were generally not successful, however. Cyclohexanone did reduce slowly with 5% ruthenium on carbon to cyclohexanol but the reaction did not appear to be fast enough to be useful.

Experimental Section

Reagents. Triethylamine (Aldrich) was distilled prior to use. The formic acid (97%) was obtained from Aldrich. The platinum and palladium on charcoal catalysts were products of Matheson Coleman and Bell. The halides and nitro compounds were commercial products and purified if they had low melting points or were darkly colored.

General Procedure for Reduction of Organic Halides. In a heavy-walled 170-mL "Pyrex" bottle was placed 10 mmol of the halide, the appropriate quantity of either the palladium acetate–phosphine catalyst or 5% palladium on charcoal. The triethylamine was then added. The bottle was flushed with a stream of argon and capped with a rubber-lined cap. The formic acid was then added by syringe through the rubber liner of the cap. The mixture was heated at the appropriate reaction temperature. The progress of the reaction could be followed by noting the increase of pressure (CO_2) in the bottle. For this purpose a small pressure gauge was connected to the bottle through a syringe needle through the rubber-lined cap. The reactions were also monitored by GLC. Products could be isolated by adding sufficient methylene chloride to the product solution to dissolve the unreacted lower layer of amine formate and then filtering and distilling.

Methyl 4-Deuteriobenzoate. A mixture of 3.41 g (20 mmol) of methyl *p*-chlorobenzoate, 4 mL (28.5 mmol) of triethylamine, and 0.085 g (0.04 mmol) of 5% Pd/C was prepared in a 170-mL heavy-walled "Pyrex" bottle. The air was blown from the bottle with a stream of argon and the bottle was capped with a rubber-lined cap. The formic acid-d_2 was then injected (1.056 g, 22 mmol) by syringe through the liner and the mixture was heated in a steam bath for 29 h. Analyses by GLC now showed the chloride had all reacted. The cooled reaction mixture was diluted with ether and filtered through Celite. After rinsing the amine salt with ether, the combined filtrates were concentrated and distilled. There was obtained 2.45 g (90%) of methyl 4-deuteriobenzoate, bp 92–94 °C (20 mm). The mass spectrum of the sample showed it to be 91% monodeuterated. The NMR spectrum was as follows in $CDCl_3$: 3.95 ppm (s, 3 H), 7.62 (d, 2 H, J = 8 Hz), and 8.27 (d, 2 H, J = 8 Hz).

General Procedure for the Reduction of Nitro Compounds. In a 100-mL three-necked round-bottomed flask equipped with a condenser and dropping funnel was placed the nitro compound, the 5% palladium on charcoal, and the triethylamine. The mixture was stirred magnetically and heated on the steam bath while the 97% formic acid was added dropwise. Two layers were formed. The mixture was then heated until GLC analyses showed the absence of the nitro compound in the upper phase. Products were isolated by addition of methylene chloride, filtration, and concentration. The product was either distilled under reduced pressure, recrystallized, or, in one case, sublimed.

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Registry No.—Triethylammonium formate, 585-29-5; methyl 4-deuteriobenzoate, 13122-30-0.

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Reductive Deamination of Arylamines by Alkyl Nitrites in *N,N*-Dimethylformamide. A Direct Conversion of Arylamines to Aromatic Hydrocarbons

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Rapid deamination of arylamines by alkyl nitrites occurs in *N,N*-dimethylformamide and results in the replacement of the primary amino group by hydrogen. Consistently moderate to high yields of aromatic hydrocarbons are reported for nitrosation reactions of *tert*-butyl, benzyl, and isopentyl nitrites with 17 representative aromatic amines. *o*-Alkyl substituted aromatic amines are reductively deaminated by this method with only minor interference from indazole formation. Competing reactions that result in the production of phenols, biphenyls, or azobenzenes are minor processes in reactions that are performed in dimethylformamide. Deuterium labeling studies indicate that dimethylformamide is the sole hydrogen donor in these reductive deamination reactions. Comparative reductive deamination reactions of *p*-nitroaniline in commonly employed aprotic solvents demonstrate that dimethylformamide is superior to tetramethylurea, dioxane, tetrahydrofuran, chloroform, acetonitrile, and hexamethylphosphoramide as a hydrogen donor. The results obtained in this study are interpreted as involving aryl radicals in the formation of aromatic hydrocarbons.

