Society. In addition, the financial assistance afforded by two graduate fellowships supported by the Ethyl Corporation is gratefully acknowledged.

Summary

1. Tri-α-naphthylboron has been prepared and found to possess somewhat different properties from the product previously described in the literature.

2. Addition compounds of tri-α-naphthylboron with ammonia, methylamine and dimethylamine were prepared. Trimethylamine did not combine with tri-α-naphthylboron.

3. The dissociation pressures of the addition compounds indicate a relative stability in the order, $NH_3 > CH_3NH_2 > (CH_3)_2NH > (CH_3)_3N$. This order is the theoretical limit predicted for a reference acid with an exceedingly high F-strain factor.

4. The addition compounds exist in two polymorphic modifications. It is suggested that these modifications result from restricted rotation of the α-naphthyl groups in the addition compounds.

5. The hypothesis is advanced that the discrepancies between the properties of the tri-α-naphthylboron prepared in the present investigation and the tri-α-naphthylboron previously described may be due to the existence of two rotation isomers of the compound.

LAFAYETTE, INDIANA RECEIVED NOVEMBER 28, 1947

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Reaction of Hydrazine Hydrate on Nitro-Compounds and a New Route to Synthetic Oestrogens

BY HUANG-MINLON[1]

The reduction of nitrobenzaldehydes by alkaline treatment of the corresponding hydrazones is not successful.[2] The modified Wolff–Kishner reduction[3] has now been found to proceed normally, with the exception that nitro-groups are reduced simultaneously. *p*- or *m*-toluidine can be obtained by this method from *p*- or *m*-nitrobenzaldehyde, respectively, in good yield. The reduction of nitro compounds by hydrazine has been observed,[4] although a sealed tube or an autoclave was usually employed. The reduction by hydrazine of *p*- or *m*-nitrotoluene to the corresponding toluidines required reaction in a sealed tube at 130° for four hours.[5] In the present investigation, the reduction was found to proceed readily in refluxing diethylene glycol. *m*-Nitrotoluene can be reduced to *m*-toluidine in good yield in this way; alkali does not affect the course of the reduction. *p*-Toluidine is obtained from *p*-nitrotoluene in good yield only if alkali is absent; in the presence of alkali a dimeric product, 4,4′-diaminostilbene (I), is also formed. The action of alkali alone on *p*-nitrotoluene is known to yield a mixture of condensation products from which 4,4′-dinitrodibenzyl (II) and 4,4′-dinitrostilbene could be isolated (IV).[6] The initial products of the alkali treatment are believed to be nitroso dimeric compounds.[7] Consequently the formation of 4,4′-diaminostilbene from *p*-nitrotoluene undoubtedly proceeds through a nitro or nitroso dimeric product by reduction. The same diamino product in better yield can also be obtained from *p*-nitrobenzyl chloride by treatment with alkali and hydrazine hydrate.

4,4′-Dinitrostilbene (II) is readily reduced by hydrazine hydrate in the presence of alkali to 4,4′-diaminostilbene (I) (80% yield). If alkali is absent, the double bond is also saturated, and 4,4′-diaminodibenzyl (III) can be obtained in this way in 70% yield. Alkali also affects the reduction of 4,4′-dinitrodibenzyl (IV): Treatment with hydrazine alone yields 4,4′-diaminodibenzyl (III) in almost quantitative yield, whereas treatment with hydrazine and alkali yields 4,4′-diaminostilbene (I) in more than 90% yield. Since neither 4,4′-diaminostilbene (I) nor 4,4′-diaminodibenzyl (III) is affected by treatment with hydrazine, with or without alkali, the electron-attracting *p*-nitro group thus activates the methylene or methine group for the donation or acceptance of hydrogen.

Substitution of sulfonic acid groups in the 2,2′-positions does not alter the reaction (see chart, $R = SO_3H$).

p-Nitrophenylacetic acid can be converted to a dinitrodicarboxylic acid (m. p. 264–266°) by treatment with alkali in the presence of an oxidizing agent. This acid when treated with hydrazine gives 4,4′-diaminodibenzyl; reduction and decarboxylation both take place.

p-Nitropropylbenzene[8] on heating with hydrazine hydrate and alkali gives *meso* and racemic 4,4′-diamino-α,β-diethyldibenzyl (V) along with *p*-aminopropylbenzene. Both of these isomeric diamino compounds have been used by Carlisle and Crowfoot[9] for X-ray measurements but the methods of preparation have not been mentioned.

