nounced red shift on para substitution of that ring by the withdrawing NO_2 group.[9b] Both findings, coupled with the band's comparative intensitivity to solvent effects observed both in benzylideneaniline[7] and in **1** (Table II), render a charge transfer of the type proposed[7] rather unlikely as the cause of this absorption. We prefer to assign the band to a $\pi \rightarrow \pi^*$ transition originating from the highest occupied π level of the $N{=}CC_6H_4C{=}N$ unit. Such assignment accords with the band's bathochromic (and hyperchromic) shift on achieving coplanarity of the molecule by protonation or ring closure to the imidazole system.[9c]

(9) (a) With respect to noncoplanarity of the outer ("aniline") rings with the $N{=}CHC_6H_4CH{=}N$ segment, the same arguments (conjugation of the aniline rings' π systems with the lone-pair electrons on N)[7,9b] hold as in the case of *N*-benzylideneaniline, in which rotation of the *N*-phenyl ring out of the plane of the benzalimino chromophore has been established.[5b,7,9c–e] It is only on heteroaromatization (process **1** → **2**) that an approximate coplanarity of the molecule's benzene rings can result. (b) V. A. Ismailski and E. A. Smirnov, *Zh. Obshch. Khim.*, **26**, 3389 (1956). (c) P. Brocklehurst, *Tetrahedron*, **18**, 299 (1962). (d) W. F. Smith, *ibid.*, **19**, 445 (1963). (e) H. B. Bürgi and J. D. Dunitz, *Chem. Commun.*, 472 (1969); *Helv. Chim. Acta*, **54**, 1255 (1971).

(10) In the KBr spectra of several crude or too rapidly recrystallized products we found the C=N band in reduced intensity; at the same time, two new nonbonded and bonded N–H stretching peaks appeared at 3440 and 3350 cm^{-1} in addition to the aforementioned two bands of these origins. This suggests that product separating from solution under nonequilibrium conditions may indeed contain some imidazoline tautomers.

(11) The facile formation of *N*-benzyl substituted benzimidazoles (aldehydines) from bis-Schiff bases of aromatic *o*-diamines is on record: J. B. Wright, *Chem. Rev.*, **48**, 397 (19651).

(12) (a) The oxidative heteroaromatization of *o*-aminoanils to benzimidazoles has been achieved in the presence of cupric salts,[12b] lead tetraacetate,[12c] and active MnO_2,[12d] and some mechanistic implications have been discussed.[12e] These methods, however, requiring large quantities of oxidants and inefficient separation techniques for the imidazole products, give inferior yields and are not adaptable to polymerization chemistry. (b) R. Weidenhagen, *Chem. Ber.*, **69**, 2263 (1936); R. Weidenhagen and U. Weedon, *Ibid.*, **71**, 2347 (1938); R. Weidenhagen and G. Train, *Ibid.*, **75**, 1936 (1942). (c) F. F. Stephens and J. D. Bower, *J. Chem. Soc.*, 2971 (1949). (d) I. Bhatnagar and M. V. George, *Tetrahedron*, **24**, 1293 (1968). (e) W. G. Nigh in "Oxidation in Organic Chemistry", W. S. Trahanovsky, Ed., Academic Press, New York, N.Y., 1973, p 59.

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(14) (a) The product most likely is a mixture of two positional isomers. Electron density determinations by MO calculations[14b] show the two *m*-amino groups in the tetramine starting compound to be somewhat more basic than the two *p*-amino groups. The calculated difference in electronic charge (1.862 vs. 1.856) is, however, not significant enough to justify a prediction of predominance of the 3,3′-di(benzylideneimino) compound over the 4,4′ isomer. (b) D. A. Bochvar, I. V. Stankevich, V. V. Korshak, and A. L. Rusanov, *Dokl. Akad. Nauk SSSR*, **184**, 95 (1969).

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(16) An attempt to differentiate between solid **a** and **b** by N(1s) x-ray photoelectron spectroscopy failed, only a single, albeit broad (width at half-height 3.0–3.5 eV) band ($E_b = 399.5 \pm 0.5$ eV) being shown by both **1** and **8**. The binding energies of $\mathbf{NH_2}$ and **NH**, on the one hand, and of CH=**N**, on the other, in these compounds obviously are within the experimental error limits of the method. Accordingly, E_b values of 398.9, 399.5, and 399.2 eV were found respectively for **3**, **4**, and *o*-phenylenediamine. 2-Phenylbenzimidazole gave a peak corresponding to $E_b = 400.0$ eV.