Common procedures for the replacement of an aromatic primary amino group by hydrogen involve preliminary diazotization of the aromatic amine followed by reductive substitution by a hydrogen donor.[2] Although first in the extensive list of reducing agents to be thoroughly investigated,[3] primary alcohols are recognized as unsatisfactory for reductive deamination of a great variety of arylamines primarily because of competing ether formation.[3] Alkaline solutions of formaldehyde have also been used for reductive deamination of arylamines and are advantageous for reductions of diazonium ions that could not be effected by primary alcohols;[4] however, this reductive method has been restricted to a narrow range of aromatic amines, since diazo oxides are formed from ortho- and para-substituted diazonium salts by hydrolytic cleavage

Table I. Product Yields from Reactions of Arylamines with Alkyl Nitrites in Dimethylformamide at 65 °C[a]

			Product yield[b] from reaction of $ArNH_2$ with		
	Registry		$(CH_3)_3CONO$	$C_6H_5CH_2ONO$	
$ArNH_2$	no.	ArH	% ArH[c]	% ArH	% C_6H_5CHO[d]
2,4-Dinitro-5-fluoroaniline	367-81-7	2,4-$(NO_2)_2C_6H_3F$	63	52	27
2,4-Dinitroaniline	97-02-9	*m*-$C_6H_4(NO_2)_2$	(68)		
4,5-Dichloro-2-nitroaniline	6641-64-1	4-NO_2-1,2-$C_6H_3Cl_2$	(68)		
4-Methyl-2-nitroaniline	89-62-3	*m*-$NO_2C_6H_4CH_3$	(58)		
p-Nitroaniline	100-01-6	$C_6H_5NO_2$	82 (69)	83	33
m-Nitroaniline	99-09-2	$C_6H_5NO_2$	60		
o-Nitroaniline	88-74-4	$C_6H_5NO_2$	72		
2,4,6-Trichloroaniline	634-93-5	1,3,5-$C_6H_3Cl_3$	85	87	16
2,5-Dichloroaniline	95-82-9	*p*-$C_6H_4Cl_2$	80 (72)		
p-Aminoacetophenone	99-92-3	$C_6H_5COCH_3$	65		
p-Aminobenzophenone	1137-41-3	$(C_6H_5)_2CO$	76		
o-Aminobenzophenone	2835-77-0	$(C_6H_5)_2CO$	69	61	24
p-Anisidine	104-94-9	$C_6H_5OCH_3$	75	70	16
4-Nitro-1-aminonaphthalene	776-34-1	1-$C_{10}H_7NO_2$	72[e]		
4-Chloro-1-aminonaphthalene	4684-12-2	1-$C_{10}H_7Cl$	44		
2,4,6-Trimethylaniline	88-05-1	1,3,5-$C_6H_3(CH_3)_3$		44[f]	9
2-Methyl-6-Chloroaniline	87-63-8	*m*-$ClC_6H_4CH_3$	41 (35)		

[a] Unless indicated otherwise, reactions were performed by adding 10.0 mmol of the amine in DMF to 15.0 mmol of the alkyl nitrite in DMF at 65 °C. The total volume of DMF was 50 mL. [b] Absolute yield of the aromatic hydrocarbon after extraction; yields were generally determined by GLC analysis through comparison to an internal standard. From duplicate runs experimentally determined percentage yields were accurate to within ±3% of the reported values. [c] Isolated yields of the purified (distillation or recrystallization) aromatic hydrocarbon from reactions that employed between 0.01 and 0.10 mol of the reactant amine are given in parentheses. [d] Yield of benzaldehyde was determined by GLC and ^1H NMR analyses. Benzyl alcohol was the only other product derived from benzyl nitrite; % C_6H_5CHO + % $C_6H_5CH_2OH$ = 95 ± 3% of reacted benzyl nitrite. [e] Reaction with isopentyl nitrite. [f] 39% yield from reaction with isopentyl nitrite in DMF.

in alkaline media.[2] Hypophosphorus acid, as a result of extensive investigations by Kornblum,[2,5] has proven to be a conveniently employed and generally effective reducing agent for diazonium salts. Although other reduction methods and reducing agents for replacement of an aromatic primary amino group by hydrogen have been promoted in recent years,[6-9] hypophosphorus acid remains the standard reagent for reductions of diazonium salts.