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[1] On leave of absence from the National Research Institute of Chemistry, Academia Sinica.

[2] Lock and Stach, *Ber.*, **76**, 1252 (1943).

[3] Huang-Minlon, THIS JOURNAL, **68**, 2487 (1946).

[4] Curtius, *J. prakt. Chem.*, **76**, 238, 281 (1907).

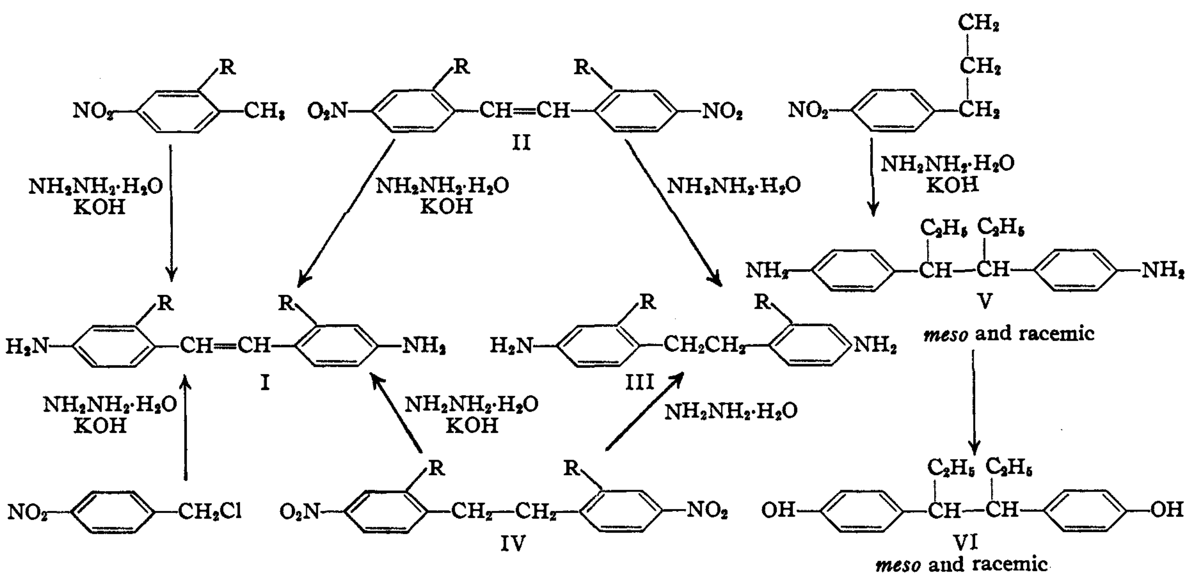
[5] Müller, *ibid.*, **111**, 278, 281 (1925).

[6] Fischer and Hepp, *Ber.*, **26**, 2231 (1893).

[7] Green. Davies and Horsfall, *J. Chem. Soc.*, **91**, 2076 (1907).

[8] Baddeley and Kenner. *J. Chem. Soc.*, 303 (1935); *cf.* Kondo and Uyeo. *Ber.*. **70**, 1087 (1937).

[9] Carlisle and Crowfoot, *J. Chem. Soc.*, 6 (1941).



(R = H or SO$_3$H)

Baker[10] prepared these compounds from p-propiopropionanilide in several steps.

The *meso* and racemic 4,4′-diamino-α,β-diethyldibenzyls on diazotization followed by heating with water give *meso*-4,4′-dihydroxy-α,β-diethyldibenzyl (VI) (hexestrol)[11] and its racemic isomer (isohexestrol),[12] respectively.

It is remarkable that p-nitrotoluene and 4-nitrotoluene-2-sulfonic acid on heating with hydrazine hydrate and alkali give the stilbene derivatives whereas p-nitropropylbenzene under the same conditions gives the isomeric dibenzyl derivatives.

