[CONTRIBUTION NO. 163 FROM JACKSON LABORATORY, E. I. DU PONT DE NEMOURS & COMPANY]

# Hydrogen Fluoride as a Condensing Agent. IV. Hydrogen Fluoride as a Solvent for Catalytic Reduction[1]

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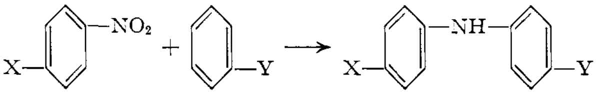
Substituted diphenylamines, aminobiphenyls and N-alkylanilines are obtained when certain aromatic and aliphatic nitro compounds are catalytically hydrogenated in hydrogen fluoride and in the presence of reactive compounds, especially phenols.

Hydrogen fluoride[2] forms a suitable solvent in which catalytic hydrogenations can be carried out. Its well-known condensing action[3] becomes a dominant factor when nitro compounds are hydrogenated by themselves or in the presence of second reactive components. Thus diphenylamines are obtained when aromatic nitro bodies substituted in the *para* position are hydrogenated in the presence of reactive second components.



$X = OCH_3, OC_2H_5, CH_3, C_2H_5, C_6H_5$

$Y = OH, OCH_3, NH_2, NHC_6H_5$

In a typical condensation, 4-hydroxy-4′-methoxydiphenylamine was obtained in a 66% yield when *p*-nitroanisole and phenol were hydrogenated in hydrogen fluoride at 50° and a pressure of 13 to 20 atmospheres.

Mixtures of diphenylamines and aminobiphenyls are obtained from nitro bodies not substituted in the *para* position to the nitro groups. Aliphatic nitro compounds react in a similar manner to give N-alkylanilines. The condensing action of hydrogen fluoride is also apparent when naphthalene is hydrogenated to tetrahydronaphthalene where a small amount of a dimer of a hydrogenated naphthalene is formed.

Nitro compounds substituted in the *para* position with halogens and amino, or carboxy groups, or polynitrobenzenes or nitroanthraquinones appear not to condense with phenol (the most reactive second component) but mainly are reduced to the normally expected amines.

*o*-Nitrodiphenyl condenses with itself with surprising ease to form a diaminoquaterphenyl. Based on a limited amount of evidence we conclude that this compound is a diamino derivative of 2,2′-diphenylbiphenyl with the exact position of the amino groups uncertain. Deamination by the alcoholic reduction of the tetraazo compound[4] gives a hydrocarbon melting from 115–122° which closely corresponds to the melting point given for 2,2′-diphenylbiphenyl (119°). The melting points reported for 3,3′-diphenylbiphenyl and 4,4′-diphenylbiphenyl are 86 and 310°, respectively.[5] The diaminoquaterphenyl is not the well-known 3,3′-diphenylbenzidine (m.p. 152°) which on deamination would have given the 3,3′-diphenylbiphenyl. It has been observed that the 2′-position in *o*-aminobiphenyl is the reactive position as illustrated by the ease with which carbazole is formed upon the oxidation of *o*-aminobiphenyl with nitro bodies.[6] A condensation in that position would lead to the formation of a diamino derivative of 2,2′-diphenylbiphenyl.

The reaction mechanism of the typical *p*-nitroanisole–phenol condensation remains uncertain. According to Bamberger,[7] hydroxylamine condenses in moderately strong sulfuric acid with phenol to give hydroxydiphenylamine. We were unable to detect diphenylamines when *p*-tolylhydroxylamine and phenol were allowed to react in hydrogen fluoride. Essentially only aniline and 1-aminoanthraquinone are obtained when nitrobenzene or nitroanthraquinone is hydrogenated in hydrogen fluoride under conditions which form *p*-aminophenol or 1-amino-4-hydroxyanthraquinone in sulfuric acid.

An azobenzene appears to be an unlikely intermediate because 4,4′-dimethoxyazobenzene is reduced with simultaneous rearrangement to form benzidine. It is further made unlikely that azobenzene can be the responsible intermediate because only aniline and traces of *p*-aminophenol but no benzidine are obtained when nitrobenzene alone is hydrogenated in hydrogen fluoride. 4-Amino-4′-hydroxybiphenyl and traces of hydroxydiphenylamine are obtained when nitrobenzene is hydrogenated in the presence of phenol.