In contrast to procedures that utilize or require a sequential two-step amino-group replacement by hydrogen (diazotization-hydrogen transfer), Cadogan and Molina have recently reported the successful use of pentyl nitrite in boiling tetrahydrofuran for direct reductive deamination of primary aromatic amines.[10] In their in situ reductive deamination procedure Cadogan and Molina rely on the efficiency of hydrogen abstraction from a carbon position that is adjacent to an ether oxygen.[11] Although their results do not generally compare favorably with those from reductive deaminations that employ hypophosphorus acid, particularly in reactions with *o*-alkyl substituted arylamines, the convenience of their in situ method and their use of anhydrous media are attractive.

Our investigations of copper(II) halide promoted reactions of alkyl nitrites with arylamines prompted this investigation of a reaction process that is potentially competitive with substitutive deamination and related reactions.[12,13] In this paper, we report that treatment of arylamines with alkyl nitrites in *N,N*-dimethylformamide results in reductive deamination and that this procedure compares favorably with Kornblum's hypophosphorus acid procedure as a generally effective method for the replacement of an aromatic primary amino group by hydrogen.[14] The use of *N,N*-dimethylformamide as the hydrogen donor effectively minimizes those side reactions that accompany similar reactions that occur in tetrahydrofuran or dioxane.

Results and Discussion

We have reported that *tert*-butyl nitrite reacts slowly with *p*-nitroaniline in acetonitrile at 65 °C to produce nitrobenzene.[12a] However, the yield of nitrobenzene is less than 50%, which indicates that this procedure is unsuitable as a general method for reductive deamination. Surprisingly, when this same reaction is performed in *N,N*-dimethylformamide (DMF) at 65 °C, gas evolution is rapid and nitrobenzene is formed in 82% yield. Compared to reactions in acetonitrile at 65 °C, which are generally complete only after 1 h, those in DMF are immediate and are complete within 10 min following complete addition of the amine. Table I presents the yields of aromatic compounds that are obtained from reactions of representative arylamines with *tert*-butyl nitrite in DMF (eq 1).

$$ArNH_2 + RONO \xrightarrow{DMF} ArH + ROH + N_2 + H_2O \quad (1)$$

Consistently moderate to high yields of the reductive deamination product are observed in nitrosation reactions that occur in DMF with the varied selection of aromatic amines. Indeed, even *o*-alkyl substituted arylamines are effectively deaminated by this procedure. In tetrahydrofuran, 2-methyl-6-chloroaniline does not form *m*-chlorotoluene, but, instead, yields 7-chloroindazole;[10] in DMF, 7-chloroindazole is formed as a minor side product (10% yield). Comparison of the product yields from nitrosative deamination of structurally similar arylamines in THF[10] and in DMF (Table I) indicates that dimethylformamide is a more effective hydrogen donor than is tetrahydrofuran. Side reactions that lead to the production of phenols, biphenyls, and azobenzenes are minor competing processes in DMF.[15] However, a dark resinous material is formed in these reactions in amounts that reflect the difference between 100% and the percentage yields of arenes that are reported in Table I; similar red or red-brown residues have been reported to result from nitrosative deamination by other reductive procedures.[5,8] Although no attempt was made in this study to optimize the yields of individual products, the yields of purified arenes that were obtained by reductive deamination in DMF were similar to those obtained by the hypophosphorus acid reduction of diazonium salts.[2,5]

Isopentyl nitrite and benzyl nitrite were reacted with a se-

Table II. Deuterium Content of Aromatic Hydrocarbons Formed by Nitrosative Deamination of Arylamines[a]