Further work is in progress for the conversion of p-nitropropylbenzene into the corresponding dimeric nitro product to explore the possibilities of obtaining diethylstilbestrol and hexestrol by using hydrazine hydrate in the presence or absence of alkali, similar to the conversion of the dinitrostilbenes or dinitrodibenzyls into diaminostilbenes and diaminodibenzyls as shown in the chart, followed by diazotization.

I am indebted to Prof. L. F. Fieser for his encouragement in the pursuance of this investigation and to Mary Fieser for help in the preparation of this manuscript.

Experimental[13]

All the compounds were reduced by the following general methods with the variations described in the notes.

A mixture of nitro compounds, diethylene glycol and 85% hydrazine hydrate with or without addition of alkali hydroxide was refluxed for about half an hour and the condenser was then removed to allow the aqueous liquor to evaporate and the temperature of the reaction mixture to rise to about 200°. Refluxing at this temperature was continued until the dark colored solution became nearly colorless or light brown (one to three hours). The reaction mixture was cooled and diluted with water and the separated amino product was filtered or extracted with ether.

Note 1.—In reduction of alkali-sensitive compounds such as nitro aldehydes it is advisable to reflux the solution of starting material in diethylene glycol with hydrazine hydrate for about half an hour and then a concentrated aqueous soution of alkali hydroxide is added slowly through the condenser and after refluxing for about twenty minutes longer the aqueous liquor is evaporated as described above.

Note 2.—In cases where either the starting material or the reduced product is volatile a take-off adapter was used instead of removing the condenser to evaporate aqueous liquor.

Note 3.—In some cases a mixture of nitro compound, diethylene glycol and hydrazine hydrate was allowed to stand for a while and then alkali hydroxide in solid form or dissolved in a small amount of water was added.

Note 4.—In cases where the reduced product is acidic, such as amino sulfonic acids, the cooled and diluted reaction mixture was acidified with warm concentrated hydrochloric acid.

p-Toluidine.—(a) From p-nitrobenzaldehyde (Notes 1 and 2): p-Nitrobenzaldehyde (7.5 g.) dissolved in 100 cc. of diethylene glycol with addition of 15 cc. of hydrazine hydrate and 11 g. of potassium hydroxide gave 3.79 g. (70.8%) of p-toluidine, b. p. 116–117° at 53 mm., m. p. 44–45° not depressed with an authentic sample; acetyl compound, m. p. 148–149°, not depressed with N-acetyl-p-toluidine. A reduction made with 6.1 g. of p-nitrobenzaldehyde without addition of alkali hydroxide gave only 1.8 g. (41.3%) of p-toluidine.

(b) From p-nitrotoluene (Note 2): 13.7 g. of p-nitrotoluene, 200 cc. of diethylene glycol and 20 cc. of hydrazine hydrate (without addition of alkali) gave 9.55 g. (89.2%) of p-toluidine, b. p. 106–107° at 34 mm., m. p. 44–45°. Acetyl compound, m. p. 147–148°, not depressed with N-acetyl p-toluidine.

m-Toluidine.—(a) From m-nitrobenzaldehyde (Notes 1 and 2): 7.5 g. of m-nitrobenzaldehyde, 100 cc. of diethylene glycol, 15 cc. of hydrazine hydrate and 11 g. of potassium hydroxide gave 3.54 g. (66.6%) of m-toluidine, b. p. 118–119° at 53 mm., n^{25}_D 1.5659; acetyl compound, m. p. 67–68°, not depressed with N-acetyl-m-toluidine.

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[10] Baker, THIS JOURNAL, 65, 1572 (1943).

[11] For literature or review of syntheses of hexestrol, see Sisido and Nozaki, *ibid.*, 70, 778 (1948); Solmssen, *Chem. Rev.*, 37, 481 (1945).

[12] My thanks are due to Prof. E. C. Dodds, Dr. W. Lawson and Dr. C. W. Sondern for a sample of isohexestrol, to Dr. C. H. Carlisle for a sample of *meso*-4,4′-diamino-α,β-diethyldibenzyl, and to Dr. B. R. Baker for the samples of dipropionyl compounds of *meso* and racemic 4,4′-diamino-α,β-diethyldibenzyl.