4,4′-Dimethoxyazoxybenzene condenses with two moles of phenol without reducing or rearranging to a diphenylamine. Nitrosophenols react with phenols to give highly colored products which cannot be hydrogenated.

## Experimental

**Preparation of Hydrogenation Grade Hydrogen Fluoride.**—The commercial grade of hydrogen fluoride is not suitable as a solvent because of its content of sulfur dioxide. It is readily purified by an oxidative treatment as follows.

Hydrogen fluoride (16.5 kg.) containing 0.13% sulfur dioxide (determined iodometrically) and manganese dioxide (900 g.) were agitated in a steel autoclave for eight hours at 80° (maximum observed pressure 6.5 atmospheres). The hydrogen fluoride was then distilled into small cylinders (recovery 15.75 kg. hydrogen fluoride free of sulfur dioxide) but the first 200 g. of distillate was discarded because it still contained an impurity other than sulfur dioxide which slightly retarded hydrogenation. Hydrogen fluoride heated with manganese dioxide as above was frequently used for condensations without distilling it from the manganese dioxide without in any way changing the results. Potassium chlorate was an equally suitable oxidizing agent.

**4-Hydroxy-4′-methoxydiphenylamine.**—A steel shaker tube (volume 500 cc.) containing *p*-nitroanisole (115 g.), phenol (94 g.) and palladium catalyst (5 g.) (3% on Nu-

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[1] For the previous paper of this series see V. Weinmayr, THIS JOURNAL, **72**, 918 (1950).

[2] Hydrogen fluoride used in this work was anhydrous unless otherwise stated.

[3] W. S. Calcott, J. M. Tinker and V. Weinmayr, THIS JOURNAL, **61**, 949 (1939); D. I. Randell and S. Archer, *ibid.*, **61**, 1795 (1939).

[4] G. H. Coleman and W. F. Talbot, *Org. Syntheses*, **13**, 96 (1933).

[5] S. Th. Bowden, *J. Chem. Soc.*, 1111 (1931).

[6] V. Weinmayr, U. S. Patent 2,351,171 (1944).

[7] E. Bamberger, *Ann.*, **390**, 131 (1912).

TABLE I

| Starting materials | | Temp., °C. | Reaction products | Yield, %[a] | M.p., °C. | Analyses, % | |
|---|---|---|---|---|---|---|---|
| | | | | | | Calcd. | Found |
| *p*-Nitroanisole | Anisole[b] | 50–90 | 4,4′-Dimethoxy-d.p.a. | 21 | 100 | [8] | |
| *p*-Nitroanisole | Aniline[c] | 25[d] | 4-Amino-4′-methoxy-d.p.a. | 12 | 99 | [9] | |
| *p*-Nitroanisole | d.p.a. | 40 | N-*p*-Methoxyphenyl-N′-phenyl-*p*-phenylenediamine | 13.8[e] | 126 | N, 9.66<br>M.W., 290 | N, 9.67<br>M.W., 312 |
| *p*-Nitrophenetole | Phenol | 50 | 4-Ethoxy-4′-hydroxy-d.p.a. | 50 | 83 | C, 73.50<br>H, 6.59<br>N, 6.11 | C, 73.29<br>H, 6.15<br>N, 5.90 |
| *p*-Nitrotoluene | Phenol | 100 | 4-Hydroxy-4′-methyl-d.p.a. | 30 | 121 | [10] | |
| *p*-Nitrobiphenyl | Phenol | 60 | 4-Hydroxy-4′-phenyl-d.p.a.[f] | 82 | 149 | N, 5.37 | N, 5.52 |
| *p*-Nitrobiphenyl | Anisole | 60 | 4-Methoxy-4′-phenyl-d.p.a. | 36 | 205 | N, 4.49<br>Cl, 11.39 | N, 4.42<br>Cl, 11.30 |
| Nitromethane | Phenol | 95 | N-Methyl-*p*-aminophenol | 6 | 88 | [11] | |
| 1-Nitro-*n*-propane | Phenol | 80 | N-*n*-Propyl-*p*-aminophenol | 6 | 85 | C, 71.4<br>H, 8.61<br>N, 9.2 | C, 70.99<br>H, 8.4<br>N, 8.8 |
| Nitrobenzene | Phenol | 100 | 4-Amino-4′-hydroxybiphenyl and traces of a hydroxy-d.p.a. | 14 | 270 | [12] | |
| *o*-Nitrobiphenyl | Phenol | 50 | 2-Amino-x′-(*p*-hydroxyphenyl)-biphenyl | 41 | 162[h] | C, 82.8<br>H, 5.75<br>N, 5.3 | C, 83.03<br>H, 5.93<br>N, 5.15 |
| | | | | | 195[g] | Cl, 11.93<br>N, 4.71 | Cl, 11.27<br>N, 4.66 |
| *o*-Nitroethylbenzene | Phenol | 40 | x-Amino-x-ethyl-x′-hydroxy biphenyl | 40 | 150[i] | C. 78.9<br>H, 7.05<br>N, 6.57<br>M.W., 213 | C, 78.90<br>H, 7.10<br>N, 6.40<br>M.W., 212 |