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(18) (a) Although conventionally[13,17] represented by structure **9** comprising a 5,5′ linkage between the two benzimidazole units, the compound in the solid state almost certainly is a mxture of tautomers in which the benzazole groups are connected via 5,5′, 6,6′, and 5,6′ bonds. In (neutral) solutions, however, the NH protons of benzimidazoles are known[18b] to undergo rapid 1,3-exchange, rendering such distinctions meaningless. (b) H. A. Staab and A. Mannschreck, *Tetrahedron Lett.*, 913 (1962).

(19) Melting points, uncorrected, were taken in sealed capillaries. IR spectra were taken on a Perkin-Elmer 521 spectrophotometer. ^1H NMR spectra were obtained with a Hitachi Perkin-Elmer R20 NMR spectrometer operating at 60 MHz; chemical shifts, δ, are in parts per million relative to internal Me_4Si. Electronic absorption spectra were recorded on a Unicam SP1800 spectrophotometer. Mass spectra (MS) were scanned with a Varian-MAT CH5 mass spectrometer at 70 eV ionizing voltage. N(1s) x-ray photoelectron spectra (Mg Kα radiation) were obtained at −100 °C with the aid of an AEI Scientific ES200 electron spectrometer; peaks were calibrated by reference against internal NH_4NO_3 [$E_{b(NH_4)} = 402.3$ eV]; precision, ±0.2 eV. Thin layer chromatography (TLC) was performed on precoated SiO_2 plates, Merck silica gel 60 F_{254}, in 4:5 acetone/hexane. Microanalyses were by Robertson Laboratory, Florham Park, N.J.

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(23) A sample isolated from large-scale runs by column chromatography (0.5%) had mp 255–260 °C dec; ν_{CO} (KBr) 1703 cm^{-1}; λ_{max} (DMAC) 341 nm; *m/e* 222 (P^+), 193 ($P^+ - H - CO$). The aldehyde probably resulted from partial hydrolysis of **1** and subsequent cyclodehydrogenation.

Palladium-Catalyzed Reductions of Halo- and Nitroaromatic Compounds with Triethylammonium Formate

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Aromatic halides and nitro compounds are readily reduced at 50–100 °C to hydrocarbons and amines, respectively, with triethylammonium formate in the presence of either palladium on charcoal or a soluble triarylphosphine–palladium acetate catalyst. Aryl halides are reduced to deuterio derivatives with dideuterioformic acid.

The reducing ability of alkylammonium formates in the palladium-catalyzed reductive dimerization of conjugated dienes has been noted by Roffia et al.[1] In subsequent studies we also became interested in this reducing system[2] and now report applications of it to the reduction of aromatic halides and nitro compounds.

Results and Discussion

Aryl Halides. We initially employed a soluble catalyst, a combination of palladium acetate with a triarylphosphine, for the reductions with triethylammonium formate. We later found that palladium on charcoal was often as useful and, of course, had the advantage of being easily removable from the reaction mixture. The results of these experiments with organic halides are shown in Table I.

It appears that aromatic halide groups may be removed with extreme ease by the palladium-catalyzed reduction with triethylammonium formate at 50–100 °C. The other products of the reaction are the triethylamine hydrohalide and carbon dioxide. Other reducible groups such as nitrile and nitro are not reduced as readily as the halo substituent. Double bonds are apparently reduced at rates comparable to those with the chloro group, and mixtures resulted from the reduction of

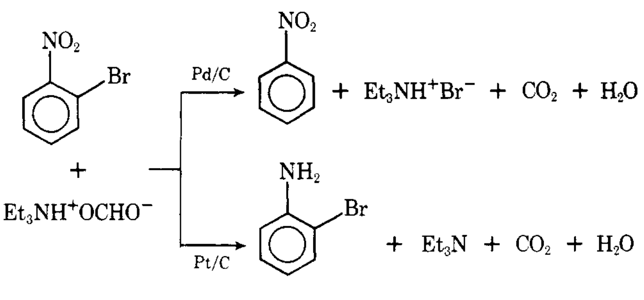


Table I. Reduction of Aromatic Halides of Triethylammonium Formate[a]