[13] The microanalyses were carried out by Shirley Katz of this Laboratory.

(b) From *m*-nitrotoluene (Note 2): The reduction of 13.7 g. of *m*-nitrotoluene with 20 cc. of hydrazine hydrate in 200 cc. of diethylene glycol in absence and in presence of alkali gave 8.26 g. (77.2%) and 8.59 g. (80.3%), respectively, of *m*-toluidine b. p. 107–109° at 34 mm., $n^{25}\text{D}$ 1.5658; acetyl compound m. p. and mixed m. p. 67°.

4,4'-Diaminostilbene.—(a) From *p*-nitrotoluene (Note 3): On reduction of 13.7 g. of *p*-nitrotoluene in 200 cc. of diethylene glycol with 20 cc. of hydrazine hydrate and 22 g. of potassium hydroxide and extraction of the reaction product with ether there was obtained 3.1 g. (30%) of crystalline basic product separated from the ethereal solution, m. p. 223–225°. Recrystallization from acetone–alcohol gave pure product (short prisms), m. p. 226–228° not depressed by admixture with 4,4'-diaminostilbene prepared from 4,4'-dinitrostilbene.[14,15]

Anal. Calcd. for $C_{14}H_{14}N_2$: N, 13.32. Found: N, 13.71.

It furnished a dibenzal compound,[14] m. p. and mixed m. p. 253–254°. From the ethereal mother liquor, 3.17 g. of *p*-toluidine was obtained.

(b) From *p*-nitrobenzyl chloride: To a warm solution of 5 g. of *p*-nitrobenzyl chloride in 20 cc. of alcohol a solution of 1.8 g. of potassium hydroxide in 1.5 cc. of water and 8 cc. of alcohol was added dropwise at about 50°. After cooling to room temperature 120 cc. of diethylene glycol, 12 cc. of hydrazine hydrate and 8 g. of potassium hydroxide were added and the reaction mixture was treated as described for the general method. On extraction with ether and evaporation of the ethereal solution there was obtained 2.17 g. (70.5%) of crystalline product, m. p. 212–220°; 227–228° after recrystallization from alcohol, not depressed by admixture with 4,4'-diaminostilbene prepared from *p*-nitrotoluene and from 4,4'-dinitrostilbene.[15] It furnished a dibenzal compound, m. p. 253°.

(c) From 4,4'-dinitrostilbene: The reduction of 1 g. of 4,4'-dinitrostilbene (prepared from *p*-nitrobenzyl chloride[16]) in 40 cc. of diethylene glycol with 2.5 cc. of hydrazine hydrate and 2 g. of potassium hydroxide gave 0.62 g. (80.5%) of 4,4'-diaminostilbene, m. p. 227–228° (228–229° after recrystallization from alcohol) not depressed by admixture with the authentic samples from other sources.

(d) From 4,4'-dinitrodibenzyl: The reduction of 1 g. of 4,4'-dinitrodibenzyl (prepared from dibenzyl by nitration[17]) by the general procedure gave 0.72 g. (93.2%) of 4,4'-diaminostilbene, m. p. 222–224°, and 0.57 g. (74%) of once-recrystallized material, m. p. 228–229° (no depression in mixed m. p. with authentic samples). It gave the dibenzal compound, m. p. and mixed m. p. 252–254°.

4,4'-Diaminodibenzyl.—(a) From 4,4'-dinitrostilbene: On reduction of 2.7 g. of 4,4'-dinitrostilbene in 100 cc. of diethylene glycol with 4 cc. of hydrazine hydrate in absence of alkali there was obtained 1.5 g. (71%) of 4,4'-diaminodibenzyl, m. p. 135–136° (white glistening plates, m. p. 137–138°, recrystallized from dilute alcohol after treatment with charcoal), not depressed by admixture with the authentic sample prepared from 4,4'-dinitrodibenzyl by reduction with tin and hydrochloric acid.[18]

Anal. Calcd. for $C_{14}H_{16}N_2$: N, 13.20. Found: N, 13.41.