Amine	Nitrite	Solvent	Arene[b]	
			d_0, %	d_1, %
2,4,6-$Cl_3C_6H_2NH_2$	$C_6H_5CD_2ONO$	DMF	100	
2,4,6-$Cl_3C_6H_2ND_2$	$(CH_3)_3CONO$	DMF[c]	100	
2,4,6-$Cl_3C_6H_2NH_2$	$(CH_3)_3CONO$	DMF + 1.0 equiv of D_2O[d]	100	
2,4,6-$Cl_3C_6H_2NH_2$	$C_6H_5CD_2ONO$	CH_3CN	70	30
2,4,6-$Cl_3C_6H_2NH_2$	$C_6H_5CH_2ONO$	CD_3CN[e,f]	83	17
2,4,6-$Cl_3C_6H_2NH_2$	$(CH_3)_3CONO$	CD_3CN[f,g]	43	57
4,5-Cl_2-2-$(NO_2)C_6H_2NH_2$	$(CH_3)_3CONO$	CD_3CN[g]	59	41

[a] Reactions were performed at 65 °C. [b] Determined by mass spectral analysis of the arene isolated by GLC collection. Percentage deuterium content was averaged from at least two separate determinations. [c] 84% yield of 1,3,5-trichlorobenzene. [d] 85% yield of 1,3,5-trichlorobenzene. [e] 64% yield of 1,3,5-trichlorobenzene + 63% benzaldehyde. [f] Reactions were run with 2 mmol of the amine in 3.0 mL of the deuterated acetonitrile. [g] 55% yield of 1,3,5-trichlorobenzene.

Table III. Reductive Deamination of p-Nitroaniline in Aprotic Solvents[a]

Solvent	RONO	Registry no.	$C_6H_5NO_2$, %[b]
Dimethylformamide	t-BuONO		82
Tetramethylurea[c]	t-BuONO		75
Dioxane	t-BuONO		65
Tetrahydrofuran	PentONO	463-04-7	65[d]
Chloroform[e]	t-BuONO		52[f]
Chloroform + 2 eq DMF[e]	t-BuONO		51[g]
Acetonitrile	t-BuONO	540-80-7	50
Hexamethylphosphoramide	i-PentONO	110-46-3	30

[a] Reactions were performed by adding 10.0 mmol of the amine in the indicated solvent to 15.0 mmol of the alkyl nitrite in the same solvent at 65 °C or at reflux (THF and $CHCl_3$). Unless indicated otherwise, the total volume of the solvent was 50 mL. [b] Absolute yield of nitrobenzene determined by GLC analysis after extraction. [c] Total volume was 30 mL. [d] Ref 10. [e] Amine was added in portions as a solid. [f] +34% p-Nitro-α,α,α-trichlorotoluene. [g] +36% p-Nitro-α,α,α-trichlorotoluene.

ries of arylamines in DMF at 65 °C to determine whether the structure of the alkyl nitrite had a pronounced effect on the extent of reductive deamination. Isopentyl nitrite gave results that were nearly identical to those obtained with *tert*-butyl nitrite under the same reaction conditions. Product yields from reactions with benzyl nitrite are given in Table I and similarly indicate no dependence of the reductive deamination process on the structure of the alkyl nitrite. Benzaldehyde was formed together with benzyl alcohol as the only identifiable products emanating from benzyl nitrite. The combined yields of benzaldehyde (Table I) and benzyl alcohol were nearly quantitative.

The formation of benzaldehyde in aromatic amine reactions with benzyl nitrite suggested that this nitrite may be a hydrogen donor in reductive deamination reactions. In order to determine the nature of benzaldehyde production and to identify the probable source of the hydrogen that is transferred in these reactions, α,α-dideuteriobenzyl nitrite was prepared and reacted with 2,4,6-trichloroaniline in dimethylformamide. The reduced product 1,3,5-trichlorobenzene was isolated by GLC separation and its deuterium content was determined by mass spectral analysis. Similarly, *N,N*-dideuterio-2,4,6-trichloroaniline was prepared and subjected to reductive deamination by *tert*-butyl nitrite in DMF. In a third experiment, 1.0 molar equiv of D_2O (based on the amine) was employed with undeuterated reactants. Within the limits of our detection, only 1,3,5-trichlorobenzene that did not contain deuterium was formed (Table II). These results strongly suggest that *N,N*-dimethylformamide is the sole hydrogen donor in deamination reactions that are performed in that aprotic solvent. Benzaldehyde formation is independent of the reductive deamination process. Indeed, in control experiments in which benzyl nitrite was heated at 65 °C in DMF for 1 h and then isolated by the usual workup procedure, benzaldehyde (21%) and benzyl alcohol (47%) were formed, and benzyl nitrite (32%) was recovered.[16]

