analyzed by infrared spectrometry. Later[11] most of the samples were reanalyzed by gas chromatography essentially as described previously.[5] The retention volumes of the amine components were always much greater than those of the olefin components (on Perkin–Elmer packing B) so that the two fractions could be very cleanly separated by gas chromatography. The results of these analyses indicated that the separation by distillation alone was not as complete as might be desired but for most practical purposes was adequate.

For the isomerization studies described in Table IV, the crude pyrolysate was washed with cold, dilute hydrochloric acid, cold 5% sodium bicarbonate, and water, dried over magnesium sulfate and analysed without further treatment. In some experiments the olefin was picked up in *n*-pentane prior to the washing. The presence of the *n*-pentane did not interfere in any way with the analysis by gas chromatography.

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Reduction of Vinylaromatic Nitro Derivatives[1]

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Using either zinc and ammonium chloride, or aluminum amalgam in moist ether, *o*, *m* and *p*-nitrostyrenes, stilbenes and -cinnamic acids are reduced to corresponding amines. Intermediate hydroxylamines cannot be isolated.

Derivatives of nitrosobenzene with vinyl or substituted vinyl side-chains are desired monomers in investigations on polymers containing nitroso groups. There are apparently no known examples of such polymerizable monomers; however, the literature describes nitrosocinnamic acids and esters[2] and contains disputed reports for 4,4′-dinitrosostilbene and derivatives.[3]

A transformation of a nitro group into a nitroso group requires initial reduction into an hydroxylamine followed by oxidation. In the present work reduction of nitrostyrenes, -stilbenes and -cinnamic acids using either zinc and ammonium chloride or aluminum amalgam in moist ether has been investigated. These reagents are known to reduce nitrobenzene,[4] and derivatives with deactivating[5] or weakly activating[6] substituents attached to the aromatic ring, into corresponding β-arylhydroxylamines. In contrast, strongly activating ring substituents on nitrobenzene promote reduction by these mild reagents into anilines.[7] The reduction of *m*-nitroaniline into *m*-phenylenediamine using aluminum amalgam has now confirmed that even in a *m*-position the amino group may not allow chemical reduction of an aromatic nitro group to stop at the hydroxylamino stage.

A vinyl substituent attached at any available ring position in nitrobenzene has now been observed to promote chemical reduction to a primary amine. In no case was it possible to detect hydroxylamines in reductions, using zinc and ammonium chloride, of nitrostyrenes, -stilbenes[8] or -cinnamic acids. Instead, corresponding amines were obtained in good to excellent yields. Similar results were obtained in good to excellent yields. Similar results were obtained from experiments on nitrostyrenes and aluminum amalgam in moist ether. These results were unexpected insofar as negatively substituted vinyl groups, such as is present in cinnamic acid and presumably stilbene, deactivate an attached aromatic ring.[9] In contrast *p*-nitrobiphenyl has been reduced to *p*-hydroxylaminobiphenyl with zinc and ammonium chloride[10] and with aluminum amalgam.[11]

Experimental

o- and *p*-nitrostyrenes were prepared by dehydrobromination of the corresponding bromides[12] and *m*-nitrostyrene by decarboxylation of *m*-nitrocinnamic acid with copper powder and quinoline.[13] *cis*-*o*-Nitrostilbene was prepared by decarboxylation of *trans*-β-phenyl-*o*-nitrocinnamic acid with Ad-

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[2] F. J. Alway and W. D. Bonner, *Amer. Chem. J.*, **32**, 392 (1904), claimed the preparation of *m*- and *p*-nitrosocinnamic acids and esters by the oxidation, using ferric chloride, of corresponding unisolated hydroxylamines, in turn prepared in unspecified poor yield by the reduction of nitro compounds using zinc and acetic acid. In contrast, G. Heller, *Ber.*, **43**, 1918 (1910), found that *o*-nitrocinnamic acid was reduced by zinc and acetic acid buffered with sodium acetate into *o*-aminocinnamic acid.