(b) From 4,4'-dinitrodibenzyl: The reduction of 1 g. of 4,4'-dinitrodibenzyl in absence of alkali as above gave 0.77 g. (99%) of 4,4'-diaminodibenzyl, m. p. 130–133°. Recrystallization from dilute alcohol (charcoal) gave 0.62 g. (79.5%) of pure product, m. p. 136–137°, not depressed by admixture with an authentic sample.

(c) From *p*-nitrophenylacetic acid: To a warm solution (40°) of 4.2 g. of *p*-nitrophenylacetic acid in 20 cc. of water containing a few drops of 30% sodium hydroxide solution a mixture of 10 g. of sodium hydroxide in 9 cc. of water and 25 cc. of sodium hypochlorite (5% available chlorine) was added slowly so that the temperature was not over 45°. After addition of the alkaline oxidizing agent, stirring was continued for three to five hours at 45–50°. The clear diluted solution was acidified with dilute hydrochloric acid and the separated yellowish white crystalline product was filtered (4.04 g.), melting at 258–261° (decomposing). After recrystallization from a large volume of acetic acid the melting point could be raised to 261–262° or 264–266°, depending on the rate of heating. Titration of this compound roughly indicated the presence of two carboxyl groups. Without further identification the dibasic acid (1 g.) was heated in 25 cc. of triethylene glycol with 4 cc. of hydrazine hydrate in absence of alkali (general method). Cooling and dilution of the reaction mixture gave 4,4'-diaminodibenzyl melting at 131–132°. On recrystallization from dilute alcohol, there was obtained 0.51 g. (white plates) of pure product, melting and mixed melting point 137–138°.

4,4'-Dinitrostilbene-2,2'-disulfonic Acid.—This was prepared according to Green and Wahl[19] with the following modifications.

To a warm solution (40–45°) of 5 g. of *p*-nitrotoluene-*o*-sulfonic acid[20] (recrystallized from acetone–benzene, m. p. 137–138°) in 30 cc. of diethylene glycol, a mixture of 50 cc. of sodium hypochlorite (5% available chlorine) and a solution of 6 g. of sodium hydroxide in 8 cc. of water was added slowly under stirring (inside temperature 45–55°). After addition stirring was continued and the temperature was kept at 50–55°. After about fifteen minutes the clear solution became turbid and fine yellow needles began to separate. After about twenty minutes the reaction was complete and the sodium hypochlorite was consumed (iodide starch paper). On cooling and filtration there was obtained 4.9 g. of the sodium salt of 4,4'-dinitrostilbene-2,2'-disulfonic acid which was converted to the free acid,[21] m. p. 266° after recrystallization from acetic acid.

Anal. Calcd. for $C_{14}H_{10}O_{10}N_2S_2$: N, 6.51. Found: N, 6.23.

4,4'-Diaminostilbene-2,2'-disulfonic Acid.—(a) From 4,4'-dinitrostilbene-2,2'-disulfonic acid (Note 4): One gram of 4,4'-dinitrostilbene-2,2'-disulfonic acid was treated with hydrazine hydrate and alkali as described in the preparation of 4,4'-diaminostilbene (c) and there was obtained 0.63 g. (73.3%) of diamino product (fine yellowish needles, m. p. over 300°) which appeared to be identical with 4,4'-diaminostilbene-2,2'-disulfonic acid[6,19,22] (prepared from the same starting material by reduction with tin and hydrochloric acid), from its crystal form, high melting point, solubility and decolorization of cold alkaline potassium permanganate solution.

Anal. Calcd. for $C_{14}H_{14}O_6N_2S_2$: N, 7.56. Found: N, 7.47.

(b) From 4,4'-dinitrodibenzyl-2,2'-disulfonic acid (Note 4): One gram of this starting material (prepared from *p*-nitrotoluene-*o*-sulfonic acid[19]) treated with hydrazine hydrate and alkali as above gave 0.58 g. (67.5%) of 4,4'-diaminostilbene-2,2'-disulfonic acid.

Titration: 96.01 mg. consumed 0.1 *N* sodium hydroxide 5.180 cc. Calcd. for $C_{14}H_{14}O_6N_2S_2$: 5.184 cc.