Similar deuteration studies were performed for nitrosative deamination reactions that employed acetonitrile as the solvent and potential hydrogen donor, and their results are reported in Table II. Benzyl nitrite is a surprisingly effective hydrogen donor in acetonitrile; acetonitrile is surprisingly ineffective as a hydrogen donor. Use of α,α-dideuteriobenzyl nitrite in the reaction with 2,4,6-trichloroaniline leads to 30% deuteration in 1,3,5-trichlorobenzene. However, in a separate experiment with acetonitrile-d_3 only 17% of monodeuterated 1,3,5-trichlorobenzene is formed. In view of the relatively low yield of deuterated arene in acetonitrile-d_3 for reactions of arylamines with *tert*-butyl nitrite, the results with benzyl nitrite may be explained as a consequence of the isotope effect for hydrogen (and deuterium) transfer from the benzylic position.[17] Due to the complex nature of hydrogen transfer and the relatively low yield of products from reductive deamination in acetonitrile, however, no definitive conclusion other than that related to the effectiveness of DMF and acetonitrile as hydrogen donors can be drawn from these investigations.

An increasing number of solvents, including tetramethylurea,[8] dioxane,[6] and tetrahydrofuran,[10] have been promoted in recent years as effective hydrogen donors for the reduction of diazonium compounds. However, only tetrahydrofuran has been employed in a direct reductive deamination process.[10] To compare hydrogen-donor capabilities, *p*-nitroaniline was subjected to nitrosative deamination in a representative series of solvents under reaction conditions identical to those that are reported for reactions in DMF. The results of this investigation are described in Table III. Although results from reductive deamination of only one amine are reported, DMF is clearly the superior hydrogen donor among the aprotic solvents employed in this study.

Tetramethylurea approaches DMF in its effectiveness as a hydrogen donor, and this similarity suggests that reduction occurs primarily by hydrogen transfer from the *N*-methyl group rather than solely from the formyl position. This explanation also accounts for the relative absence of carbon dioxide in the gaseous products. Deamination of *p*-nitroaniline by *tert*-butyl nitrite in DMF at 65 °C yields a mixture of gaseous products that is composed of nitrogen (93%), nitrous oxide (2%),[18] and carbon dioxide (5%). We have been unable, however, to isolate product(s) that are formed from DMF following hydrogen transfer.

The results obtained in this study of reductive deamination

Scheme I

$$\mathrm{ArNH_2 + RONO \rightarrow ArN{=}N\text{-}OR + H_2O} \tag{2}$$

$$\mathrm{ArN{=}N\text{-}OR \rightarrow ArN_2\cdot + RO\cdot} \tag{3}$$

$$\mathrm{ArN_2\cdot \rightarrow Ar\cdot + N_2} \tag{4}$$

$$\mathrm{Ar\cdot + SolH \rightarrow ArH + Sol\cdot} \tag{5}$$

of aromatic amines are consistent with the involvement of aryl radicals (Scheme I).[20] Additional evidence for the operation of the radical pathway was obtained through trapping experiments in which equal volumes of acrylonitrile and acetonitrile were employed as the solvent for the reaction between *p*-nitroaniline and *tert*-butyl nitrite; only a trace amount of nitrobenzene was formed and polymerization of acrylonitrile was observed. The amount of gaseous products was only two-thirds of that obtained from reactions without added acrylonitrile, suggesting that the aryldiazo radical is an intermediate in this reaction process. Furthermore, the observation of *p*-nitro-α,α,α-trichlorotoluene from reactions in chloroform (Table III) suggests a radical coupling mechanism for the formation of this unusual product.[21]

Our results do not distinguish the mechanism proposed in Scheme I from one that involves the intermediacy of aryldiazenes (Scheme II). Hydrocarbons are the predominant products from bimolecular decomposition of aryldiazenes.[22] However, if aryldiazenes are reaction intermediates in reductive nitrosation reactions of arylamines, they cannot be solely responsible for hydrocarbon formation. Nitro substituents inhibit aryldiazene decomposition to the corresponding aromatic hydrocarbon,[22] whereas nitro substituents do not measurably affect the yield of the reduced product in nitrosation reactions (Table I).