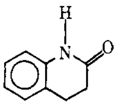
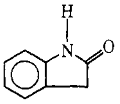
Registry no.	Substituted benzene	Registry no.	Catalyst	Mol % Pd based on organic halide	Temp, °C	Reaction time, h	Product, % yield[b]
623-03-0	1-CN, 4-Cl	7440-05-3	5% Pd/C	0.2	100	23.5	C_6H_5CN, 80
1126-46-1	1-CO_2CH_3, 4-Cl		5% Pd/C	0.2	100	42	$C_6H_5CO_2CH_3$, 93
7560-44-3	1-$CH{=}CHCO_2CH_3$, 4-Cl		5% Pd/C	0.2	100	1.5	$C_6H_5CH{=}CHCO_2CH_3$, 22 $C_6H_5CH_2CH_2CO_2CH_3$, 55
100-00-5	1-NO_2, 4-Cl		5% Pd/C	0.2	100	1	$C_6H_5NO_2$, 91
						6	$C_6H_5NO_2$, 83 $C_6H_5NH_2$, 3
						48	$C_6H_5NH_2$, 85[e]
106-47-8	1-NH_2, 4-Cl		5% Pd/C	0.2	100	<1	$C_6H_5NH_2$, 87[e]
	1-CO_2CH_3, 4-Cl		5% Pd/C	0.2	100	29	1-CO_2CH_3, 4-D, 90[e]
108-86-1	Br	3375-31-3	$Pd(OAc)_2$ + 2P(o-tol)$_3$[f]	1	50	4.5	C_6H_6, 92
623-00-7	1-CN, 4-Br		$Pd(OAc)_2$ + 2P(o-tol)$_3$	1	50	20	C_6H_5CN, 83
3650-78-0	1-CN, 4-Br		5% Pd/$BaSO_4$	1	50	20	C_6H_5CN, 53
2859-78-1	1-$CH{=}CHCO_2CH_3$, 4-Br[c]		5% Pd/C	0.2	100	7	$C_6H_5CH{=}CHCO_2CH_3$, 93[e]
585-79-5	1,2-$(OCH_3)_2$, 4-Br		5% Pd/C + 4P(o-tol)$_3$	1	50	15	1,2-$(CH_3O)_2C_6H_4$, 68
	1-NO_2, 3-Br[d]		$Pd(OAc)_2$ + 2P(o-tol)$_3$	1	50	1.5	$C_6H_5NO_2$, 81 $C_6H_5NH_2$, 2
	1-NO_2, 3-Br[d]		$Pd(OAc)_2$ + $2PPh_3$	1	50	23	$C_6H_5NO_2$, 55 $C_6H_5NH_2$, 12
	1-NO_2, 3-Br[d]		$Pd(OAc)_2$ + 2P(2,5-i-$pr_2C_6H_3)_3$	1	50	23	$C_6H_5NO_2$, 54 $C_6H_5NH_2$, 25
	1-NO_2, 3-Br[d]		5% Pd/C	1	50	1.5	$C_6H_5NO_2$, 46 $C_6H_5NH_2$, 15
	1-NO_2, 3-Br[d]		5% Pd/C + 2P(o-tol)$_3$	1	50	20	$C_6H_5NO_2$, 44 $C_6H_5NH_2$, 16
577-19-5	1-NO_2, 2-Br[d]		5% Pd/C	1	50	48	$C_6H_5NO_2$, 78 $C_6H_5NH_2$, 8
106-40-1	1-NH_2, 4-Br		$Pd(OAc)_2$ + 2P(o-tol)$_3$	1	50	1	$C_6H_5NH_2$, 69[e]
615-57-6	1-NH_2, 2,4-Br_2		5% Pd/C	1	50	0.5	$C_6H_5NH_2$, 50 2-$BrC_6H_4NH_2$, 10 4-$BrC_6H_4NH_2$, 4
6630-33-7	1-CHO, 2-Br		$Pd(OAc)_2$ + 2P(o-tol)$_3$	1	50	2	C_6H_5CHO, 43 $C_6H_5CH_2OH$, 10 $C_6H_5CH_3$, 10
	1-CHO, 2-Br		5% Pd/C	1	50	20	C_6H_5CHO, 44 $C_6H_5CH_2OH$, 8
103-64-0	$CH{=}CHBr$[d]		$Pd(OAc)_2$ + 2P(o-tol)$_3$	1	50	1.5	$C_6H_5CH{=}CH_2$, 32 $C_6H_5CH_2CH_3$, 9
			5% Pd/C		50	19.5	$C_6H_5CH{=}CH_2$, 34 $C_6H_5CH_2CH_3$, 31
2687-12-9	$CH{=}CHCH_2Cl$		$Pd(OAc)_2$ + 4P(o-tol)$_3$	1	50	24	(E)-$C_6H_5CH{=}CHCH_3$, 34 (Z)-$C_6H_5CH{=}CHCH_3$, 3 $C_6H_5CH_2CH{=}CH_2$, 23 $C_6H_5CH{=}CHCH_2OCHO$, 28
389-87-7	1-Br, 4-I		5% Pd/C	0.2	100	1.5	C_6H_5Br, 58
619-44-3	1-CO_2CH_3, 4-I		5% Pd/C	0.2	100	48	$C_6H_5CO_2CH_3$, 91