[3] O. Fischer and E. Hepp, *ibid.*, **26**, 2231 (1893); **28**, 2281 (1895), reported that *p*,*p*,-dinitrostilbene resulted from *p*-nitrotoluene and strong alkali in methanol; F. Bender, *ibid.*, **28**, 422 (1895), claimed that alkaline treatment of 4-nitrotoluene-2-sulfonic acid resulted in the formation of a mixture of dinitrodibenzyldisulfonic acid and azoxystilbenedisulfonic acid; A. G. Green, A. H. Davies and R. S. Horsfall, *J. Chem. Soc.*, **91**, 2076 (1907), suggested that "*p*,*p*′-dinitrosostilbene" and derivatives were, instead, dinitroazodistilbenes.

[4] G. H. Coleman, C. M. McCloskey and F. A. Stuart, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 668, used zinc and ammonium chloride; H. Wislicenus and L. Kaufmann, *Ber.*, **28**, 1323 (1895), used aluminum amalgam.

[5] F. J. Alway and A. B. Walker, *ibid.*, **36**, 2312 (1902), reduced *o*- and *m*-nitrobenzoic esters using zinc and acetic acid; E. Bamberger and F. L. Pyman, *ibid.*, **36**, 2700 (1903), **42**, 2306 (1909), used zinc and ammonium chloride; for a similar reduction of nitrobenzaldehydes see A. Kirpal, *ibid.*, **30**, 1597 (1897), and F. J. Alway, **36**, 2312 (1902), and for reductions of halonitrobenzenes see R. D. Haworth and A. Lapworth, *J. Chem. Soc.*, **119**, 768 (1921).

[6] E. Bamberger and A. Rising, *Ann.*, **316**, 278 (1901), reduced nitrotoluenes.

[7] With zinc dust and water, or zinc dust, water and calcium chloride, *o*- and *p*-nitrophenols and *o*- and *p*-nitroanilines were reduced to corresponding aminophenols and diamines; E. Bamberger, *Ber.*, **28**, 245 (1895), and M. Lumière and A. Seyewetz, *Bull. soc. chim.*, [3] **11**, 1038 (1894); see also R. D. Haworth and A. Lapworth, ref. 5.

[8] G. Drefahl, O. Henning and G. Rudakoff, *Chem. Ber.*, **91**, 286 (1958), reduced 4-nitrostilbene into azoxystilbene using magnesium and ammonium chloride.

[9] F. G. Bordwell and K. Rohde, THIS JOURNAL, **70, 1191** (1948).

[10] H. Gilman and H. E. Kirby, *ibid.*, **48**, 2192 (1926).

[11] F. Bell, J. Kenyon and P. H. Robinson, *J. Chem. Soc.*, 1239 (1926).

[12] R. W. Strassburg, R. A. Gregg and C. Walling, THIS JOURNAL, **69**, 2142 (1947); E. L. Foreman and S. M. McElvain, *ibid.*, **62**, 1435 (1940).

[13] R. H. Wiley and N. R. Smith, *Org. Syntheses*, **33**, 62 (1953); W. J. Dale and C. W. Strobel, THIS JOURNAL, **76**, 6173 (1954).

kin catalyst,[14] *trans-m*-nitrostilbene by the Meerwein reaction,[15] *trans-p*-nitrostilbene by condensation of benzaldehyde with *p*-nitrophenylacetic acid[16] and *trans-p-, p'*-dinitrostilbene by treating *p*-nitrobenzyl chloride with potassium hydroxide.[17] *o*-Nitrocinnamic acid was prepared by condensation of *o*-nitrobenzaldehyde with acetic anhydride.[18] The *m*-isomer was prepared according to Wiley and Smith[13] and commercial *p*-nitrocinnamic acid was used.

Reduction of *o*-, *m*-, and *p*-Nitrostyrenes with Aluminum Amalgam.—To 10.0 g. of aluminum amalgam[19] and 400 ml. of ether in a 1-liter, 2-necked flask equipped with a reflux condenser and a dropping funnel, 12.0 g. of nitrostyrene dissolved in 50 ml. of ether is poured into the flask in small portions from the top of the condenser. The flask is occasionally shaken while 8 ml. of water is added slowly from the dropping funnel. A vigorous reaction occurs and addition of the nitrostyrene is regulated to give a gentle reflux. After all of the nitrostyrene and water have been added the mixture is left until the reaction subsides, refluxed for 10 minutes on a water-bath, and filtered. The precipitate is washed several times with ether and the washings are combined with the filtrate which is dried with anhydrous sodium sulfate and evaporated first on a water-bath and later under reduced pressure.

