethyl-6-amino-5-nitrosouracil (**4**).



1 **2** **3**

Addition of lead tetraacetate to an acetic acid solution of **4** at room temperature resulted in nitrogen evolution, rapid discharge of the purple color of **4**, and the separation of a yellow, crystalline solid, mp 360–362° dec. Evaporation of the filtrate and recrystallization of the residue gave the expected[4] product, 4,6-dimethyl-5,7(4*H*,6*H*)-furazano[3,4-*d*]pyrimidinedione (**5**), in low (19%) yield. Microanalytical and mass spectral data on the yellow solid, mp 360–362° dec, established the molecular formula $C_{12}H_{12}N_6O_5$, while a strong M − 16 peak in the mass spectrum indicated the presence of a labile oxygen, most probably an *N*-oxide.[5] This conclusion was confirmed by chemical reduction with sodium dithionite at room temperature to give a pale yellow solid, mp 385°, which was shown to be 1,3,6,8-tetramethyl-2,4,5,7(1*H*,3*H*,6*H*,8*H*)-pyrimido[5,4-*g*]pteridinetetrone (**8**) by comparison with an authentic sample fortuitously available in our own laboratory.[6] Thus the lead tetraacetate oxidation product of **4** must be one of the two possible *N*-oxides **6** or **7** of **8**. That the major oxidation product of **4** was the 10-oxide (**6**) and not the 9-oxide (**7**) was demonstrated unequivocally by hydrolytic and other degradative reactions which are summarized below.

Although dilute alkaline hydrolysis of **8** is known to give 3,5-bis(methylamino)-*N*,*N*′-dimethylpyrazine-2,6-dicarboxamide (**9**) in excellent yield,[6] analogous hydrolysis of **6** yielded three products, 3,5-bis(methylamino)-*N*,*N*′-dimethylpyrazine-2,6-dicarboxamide 1-oxide (**10**), 3,5-bis(methylamino)-6-carboxy-*N*-methylpyrazine-2-carboxamide 1-oxide (**11**), and 1,3-dimethyl-5-methylaminocarbonyl-6-methylamino-1*H*-imidazo-[4,5-*b*]pyrazin-2(3*H*)-one (**12**) in yields of 20, 20, and 50%, respectively. Compound **10** was readily deoxygenated to the known **9** with triethyl phosphite. Re-

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(4) E. C. Taylor, G. P. Beardsley, and Y. Maki, *J. Org. Chem.*, **36**, 3211 (1971).

(5) T. A. Bryce and J. R. Maxwell, *Chem. Commun.*, 206 (1965).

(6) E. C. Taylor, C. K. Cain, and H. M. Loux, *J. Amer. Chem. Soc.*, **76**, 1874 (1954). The melting point of **8** was reported to be 403–404°, but a redetermination using a corrected thermometer showed it to be 385°.