(c) From *p*-nitrotoluene-*o*-sulfonic acid (Note 4): 2.2 g. of this starting material with 20 cc. of diethylene glycol, 2.5 cc. of hydrazine hydrate and 3 g. of potassium hydroxide gave 0.5 g. (27%) of 4,4'-diaminostilbene-2,2'-disulfonic acid.

Titration: 152 mg. consumed 0.1 *N* sodium hydroxide 8.21 cc. Calcd. for $C_{14}H_{14}O_6N_2S_2$: 8.20 cc.

4,4'-Diaminodibenzyl-2,2'-disulfonic Acid.—(a) From 4,4'-dinitrodibenzyl-2,2'-disulfonic acid (Note 4): One gram of this starting material with 25 cc. of diethylene glycol and 4 cc. of hydrazine hydrate gave 0.63 g. (70%) of

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(14) Ruggli and Lang, *Helv. Chim. Acta*, **19**, 996 (1936).

(15) Calvin and Buckles, THIS JOURNAL, **62**, 3326 (1940).

(16) Walden and Kernbaum, *Ber.*, **23**, 1959 (1890).

(17) Rinkenbach and Aaronson, THIS JOURNAL, **52**, 5041 (1930).

(18) Stelling and Fittig, *Ann.*, **137**, 262 (1866).

(19) Green and Wahl, *Ber.*, **30**, 3097 (1897).

(20) I am indebted to E. I. du Pont de Nemours and Company for this material.

(21) Ruggli and Welge, *Helv. Chim. Acta*, **15**, 576 (1932).

(22) Bender and Schultz, *Ber.*, **19**, 3235 (1886).

4,4′-diaminodibenzyl-2,2′-disulfonic acid (white pointed flat needles) which was found to be identical with an authentic sample prepared from the same starting material by reduction with tin and hydrochloric acid.[23]

Anal. Calcd. for $C_{14}H_{16}O_6N_2S_2$: N, 7.53. Found: N, 7.13. *Titration:* 99.03 mg. consumed 0.1 *N* sodium hydroxide 5.295 cc. Calcd. for $C_{14}H_{16}O_6N_2S_2$: 5.318 cc.

(b) From 4,4′-dinitrostilbene-2,2′-disulfonic acid (Note 4): 2 g. of 4,4′-dinitrostilbene-2,2′-disulfonic acid in 40 cc. of diethylene glycol with 8 cc. of hydrazine hydrate gave 0.8 g. (46.2%) of 4,4′-diaminodibenzyl-2,2′-disulfonic acid (white pointed flat needles).

Titration: 95.80 mg. consumed 0.1 *N* sodium hydroxide 5.12 cc. Calcd. for $C_{14}H_{16}O_6N_2S_2$: 5.14 cc.

4,4′-Diamino-α,β-diethyldibenzyl.—The reduction of 19.8 g. of *p*-nitropropylbenzene with 180 cc. of triethylene glycol, 30 g. of potassium hydroxide and 24 cc. of hydrazine hydrate gave 14 g. of dark oily product which was fractionally distilled.

Fraction I: 3.5 g. boiling at 86–87° at 4 mm., identical with *p*-aminopropylbenzene. It furnished an acetyl compound (plates), m. p. 95–96°.

Anal. Calcd. for $C_{11}H_{15}ON$: C, 74.53; H, 8.53; N, 7.90. Found: C, 74.68; H, 8.49; N, 8.03.

Fraction II: 5.1 g. boiling at 178–188° at 0.3 mm.; it solidified after standing. Recrystallization from a mixture of ether and petroleum ether (70–90°) and then from methanol gave about 2 g. of *meso*-4,4′-diamino-α,β-diethyldibenzyl (rhombic plates), m. p. 141–142°, not depressed by admixture with an authentic sample.[12]

The ether–petroleum ethereal mother liquor obtained above on concentration gave the racemic isomer in leaflets. Recrystallization from ether–petroleum ether gave 1.7 g., m. p. 97–98.5° (one sample recrystallized from methanol melting at 98–99°).

Anal. Calcd. for $C_{18}H_{24}N_2$: C, 80.54; H, 9.01; N, 10.43. Found: (*meso* form) C, 80.68; H, 9.12; N, 10.63; (racemic form) C, 80.50; H, 8.82; N, 10.71.