[a] Reactions were carried out with 20 mmol of organic halide, 22 mmol of HCO_2H, and 28.5 mmol of Et_3N, except as indicated. [b] GLC yield except where indicated. [c] Reaction was carried out with 50 mmol of organic halide, 220 mmol of HCO_2H, and 285 mmol of Et_3N. [d] Reactions were carried out with 10 mmol of organic halide, 22 mmol of HCO_2H, and 28.5 mL of Et_3N. [e] Isolated yield. [f] P(o-tol)$_3$ = tri-o-tolylphosphine.

methyl 4-chlorocinnamate. Methyl 4-bromocinnamate could be reduced selectively in 93% yield, however. When compared under identical conditions, 4-chlorobenzonitrile reduced considerably more rapidly than 4-bromobenzonitrile. Reduction with the soluble catalysts was somewhat dependent upon the phosphine groups present in the catalyst. At 50 °C, m-bromonitrobenzene in 1.5 h gave an 81% yield of nitrobenzene with only 2% aniline formed, employing 1 mol % of 2:1 tris(o-tolylphosphine)–palladium acetate as catalyst. Less selectivity was seen with either triphenylphosphine or tris(2,5-diisopropylphenylphosphine) catalysts or with 5% palladium on charcoal alone. o-Bromonitrobenzene reduced in 78% yield to nitrobenzene even with the 5% palladium on charcoal catalyst. The use of 5% platinum on charcoal led to the exclusive formation of o-bromoaniline in 94% yield.

Methyl 4-chlorobenzoate was reduced with dideuterioformic acid to give a 90% yield of pure methyl 4-deuteriobenzoate. A related deuteration has been reported by Bosin,[3] but stoi-

Table II. Reductions of Aromatic Nitro Compounds with Triethylammonium Formate[a]

Registry no.	Substituted Benzene (50 mmol)	Catalyst, 0.2 mol %	Mol of Et_3N	Mol of HCO_2H	Time, h	Product (substituted benzene), % yield
98-95-3	NO_2	5% Pd/C[b]	0.214	0.165	2.3	NH_2, 100
619-50-1	1-CO_2CH_3, 4-NO_2	5% Pd/C[b]	0.214	0.165	2	1-CO_2CH_3, 4NH_2, 97[c]
91-23-6	1-OCH_3, 2-NO_2	5% Pd/C	0.214	0.165	4	1-OCH_3, 2-NH_2, 94[c]
100-17-4	1-OCH_3, 4-NO_2	5% Pd/C	0.214	0.165	4	1-OCH_3, 4-NH_2, 89
104-04-1	1-$NHCOCH_3$, 4-NO_2	5% Pd/C	0.214	0.165	4.5	1-$NHCOCH_3$, 4-NH_2, 85[c]
	1-NO_2, 2-Br[d]	5% Pt/C	0.039	0.033	1.3	1-NH_2, 2-Br, 94[c]
612-41-9	1-CH=$CHCO_2H$, 2-NO_2	5% Pd/C	0.285	0.220	5.3	 , 72[c]
555-68-0	1-CH=$CHCO_2CH_3$, 3-NO_2	5% Pd/C	0.194	0.150	3.5	1-CH=$CHCO_2CH_3$, 3-NH_2 1-$(CH_2)_2CO_2CH_3$ } ~75
3740-52-1	1-CO_2H, 2-NO_2	5% Pd/C	0.214	0.165	23	 , 75[e]
577-59-3	1-$COCH_3$, 2-NO_2	5% Pd/C	0.357	0.275	25	1-CH_2CH_3, 2-NH_2, 50

[a] Carried out at reflux temperature. [b] 0.1 mol % catalyst used. [c] Yield of pure isolated product. [d] 10 mmol used. [e] After sublimation.

chiometric quantities of palladium chloride and sodium borodeuteride in methanol-d_1 were required.

4-Bromo- and 2,4-dibromoaniline reduced readily also. Attempts to selectively reduce the dibromoaniline were not promising. There was a slight preference for reduction of the 4-bromo group rather than the 2-, but the difference was not large enough to be preparatively useful.