Several attempts were made to convert primary alkylamines to their corresponding hydrocarbons through reactions with *tert*-butyl nitrite in DMF at 65 °C. However, as expected from prior investigations of aprotic diazotization of aliphatic amines,[19] low product yields were obtained. For example, adamantane was formed from 1-adamantamine in only 5% yield, and 1-amino-4-phenylbutane produced 1-phenylbutane and tetrahydronaphthalene in 6 and 2% yield, respectively.[23]

Reductive deamination by alkyl nitrites in DMF is not limited to primary aromatic amines. Preliminary results in our laboratory have demonstrated that arylhydrazines are reduced to the corresponding aromatic hydrocarbons without competing formation of aryl azides. These and related transformations are presently under investigation.

Experimental Section

General. Instrumentation has been previously described.[12a] Mass spectra were obtained using a Fannigan Model 1015 gas chromatograph–mass spectrometer operated at 70 eV. *tert*-Butyl nitrite was prepared from *tert*-butyl alcohol according to the procedure of Noyes;[24] isopentyl nitrite was obtained commercially. Benzyl nitrite was formed from benzyl alcohol, sodium nitrite, and aluminum sulfate according to the published procedure,[25] and its purity was monitored regularly by ^{1}H NMR spectral analysis.[26] α,α-Dideuteriobenzyl nitrite was similarly prepared from α,α-dideuteriobenzyl alcohol. The amines that were employed in this study were commercially available and, with the exception of *p*-anisidine, were used without prior purification. Reagent grade *N*,*N*-dimethylformamide, acetonitrile, and hexamethylphosphoramide were distilled from calcium hydride prior to their use as reaction solvents. Dioxane was distilled from lithium aluminum hydride, and chloroform was washed with concentrated sulfuric acid prior to distillation. Tetramethylurea was used without further purification. *N*,*N*-Dideuterio-2,4,6-trichloroaniline was prepared by hydrogen–deuterium exchange in D_2O catalyzed by sulfuric acid-d_2; ^{1}H NMR analysis verified total exchange. Acetonitrile-d_3 was obtained commercially (99 atom % ^{2}H) and was used without further purification.

Scheme II

$$\mathrm{ArN_2\cdot + SolH \rightarrow ArN{=}NH + Sol\cdot} \tag{6}$$

$$\mathrm{ArN{=}NH \rightarrow ArH + N_2} \tag{7}$$

Reductive Deamination of Aromatic Amines. General Procedure. To a rapidly stirred solution of the alkyl nitrite (15.0 mmol) and anhydrous DMF heated at 65 °C in a three-necked round-bottom flask equipped with a reflux condenser, addition funnel, and gas outlet tube was added the aromatic amine (10.0 mmol) dissolved in a minimal amount of DMF. The amine was added slowly to the reaction solution over a 5-min period. Gas evolution was immediate, continued steadily throughout the addition, and was generally complete within 10 min following complete addition of the amine. Total gas evolution was measured on the closed system by water displacement from a calibrated gas buret; with the exception of reactions with *o*-alkyl-substituted aromatic amines and the naphthylamines, the yield of gaseous products was 220 ± 20 mL (based on 10 mmol of the amine). After complete gas evolution, the reaction solution that had turned deep red from the initial yellow was cooled and then poured into 200 mL of 20% aqueous hydrochloric acid and extracted with 200 mL of ether, and the organic layer was washed once with 200 mL of aqueous hydrochloric acid. The resulting ether solution was dried over anhydrous magnesium sulfate and the ether was removed under reduced pressure. Ether solutions containing volatile products were distilled at atmospheric pressure through a 12.5-cm Vigreux column.

A similar procedure was employed for reactions of *p*-nitroaniline in those solvents that are described in Table III.

Product Analyses. Structural assignments for the aromatic hydrocarbons produced in reactions of arylamines with alkyl nitrites were made following extraction by ^{1}H NMR spectral comparisons and/or by GLC retention time and peak enhancement with authentic samples. *p*-Nitro-α,α,α-trichlorotoluene was identified by ^{1}H NMR, IR, and mass spectral analysis following isolation of this compound from the reaction mixture (see Table III) by GLC separation. The gaseous products from the reaction of *p*-nitroaniline with *tert*-butyl nitrite in dimethylformamide were analyzed by GLC retention times on a 5-ft silica gel column and by infrared spectral analysis.

