

# Communications

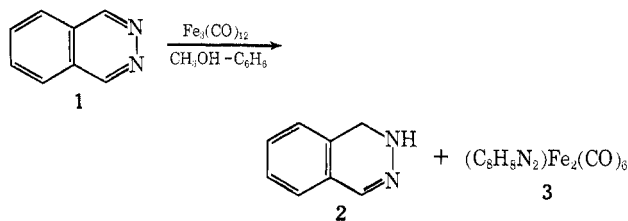
See Editorial, *J. Org. Chem.*, **37**, No. 24, 4A (1972)

## A Convenient Reduction of the Carbon-Nitrogen Double Bond

**Summary:** The carbon-nitrogen double bond can be conveniently reduced by reaction of the appropriate organic (or organometallic) compound with a mixture of triiron dodecacarbonyl [ $\text{Fe}_3(\text{CO})_{12}$ ] and methanol in benzene.

**Sir:** Recent interest in the use of hydridoiron carbonyl complexes as reagents for hydrogenating  $\alpha,\beta$ -unsaturated carbonyl compounds<sup>1</sup> and for preparing aromatic amines from nitro compounds<sup>2</sup> prompts the author to communicate a new, simple method for reducing a carbon-nitrogen double bond.

Treatment of phthalazine (1) with  $\text{Fe}_3(\text{CO})_{12}$  in refluxing methanol-benzene for 12-16 hr {conditions which generate the hydridoundecacarbonyltriferrate anion [ $\text{HFe}_3(\text{CO})_{11}^-$ ]}, followed by chromatography on Florisil, gave 1,2-dihydrophthalazine (2, mp 83.5-85.0°) in 54% yield and a small amount of complex 3. Controlled potential electrolysis is the only other reported way for effecting direct conversion of 1 to 2.<sup>3</sup>



The generality of this hydridoiron carbonyl reduction was demonstrated by similar reaction of  $\text{Fe}_3(\text{CO})_{12}-\text{CH}_3\text{OH}$  with a number of Schiff bases bearing various substituents. The results listed in Table I indicate

TABLE I

Reactant 1	Product <sup>a</sup> 2	Yield, %
<i>N</i> -( <i>p</i> -Methoxybenzylidene)aniline	<i>p</i> -Methoxy- <i>N</i> -phenylbenzylamine	54
<i>p</i> - <i>n</i> -Butyl- <i>N</i> -( <i>p</i> -methoxybenzylidene)aniline	<i>p</i> -Methoxy- <i>N</i> -( <i>p</i> - <i>n</i> -butylphenyl)benzylamine	62
<i>N</i> -Benzylideneaniline	<i>N</i> -Benzylaniline	88
<i>p</i> -Hexyloxy- <i>N</i> -(ferrocenylidene)aniline	<i>p</i> -Hexyloxy- <i>N</i> -phenylferrocenylmethylamine	83
<i>N</i> -( <i>p</i> -carbomethoxybenzylidene)aniline	<i>p</i> -Carbomethoxy- <i>N</i> -phenylbenzylamine	71
<i>N</i> -Isopropylidene- <i>n</i> -butylamine	Isopropyl- <i>n</i> -butylamine	47

<sup>a</sup> Known products were identified by comparison of melting points and spectral data with those reported in the literature. Satisfactory analytical data was obtained for new compounds.

that this transformation occurs in reasonable-very good yields and hence shows promise as a synthetically useful organic reaction.

The following procedure is typical. A mixture of  $\text{Fe}_3(\text{CO})_{12}$  (2.67 g), dry methanol (2.7 ml), and dry

benzene (35 ml) was refluxed with stirring under nitrogen for 2.25 hr. *p*-Hexyloxy-*N*-(ferrocenylidene)aniline (1.56 g, 4.0 mmol), dissolved in benzene (10 ml), was added to the hydridoiron carbonyl solution and the resulting mixture was refluxed for 15 hr. The solution was cooled and filtered, and the filtrate was evaporated *in vacuo*. The residue from evaporation was chromatographed on Florisil to give *p*-hexyloxy-*N*-phenylferrocenylmethylamine on elution with petroleum ether (bp 38-50°).

**Acknowledgments** are made to the Petroleum Research Fund, administered by the American Chemical Society, and to the Research Foundation of the State of New York, for support of this research. The author is indebted to Dr. L. Verbit for providing generous quantities of *p*-hexyloxy-*N*-(ferrocenylidene)aniline and *p*-*n*-butyl-*N*-(*p*-methoxybenzylidene)aniline.

DEPARTMENT OF CHEMISTRY  
STATE UNIVERSITY OF NEW YORK  
AT BINGHAMTON  
BINGHAMTON, NEW YORK 13901

HOWARD ALPER

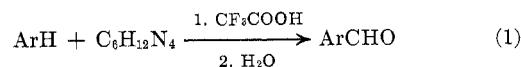
RECEIVED SEPTEMBER 6, 1972

## Formylation of Aromatic Compounds with Hexamethylenetetramine and Trifluoroacetic Acid

**Summary:** A variety of aromatic compounds have been converted to aldehydes *via* a facile formylation process employing hexamethylenetetramine and trifluoroacetic acid.