[a] Based on nitrobody charged. [b] About 0.4% boric acid had been added to the hydrogen fluoride. [c] This reaction was carried out in methanol using 1.2 moles of hydrogen fluoride per mole of aniline. [d] At a pressure of 3.5 atmospheres. [e] 71.4% on d.p.a. consumed. [f] Did not form a hydrofluoride in dilute hydrofluoric acid. [g] Purified and analyzed as the hydrochloride. [h] Crystals as obtained when the fraction distilling from 225–265° (2 mm.) was agitated in boiling carbon tetrachloride. [i] The hydrochloride melted at 166–171°; calcd.: $NH_2$, 6.42. Found: $NH_2$, 6.7.

char) was cooled with Dry Ice, and hydrogen fluoride (120 g.) was added. (If hydrogen fluoride treated with manganese dioxide, but not distilled, was used then the phenol, *p*-nitroanisole and catalyst were added to the cooled hydrogen fluoride). Hydrogenation required about two hours at 40 to 45° at a pressure of 13–20 atmospheres. The cooled mixture was poured into water (500 cc.), the catalyst was filtered off (it was reusable as recovered), the filtrate was diluted to 800 cc. and the acidity was reduced to slightly acid to congo red with 28% ammonia (175 cc.). 4-Hydroxy-4′-methoxydiphenylamine precipitated (106 g.) as an oil which quickly solidified (m.p. 108°). *p*-Anisidine was recovered by making the filtrate from the 4-hydroxy-4′-methoxydiphenylamine alkaline. The yield of 4-hydroxy-4′-methoxydiphenylamine was 66% based on *p*-nitroaniline or 100% based on the *p*-nitroaniline consumed in the condensation.

*Anal.* Calcd. for $C_{13}H_{13}NO_2$: N, 6.58. Found: N, 6.50.

Temperatures above 100° as required for poorly purified hydrogen fluoride caused demethylation to a considerable extent as indicated by the formation of 4,4′-dihydroxydiphenylamine.

The condensations summarized in Table I were made by essentially the identical procedure. The abbreviation d.p.a. is used for diphenylamine. The isolation of the compounds varied depending upon the solubility of the product formed but was obvious in all cases.

**The Hydrogenation of *p*-Nitrobiphenyl.**—*o*-Nitrobiphenyl (300 g.) was hydrogenated in hydrogen fluoride (250 g.) at 45° at a pressure of 20 atmospheres using palladium (10 g.) as the catalyst. Upon the usual dilution and partial neutralization, a tarry white precipitate was formed which was washed with warm water, dissolved in benzene and distilled. *o*-Aminobiphenyl (52 g.) was obtained from the fraction distilling from 125 to 200° (2 mm.). Diaminoquaterphenyl (140 g. 55%) distilled from 300 to 340° (2–3 mm.) leaving a residue of 45 g. The crude distillate was redistilled and the fraction distilling from 300 to 320° (2 mm.) (110 g.) was separated. This product formed a glassy mass which melted at about 70 to 80°. It could be heated to the boil at atmospheric pressure without decomposition. Two crystallizations from 95% ethanol (25 g., 900 and 750 cc.) gave a pure compound analyzing as a diaminoquaterphenyl melting at 144°. The product was free of diphenylamine type compounds.

*Anal.* Calcd. for $C_{24}H_{20}N_2$: C, 85.7; H, 5.85; N, 8.34; $NH_2$, 9.52; mol. wt., 336. Found: C, 85.56; H, 5.77; N, 8.44; $NH_2$, 9.52; mol. wt., 317.