Product yields were determined by GLC analyses for the vast majority of reactions reported in this study. Prior to workup a weighed amount of dibenzyl ether was added to the reaction solution as an internal standard. The average integrated area ratio from at least two GLC traces was employed in each yield determination. Absolute yields were calculated with the use of experimentally determined thermal conductivities for each of the aromatic hydrocarbons examined by this method. Thermal conductivity ratios were determined immediately prior to product analyses to ensure accuracy in these calculations. Yields also determined by ^{1}H NMR spectral analysis were in substantial agreement (±2%) with those obtained by the GLC method.

The absolute yields of benzaldehyde and benzyl alcohol were obtained by ^{1}H NMR spectral analysis of the reaction solutions following extraction. The average values of at least five integrations were utilized in the calculation of absolute yields. Yields obtained by the GLC method confirmed those determined by ^{1}H NMR spectral analysis.

Determination of the deuterium content in aromatic hydrocarbons was made by mass spectral comparisons of the molecular ion peaks of an authentic sample with those peaks observed from the reaction product. No difference in relative peak intensity was observed from analyses at 70 and 20 eV. For each analysis the aromatic hydrocarbon was isolated from the reaction mixture by GLC separation and this sample was inserted into the ionization chamber through the use of a solid probe. A minimum of two mass spectral traces was employed in the calculation of deuterium content for each reaction.

1,2-Dichloro-4-nitrobenzene. The procedure employed for reductive deamination of 4,5-dichloro-2-nitroaniline exemplifies those used for the preparative scale reactions that are reported in Table I (yield of distilled or recrystallized product given in parentheses). To a rapidly stirred solution of *tert*-butyl nitrite (5.47 g, 0.0530 mol) and anhydrous DMF (30 mL) heated at 50 °C in a 250-mL three-necked round-bottom flask equipped with a reflux condenser and addition funnel was added 4,5-dichloro-2-nitroaniline (7.28 g, 0.0352 mol) dissolved in 70 mL of DMF. The reaction temperature was maintained at 50 °C to minimize the loss of *tert*-butyl nitrite. The amine solution was added dropwise to the nitrite solution over a 25-min period. Gas evolution was immediate and continued steadily throughout the addition. After addition was complete, no further gas evolution was observed and the reaction solution was allowed to cool to room temperature. The resulting burnt orange reaction solution was diluted with 300 mL of ether and then poured into 300 mL of 20% aqueous hydrochloric acid. After separation, the ether solution was washed with an additional 300 mL of 20% aqueous hydrochloric acid and was dried over anhydrous magnesium sulfate. The ether was removed under reduced pressure and the residue was distilled at 0.6 Torr to give 4.56 g of a light yellow liquid (bp 107–110 °C at 0.6 Torr; lit.[27] bp 254–257 °C) that crystallized on standing (mp 40.5–41.0 °C; lit.[27] mp 43 °C): 0.0238 mol, 68% yield.

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Registry No.—Dimethylformamide, 68-12-2; $C_6H_5CH_2ONO$, 935-05-7.

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(13) Although reductive deamination does not compete with substitutive deamination when nitrosation reactions with a wide variety of arylamines are performed in the presence of at least 1 molar equiv of copper(II) halide,[12a] effective competition does occur when the $[CuX_2]/[ArNH_2]$ ratio is ≤ 0.5.

(14) Dimethylformamide has been employed for reductions of arenediazonium compounds: (a) H. Zollinger, "Azo and Diazo Chemistry", Interscience, New York, N.Y., 1961, p 168; (b) M. Schubert and R. Fleischhauer, German Patent 901 175; *Chem. Abstr.*, **49,** 10365h (1955); (c) German Patent 905 014; *Chem. Abstr.*, **50,** 12111*b* (1956).

(15) Nitrosative deamination of aniline by isopentyl nitrite in DMF at 65 °C resulted in the formation of biphenyl (<2%) and azobenzene (4%). Phenols were usually absent in reaction mixtures but in several experiments were observed in yields that were less than 5%.

(16) Benzyl nitrite is hydrolyzed to benzyl alcohol during the workup process.