**Sir:** In the Duff reaction,<sup>1-3</sup> hexamethylenetetramine is employed, usually with glyceroboric acid, to convert highly activated aromatic compounds to their formyl derivatives. The process is quite limited in scope, having been most widely used in the conversion of phenols to *o*-hydroxybenzaldehyde derivatives. The required conditions are rigorous, and the yields are generally low.

When the hexamethylenetetramine is used in conjunction with trifluoroacetic acid, a variety of aromatic compounds, including simple hydrocarbons, can be converted to imine products which are transformed to the aryl aldehydes on hydrolysis (eq 1). The required



conditions are mild, and good yields of pure products can be easily isolated. A high order of para regioselectivity is exhibited.

Thus, a mixture of 12.2 g of 2,6-xyleneol (100 mmol),

(1) R. Noyori, I. Umeda, and T. Ishigami, *J. Org. Chem.*, **37**, 1542 (1972).  
(2) J. M. Landesberg, L. Katz, and C. Olsen, *ibid.*, **37**, 930 (1972).  
(3) H. Lund and E. T. Jensen, *Acta Chem. Scand.*, **24**, 1867 (1970).

(1) J. C. Duff, *J. Chem. Soc.*, 547 (1941).  
(2) C. F. H. Allen and G. W. Leubner, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 866.  
(3) L. N. Ferguson, *Chem. Rev.*, **38**, 230 (1946).

14.0 g of hexamethylenetetramine (100 mmol), and 150 ml of trifluoroacetic acid was heated at reflux (83–90°) for 12 hr. The products were concentrated and combined with 600 ml of ice water; the resultant mixture was stirred for 15 min, made basic with Na<sub>2</sub>CO<sub>3</sub>, and extracted with ether. Evaporation of the ether solution left a yellow solid which was recrystallized from chloroform–pentane to afford 14.3 g (95% yield) of 3,5-dimethyl-4-hydroxybenzaldehyde, mp 111–112.5° (lit.<sup>4</sup> mp 113–114°).

The data for a number of these transformations are summarized in Table I.

TABLE I  
FORMYLATION OF AROMATICS BY HEXAMETHYLENETETRAMINE  
IN TRIFLUOROACETIC ACID

Aromatic	Hexamethylene- tetramine: aromatic	Product <sup>a</sup> (% yield)
<i>tert</i> -Butylbenzene	1:1	<i>p</i> - <i>tert</i> -Butylbenzaldehyde (75)
<i>p</i> -Xylene	1:1	2,4-Dimethylbenzaldehyde (55)
Toluene	1:1	<i>p</i> -Tolualdehyde (50) <i>o</i> -Tolualdehyde (11)
Benzene <sup>b</sup>	1:4	Benzaldehyde (32)
2,6-Dimethylanisole	2:1	3,5-Dimethyl-4-methoxybenzaldehyde (74)
Benzodioxane(1,4)	1:1	4'-Formylbenzodioxane(1,4) (37), 3'-formylbenzodioxane(1,4) (2)
Diphenyl ether	2:1	<i>p</i> -Phenoxybenzaldehyde (29), 4,4'-diformyldiphenyl ether (25)
2,6-Di- <i>tert</i> -butylphenol	1:1	3,5-Di( <i>tert</i> -butyl)-4-hydroxybenzaldehyde (60)
2,6-Xylenol	1:1	3,5-Dimethyl-4-hydroxybenzaldehyde (95)

<sup>a</sup> Isolated materials exhibiting correct physical and spectroscopic properties; isomer compositions were by <sup>1</sup>H nmr spectroscopy. <sup>b</sup> Sealed tube, 125–150°.

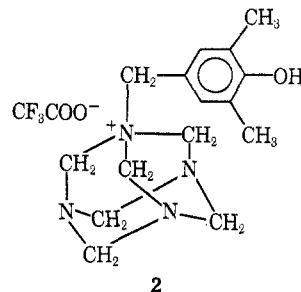
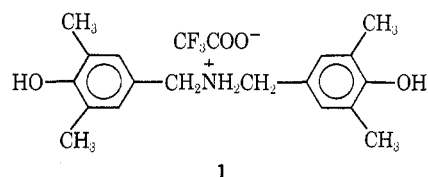
Methylimine derivatives are immediate precursors of the aldehydes. When the reaction products derived from toluene were subjected to rapid hydrolytic work-up, the *p*- and *o*-toluimines CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CH=NCH<sub>3</sub> were obtained in predominance to the carbonyl compounds. Whether such products are formed by rearrangement of the methyleneimines ArCH<sub>2</sub>N=CH<sub>2</sub> or arise in exchange reactions involving methylamine remains to be determined.