The diaminoquaterphenyl changed from the glassy form to the crystalline form by slurrying it with cold alcohol. The crystals changed again to a glassy form when melted. The product was not the known 3,3′-diphenylbenzidine (m.p. 152°) because the mixed melting point showed a strong depression. The distillation residue (100 g.) was purified by dissolving a sample at room temperature in water (350 cc.) containing concentrated sulfuric acid (167 g.), clarifying the solution, making it alkaline with 40% sodium hydroxide (320 cc.) and heating the reaction mass to 80° to change the precipitate to a readily filterable crystalline form. The product thus obtained (83 g.) melted from 128 to 160° and could not be crystallized. Based on the analysis it was a trimer of *o*-aminobiphenyl, a triaminosexiphenyl.

*Anal.* Calcd. for $C_{36}H_{28}N_3$: N, 8.33; $NH_2$, 9.52; mol. wt., 502. Found: N, 8.09; $NH_2$, 8.8; mol. wt., 563.

The diaminoquaterphenyl (5 g.) gave a diacetyl derivative (5.8 g.) quickly in acetic anhydride melting at 198° or after crystallization from 90% ethanol (100 cc.) melting at 211°. The diacetyl-3,3′-diphenylbenzidine melted at 251°.

*Anal.* Calcd. for $C_{28}H_{24}N_2O_4$: C, 80.00; H, 5.71; N, 6.64. Found: C, 80.07; H, 5.69; N, 6.57.

The diaminoquaterphenyl did not ring close to a carbazole when heated in 25% sulfuric acid to 210° for 15 hours. It was recovered unchanged.

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(8) H. Wieland, *Ber.*, **41**, 3493 (1908).

(9) P. Jacobson, M. Jaenicke and F. Meyer, *ibid.*, **29**, 2684 (1896).

(10) A. Hatschek and A. Zega, *J. prakt. Chem.*, [2] **33**, 224 (1886).

(11) R. N. Harger, THIS JOURNAL, **41**, 273 (1919).

(12) E. Taeuber, *Ber.*, **27**, 2629 (1894).

To deaminate diaminoquaterphenyl, solid sodium nitrite (30 g.) was added to a refluxing solution of diaminoquaterphenyl (34 g.) in 95% ethanol (400 cc.) and benzene (100 cc.), containing 96% sulfuric acid (55 g.). Refluxing was continued for 20 hours. The reaction mass was made alkaline with 28% ammonia and evaporated to a small volume on the steam-bath. The tarry product obtained was distilled and a pale yellow solid (11 g.) was obtained distilling from 280 to 300° (3 mm.). Upon crystallization from glacial acetic acid (9 g. in 50 cc.) crystals of presumably 2,2'-diphenylbiphenyl (4 g.) melting from 115 to 122° were obtained.

*Anal.* Calcd. for $C_{24}H_{18}$: C, 94.1; H, 5.9; mol. wt., 306. Found: C, 93.7; H, 6.1; mol. wt., 316.

**Hydrogenation of Naphthalene** (200 g.).—Naphthalene (200 g.) was hydrogenated slowly in the presence of hydrogen fluoride (127 g.) and platinum catalyst at 250° under a pressure of 200 atmospheres. Upon distillation tetrahydronaphthalene (172 g.) boiling range 198–209° was obtained. A small amount of a dimeric compound (8 g.) was obtained distilling from 180 to 186° (3 mm.) indicating some self condensation in the course of the hydrogenation.

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[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF OAK RIDGE NATIONAL LABORATORY]

# The Action of Aluminum Chloride on Ethyl-β-$C^{14}$-benzene[1a,b]

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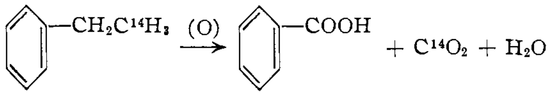
Attempted aluminum chloride-catalyzed isomerizations of the ethyl group of ethyl-β-$C^{14}$-benzene revealed no rearrangement under a variety of conditions. Ethyl-β-$C^{14}$-benzene was converted to diethylbenzene without chain rearrangement. Ethyl-β-$C^{14}$ chloride was condensed with benzene to give ethyl-β-$C^{14}$-benzene. Ethyl-β-$C^{14}$ chloride was almost completely isomerized by standing over aluminum chloride at room temperature for one hour. Possible mechanisms of the reactions are discussed.