(17) The deuterium isotope effect for hydrogen (deuterium) abstraction from toluene by a phenyl radical is 4.0 (60 °C): R. F. Bridger and G. A. Russell, *J. Am. Chem. Soc.*, **85,** 3754 (1963).

(18) The production of nitrous oxide in reactions that employ *tert*-butyl nitrite cannot be explained by a base-catalyzed oxidation similar to that proposed in reactions of aliphatic amines with isopentyl nitrite.[19]

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(20) This mechanism is supported by other recent investigations of reductive deamination reactions in aprotic media: (a) Y. Hirose, G. H. Wahl, Jr., and H. Zollinger, *Helv. Chim. Acta*, **59,** 1427 (1976); (b) J. I. G. Cadogan, D. A. Roy, and D. M. Smith, *J. Chem. Soc. C*, 1249 (1966).

(21) Cadogan has reported that deamination of *p*-nitroaniline by pentyl nitrite in refluxing chloroform yields nitrobenzene (42%) and *p*-chloronitrobenzene (28%).[20b] We obtained no evidence for the formation of *p*-chloronitrobenzene from reactions that employed *tert*-butyl nitrite.

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(25) A. Chritien and Y. Longi, *Compt. Rend.*, **220,** 746 (1945); low yields of benzyl nitrite were obtained if the aluminum salt was not rigorously excluded from the benzyl nitrite solution prior to distillation. Multiple extractions with ether and subsequent washings of the ether solution with saturated sodium bicarbonate satisfactorily removed these contaminants.

(26) When storred at 0 °C benzyl nitrite was stable over long periods of time; decomposition to benzaldehyde amounted to only 3% after 1 month.

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1,2,4-Triazine 1- and 2-Oxides. Reactivities toward Some Electrophiles and Nucleophiles

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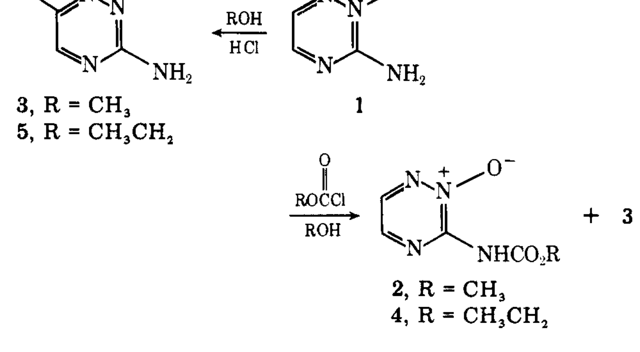
The 3-amino- (**1**), 3-methylamino- (**6**), 3-dimethylamino- (**7**), and methylthio- (**10**) 1,2,4-triazine 2-oxides undergo an addition–elimination reaction with methanol, ethanol, or 2-propanol to give the corresponding 6-alkoxy-1,2,4-triazines. The 1,2,4-triazine 1-oxides do not react with methanol under similar reaction conditions. Reaction of 3-amino-1,2,4-triazine 1-oxide (**14**) with nitrous acid in the presence of hydrobromic acid forms 3-bromo- (**19**) and 3,6-dibromo-1,2,4-triazine 1-oxide (**20**). The 3-methoxy- (**13**), 3-amino- (**14**), 3-methylamino- (**15**), and 3-dimethylamino- (**16**) 1,2,4-triazine 1-oxides react with bromine to give the respective 6-bromo-1,2,4-triazine 1-oxides (**21–24**). Possible reaction paths to account for these transformations are proposed.

1,2,4-Triazines have proven to be rather unusual π-deficient heteroaromatic compounds, as exemplified by their facile covalent hydration across the N_4–C_5 bonds,[1] their propensity for acting as dienes in Diels–Alder reactions,[2] and the tendency for ring contraction of their N-alkylated derivatives.[3]

We have described the selective N-1 and N-2 oxidation of several 1,2,4-triazine derivatives[4,5] and now wish to report some interesting chemical transformations of these compounds.

During studies involving the condensation of 3-amino-1,2,4-triazine 2-oxide (**1**) with methanolic methyl chloroformate, the expected urethane (**2**) was the minor product; the



3, R = CH_3
5, R = CH_3CH_2

1

2, R = CH_3
4, R = CH_3CH_2