Other kinds of intermediates are isolable when both heating and hydrolysis are avoided. Thus, the 2,6-xylenol–hexamethylenetetramine–trifluoroacetic acid system when kept below 30° for 3 hr yielded a complex mixture from which the dibenzylammonium salt<sup>5</sup> **1** (41%) and the hexaminium salt<sup>6</sup> **2** (15%) were isolated

(4) V. V. Ershov and G. A. Ziobina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2235 (1964).

(5) Bis(4-hydroxy-3,5-dimethylbenzyl)ammonium trifluoroacetate (**1**): mp 193–195°; <sup>1</sup>H nmr (DMSO-*d*<sub>6</sub>) δ 2.30 (s, 12), 4.08 (s, 4), 7.26 (s, 4), 9.18 (br, 2), 9.80 (br, 2); Fourier transform <sup>13</sup>C nmr (DMSO-*d*<sub>6</sub>, from TMS) 153.2, 129.4, 123.8, 121.3, 48.9, 15.7 ppm. *Anal.* Calcd for C<sub>26</sub>H<sub>24</sub>F<sub>3</sub>O<sub>4</sub>N: C, 60.14; H, 6.06; F, 14.24; N, 3.51. Found: C, 60.26; H, 6.14; F, 14.36; N, 3.51.

(6) 4-Hydroxy-3,5-dimethylbenzylhexamethylenetetrammonium trifluoroacetate (**2**): mp 154° dec; <sup>1</sup>H nmr (DMSO-*d*<sub>6</sub>) δ 2.27 (s, 6), 3.55 (br, 2) 4.05 (s, 2), 4.67 (s, 6), 5.20 (s, 6), 7.25 (s, 2), 9.20 (br, 1); Fourier transform <sup>13</sup>C nmr (DMSO-*d*<sub>6</sub>, from TMS) 155.4, 132.4, 125.1, 115.6, 77.7, 70.2, 59.6, 16.7 ppm. *Anal.* Calcd for C<sub>18</sub>H<sub>28</sub>N<sub>6</sub>O<sub>3</sub>F<sub>3</sub>: C, 51.06; H, 6.16; N, 14.89; F, 15.14. Found: C, 51.27; H, 6.03; N, 14.80; F, 15.30.



after evaporation of the acid and fractional crystallization of the residue from acetonitrile–ether. No unalkylated 2,6-xylenol was recovered.

The formation of **2** makes evident the relationship of this process to the Sommelet<sup>7</sup> and Delépine<sup>8</sup> reactions, both of which are based on transformation of *N*-benzyl derivatives of hexamethylenetetramine. Experiments with the trifluoroacetic acid system aimed at an illumination of these mechanistically obscure<sup>9</sup> facets of hexamethylenetetramine chemistry are in progress.

(7) S. J. Angyal, *Org. React.*, **8**, 197 (1954).

(8) M. Delépine, *Bull. Soc. Chim. Fr.*, **13**, 358 (1895).

(9) Methyleneimmonium<sup>10</sup> and methylenebenzylimmonium<sup>11</sup> ions have been invoked as the oxidizing agents in the Sommelet reaction, in which aldehydes are produced on hydrolysis of hexaminium salts. Both species are likely alkylating agents in the process reported here. The seemingly high sensitivity to steric effects of substituents on the aromatic nucleus does suggest, however, that the alkylation involves bulkier electrophile(s), possibly ones more immediately derived from hexamethylenetetramine.

(10) H. R. Snyder and J. R. Demuth, *J. Amer. Chem. Soc.*, **78**, 1981 (1956).

(11) S. J. Angyal, *et al.*, *J. Chem. Soc.*, 1742 (1953).

CHEMICAL LABORATORY  
GENERAL ELECTRIC RESEARCH  
AND DEVELOPMENT CENTER  
SCHENECTADY, NEW YORK 12301

WILLIAM E. SMITH

RECEIVED SEPTEMBER 20, 1972

### Facile Thermal Rearrangements of Allyl Selenides and Diselenides. [1,3] and [2,3] Shifts

*Summary:* Allyl selenides and allyl diselenides undergo [1,3] and [2,3] shifts, respectively.

*Sir:* We wish to report the selenoallylic rearrangement<sup>1,2</sup> of **1** to **2** and the [2,3] sigmatropic rearrangement–reduction<sup>3</sup> of **3** (M = Se) to **5** (M = Se) (eq 1 and 2). The secondary allyl selenide **1** (X = Ph)

(1) The analogous thioallylic rearrangement has been studied by H. Kwart and N. Johnson, *J. Amer. Chem. Soc.*, **92**, 6064 (1970).

(2) A related [1,3] silylallylic rearrangement has also been described by H. Kwart and J. Slutsky, *ibid.*, **94**, 2515 (1972).

(3) The analogous rearrangement–reduction of allylic disulfides has been studied by G. Höfle and J. E. Baldwin, *ibid.*, **93**, 6307 (1971); the synthesis of geranyl linalyl sulfide (**5**, M = S), *via* this sequence, the exact analog of reaction 2, was reported by G. M. Blackburn and W. D. Ollis, *Chem. Commun.*, 1261 (1968).