The action of Lewis acids as isomerization catalysts on alkylaromatic hydrocarbons has been a subject of much study[3] because of the preparative and commercial value of these reactions and because of the light they throw on the mechanisms of carbonium ion processes. When an alkylaromatic compound is treated with an isomerization catalyst such as aluminum chloride, several reactions involving the aliphatic groups can occur separately or in combination: (1) cleavage between the nucleus and a chain,[4] (2) re-orientation of the alkyl groups (intramolecular[5] migrations), (3) intermolecular[5] transfers of the alkyl groups, (4) fragmentation of the alkyl groups and (5) internal rearrangements of the alkyl chains.

Although no case has been reported of chain rearrangement in the absence of a group transfer, disagreement exists as to the extent of chain rearrangement occurring during re-orientation or intermolecular transfer of alkyl groups.[6]

In the present investigation, the extent of isomerization of the ethyl-β-$C^{14}$ group under the influence of aluminum chloride was studied. Unlike the studies reported above which depended upon structure proof of the products, the degree of side chain isomerization in the present work was indicated by migration of radioactivity to the α-position in the alkyl group, complete isomerization being indicated by an equal distribution of $C^{14}$ between the two positions. The extent of this migration was determined by oxidation of the recovered, purified ethylbenzene to benzoic acid and determination of its radioactivity.



The determination of the extent of isomerization depended therefore in only the most elementary way upon structure proof of the compounds.

Preliminary experiments involved the treatment of ethyl-β-$C^{14}$-benzene in nitrobenzene solution at 0° with aluminum chloride for increasing periods of time. Oxidation[7] of recovered ethylbenzene with nitric acid gave *non-radioactive* *p*-nitrobenzoic acid in every case. Increasing the temperature to 72° and the reaction time to 6 hours also gave non-isomerized ethyl-β-$C^{14}$-benzene. Neither the addition of a small amount of water[8] nor of α-chloroethylbenzene[9] caused isomerization to occur.

Since the ameliorating influence of nitrobenzene on aluminum chloride catalysis is recognized[10] and since every reported case of side chain rearrangement has been in combination with either an inter-

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[1] (a) This paper is based upon work performed under Contract Number W-7405-eng 26 for the Atomic Energy Commission at the Oak Ridge National Laboratory. (b) Presented in part before the Division of Organic Chemistry at the Los Angeles, California, Meeting of The American Chemical Society, March 15–19, 1953.

[2] (a) Visiting member in the Research Participation program sponsored jointly by the Oak Ridge Institute of Nuclear Studies and Oak Ridge National Laboratory; permanent address, Department of Chemistry, University of Texas, Austin 12, Texas. Reprint requests should be addressed to this author. (b) Present address: Nuclear Instrument and Chemical Corporation, Chicago, Illinois.

[3] For discussions of these various isomerization reactions see: (a) G. Egloff, "Reactions of Pure Hydrocarbons," Reinhold Publ. Corp., New York, N. Y., 1937; (b) C. A. Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," Reinhold Publ. Corp., New York, N. Y., 1941; (c) L. I. Smith in Adams, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 370; (d) D. Nightingale, *Chem. Revs.*, **25**, 347 (1939).

[4] Although this is usually considered to be the reversal of the Friedel–Crafts condensation reaction, there is little evidence that a true thermodynamic equilibrium exists in the alkylation reaction. See A. W. Francis, *Chem. Revs.*, **43**, 257 (1948).

[5] The terms "intramolecular" and "intermolecular" as used here imply no insight into the actual mechanisms of the reactions. "Apparent" intermolecular and intramolecular migrations should be inferred.

[6] Discussed in reference 3d; for more recent work see R. E. Kinney and L. A. Hamilton, THIS JOURNAL, **76**, 786 (1954), and references given there.

[7] In the early experiments of this series, degradations of ethylbenzene were carried out by nitric acid oxidation (*cf.* ref. 11) to give *p*-nitrobenzoic acid. In the later experiments a more elegant procedure was developed which involved the bromination of the alkylaromatic compound, treatment with sodium acetate and oxidation with potassium permanganate. This procedure gave benzoic acid in excellent yields.

[8] *Cf.* R. C. Wackher and H. Pines, THIS JOURNAL, **68**, 1642 (1946).

[9] *Cf.* H. Pines, B. M. Abraham and V. N. Ipatieff, *ibid.*, **70**, 1742 (1948).

[10] C. A. Thomas, ref. 3b, p. 873.