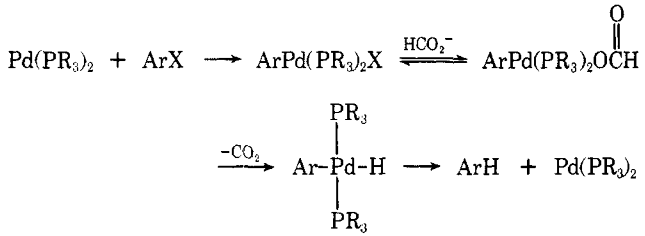
2-Bromobenzaldehyde does not reduce selectively. A mixture of benzaldehyde (43%), benzyl alcohol (10%), and toluene (10%) was obtained with 1 equiv of reducing agent. Both β-bromostyrene and cinnamyl chloride gave mixtures of products under the usual conditions. The bromostyrene gave styrene and ethylbenzene, while the cinnamyl chloride produced three isomeric phenylpropenes and cinnamyl formate. The reaction has been applied to allyl derivatives previously in the absence of amine.[4] Cyclohexyl chloride did not reduce in 26 h at 100 °C with the palladium on charcoal catalyst. Aryl iodides also were reduced by the reagent. 4-Nitroiodobenzene reacted very slowly, but 4-bromoiodobenzene gave bromobenzene in 58% yield and methyl 4-iodobenzoate gave methyl benzoate.

No reduction of nitrobenzene or bromobenzene takes place with formic acid and the catalyst without the addition of excess tertiary amine.

The reduced products were easily isolated from these reaction mixtures by diluting with ether to precipitate the triethylamine hydrohalide, filtering, and distilling the filtrate.

The results suggest a mechanism of reaction involving oxidative addition of the aryl halide to a palladium(0)–phosphine catalyst followed by displacement of halide on the metal by formate ion. Decomposition of the formate group by a deinsertion of carbon dioxide and reductive elimination of the hydrocarbon would explain the reaction.

$$(Pd(PR_3)_2(OAc)_2 + HCO_2H \longrightarrow Pd(PR_3)_2 + CO_2 + 2HOAc)$$

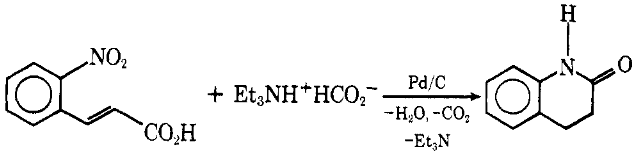


$$Pd(PR_3)_2 + ArX \longrightarrow ArPd(PR_3)_2X \xrightleftharpoons{HCO_2^-} ArPd(PR_3)_2O\overset{\overset{O}{\|}}{C}H$$

$$\xrightarrow{-CO_2} Ar\text{-}\underset{\underset{PR_3}{|}}{\overset{\overset{PR_3}{|}}{Pd}}\text{-}H \longrightarrow ArH + Pd(PR_3)_2$$

The fact that chlorobenzene does not react with tetrakis(triphenylphosphinepalladium(0)) below about ~120 °C[5] is evidence against this mechanism. However, the triphenylphosphine present no doubt strongly inhibits the oxidative addition of chlorobenzene in that reaction compared with the reduction reactions in the absence of the phosphine or with only 2 equiv per palladium.

Aromatic Nitro Compounds. The nitro group is readily reduced in very good yields with 3 mol of triethylammonium formate with palladium on charcoal as catalyst at the boiling temperature of the reaction mixture (~90–100 °C). Results are summarized in Table II. We have generally used about a 10% excess of formic acid and a 30% excess of triethylamine. The reduction is very slow or does not proceed at all without a large excess of the amine. The best procedure is to add the formic acid slowly to a boiling solution of the nitro compound in the amine. The excess amine formate remains as a separate lower phase at the end of the reaction. The products are easily isolated by adding methylene chloride to dissolve the amine salt and then filtering from the catalyst and concentrating the filtrate. The triethylamine salt is readily removed by distillation under reduced pressure and the crude product remaining can be purified by distillation or recrystallization. We have used 0.2 mol % of 5% palladium on charcoal as catalyst generally, but, of course, the reaction rates can be increased if more catalyst is used. The triethylammonium formate–palladium reducing system does not reduce methyl cinnamate significantly under the usual reaction conditions. However, o-nitrocinnamic acid is reduced by the reagent to the saturated lactam in 72% yield. Reduction of o-nitrophenylacetic acid by the reagent yields a 1:1 mixture of the lactam and o-aminophenylacetic acid. Sublimation of the product mixture produces the lactam in 75% yield. With sufficient reducing agent o-nitroacetophenone produces o-ethylaniline in 50% yield. Presumably, condensation reactions are also occurring to reduce the yield in the last reaction. Azobenzene was not reduced under our usual conditions.



The palladium–amine formate reagent is a very convenient combination for selective laboratory reductions of aryl halides and nitro compounds.[6] Attempts to reduce other functional groups with various catalysts using the amine formate reagent 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