Both *meso* and racemic isomers furnished the dipropionyl compounds melting at 264–266° (plates) and 217–218° (plates), respectively, mixed with authentic samples[12] (*meso* form m. p. 262–264°; racemic form 207–215°[10]) melted at 263–266° and 210–216°, respectively.

4,4′-Dihydroxy-α,β-diethyldibenzyl.—0.14 g. of *meso*-diamino compound, m. p. 141–142°, was dissolved in dilute sulfuric acid and diazotized with sodium nitrite. After standing at 2–5° about twenty minutes and pouring in portions into 300 cc. of boiling water, the crystalline dihydroxy compound separated on cooling, m. p. 174–178° (0.12 g.). Recrystallization from benzene gave pure product, m. p. 181–182°, not depressed by admixture with an authentic sample of hexestrol.

Diazotization of racemic diamino compound (m. p. 97–98°) under the same conditions as above gave the racemic or isohexestrol which after repeated recrystallization from ether–petroleum ether melted at 128–129°, not depressed by admixture with an authentic sample.[12]

Anal. Calcd. for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found (*meso* form): C, 80.18; H, 8.14. (racemic form): C, 80.04; H, 8.22.

Summary

1. The modified Wolf–Kishner method has been adapted for the reduction of aromatic nitroaldehydes.

2. Nitrotoluenes have been converted to the corresponding dimeric amino products and toluidines by using hydrazine hydrate.

3. Both the 4,4′-dinitrostilbenes and the 4,4′-dinitrodibenzyls have been converted to the diaminostilbenes or diaminodibenzyls by the action of hydrazine hydrate. In all of these cases the presence of alkali was a determining factor with respect to the formation of dimeric products and the persistence or the reduction of the ethylenic linkage.

4. A new synthetic route for the preparation of hexestrol has been described.

CAMBRIDGE 38, MASSACHUSETTS RECEIVED APRIL 17, 1948

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[23] Ris and Simon, *Ber.*, **30**, 2618 (1897).

[CONTRIBUTION FROM ROHM & HAAS COMPANY]

Preparation of Acetals or Ketals from Vinyl-type Esters

BY W. J. CROXALL, F. J. GLAVIS AND H. T. NEHER

In the course of an investigation of the addition of alcohols to vinyl compounds, it was observed that when vinyl acetate is added to an excess of alcohol containing a small amount of mercury oxide and boron trifluoride, heat is evolved and an acetal and acetic acid are formed in high yields. Under similar conditions isopropenyl acetate gives a ketal and acetic acid. The over-all course of the reaction is

$$CH_2{=}CHOCOCH_3 + 2ROH \longrightarrow CH_3CH(OR)_2 + CH_3COOH$$

Mixtures of mercuric oxide and the complexes formed from boron trifluoride with alcohols, ethers or carboxylic acids were found to be the most active catalysts. With these, the reaction starts promptly and is so rapid that efficient cooling is required to prevent vigorous or even violent boiling. Mercuric sulfate is a slightly less active catalyst. With mercuric phosphate no appreciable reaction occurs at room temperature, but after the mixture is refluxed for two hours, some hemiacetal acetate is formed. Coffman[1] obtained the 1-acetoxyethyl ether of a glycolic ester when equi-molar quantities of vinyl acetate and the glycolic ester were refluxed in the presence of mercuric phosphate. Mercuric oxide alone is entirely inert as a catalyst at room or elevated temperatures. Boron trifluoride diethyl etherate alone induces no exothermic reaction, but when the reaction mixture is refluxed, acetal is produced in low yield, together with acetic ester, acetaldehyde and water. Presumably, the initial reaction in this case is an alcoholysis[2] after which some of the acetaldehyde undergoes acetal formation

$$CH_2{=}CHOCOCH_3 + ROH \longrightarrow CH_3CHO + CH_3COOR$$
$$CH_3CHO + 2ROH \longrightarrow CH_3CH(OR)_2 + H_2O$$

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[1] Coffman, U. S. Patent 2,384,726 (1945).

[2] Herrmann and Deutsch, British Patent 314,646 (1929).