o-Nitrostyrene gives 9.0 g. (93%) of undistilled *o*-aminostyrene, n^{26}_{D} 1.5899, and after distillation from 0.5 g. of hydroquinone, 5.1 g. (53%), b.p. 93–96° (10 mm.), n^{26}_{D} 1.6065 (lit.[20] b.p. 102–104° (12 mm.), n^{15}_{D} 1.608). A red-brown tough polymer remained.

m-Aminostyrene, 6.2 g. (74%), distilled from hydroquinone, has b.p. 82–85° (6 mm.), n^{26}_{D} 1.6069 (lit.[21] b.p. 93.5° (8 mm.), n^{35}_{D} 1.6068); benzoyl derivative, m.p. 91° (lit.[22] m.p. 90–91°). About 0.9 g. of polymeric material is obtained.

p-Nitrostyrene yields 8.6 g. (89%) of undistilled amine, n^{25}_{D} 1.5950. After distillation from hydroquinone, 5.8 g. (61%), b.p. 74–77° (2 mm.), n^{25}_{D} 1.6185 (lit.[23] b.p. 76–81° (2.5 mm.), n^{20}_{D} 1.619), is obtained. An acetyl derivative has m.p. 135–136° (lit.[23] m.p. 135–136°).

m-Nitrostyrene is quantitatively recovered from tested aluminum amalgam in moist ether at 0° for 6 hours.

Reduction of *m*-nitroaniline with aluminum amalgam and moist ether follows the same procedure. The final hot reaction mixture is filtered and the filtrate dried with anhydrous sodium carbonate and sodium hydroxide. The solvent is removed on a water-bath and the residue is distilled under reduced pressure. The product, obtained in 80% yield, crystallizes in the receiving flask, m.p. 63°.

Reduction of *p*-Nitrostyrene with Zinc and Ammonium Chloride.—To a solution of 7.0 g. (0.05 mole) of *p*-nitrostyrene in 75 ml. of acetone is added a solution of 5.0 g. of ammonium chloride in 20 ml. of water. The mixture is heated to boiling on a water-bath. The bath is removed and 10.0 g. of zinc dust is added in small portions to maintain a moderate reaction. After the zinc is added and the reaction subsides five additional grams of zinc dust is added and the mixture refluxed on the water-bath for 30 minutes. The solution is then filtered while hot and the precipitate is washed twice with acetone. The combined washings and filtrate is concentrated on the water-bath to about 30 ml. and the crude amine is converted with sodium acetate and acetic anhydride into *p*-acetamidostyrene, m.p. 134°,[23] 5.9 g. (74%).

Reduction of mono- and di-nitrostilbenes and *o*-, *m*- and *p*-nitro-cinnamic acids with zinc and ammonium chloride is carried out in the same manner. In the case of *o*-aminostilbene the final acetone solution is evaporated on a water-bath until red droplets of the amine appear on the surface. These are taken up in ether and dried with anhydrous sodium sulfate. As the ether solution is saturated with dry hydrogen chloride the amine hydrochloride appears as a white crystalline precipitate which is filtered, washed with ether and recrystallized from a small amount of alcohol, m.p. 199–201° (lit.[14] 202–203°), (72%). The reaction carried out in alcohol gives a yield of 51%.

For each of *m*- and *p*-aminostilbenes the final acetone solution is treated with 15 ml. of 3 *N* ammonium hydroxide solution to dissolve zinc hydroxide and the solution is concentrated on a water-bath to about 30 ml. Sufficient water containing a few drops of concentrated ammonium hydroxide is added to precipitate the product. The solution is filtered and the precipitate washed with 5% ammonium hydroxide solution and with water and dried. In the case of *m*-aminostilbene the product is dissolved in ether and filtered of remaining zinc hydroxide. Removing ether by distillation on a water-bath leaves the product, m.p. 120–121° (lit.[15] m.p. 120–121°) (77%). With the *p*-isomer the yield was 84% after recrystallization from a small amount of dilute alcohol m.p. 150–151° (lit.[24] m.p. 151°). The reactions carried out in alcohol give yields of 59 and 61% for the *m*- and *p*-isomers, respectively.

The crude precipitate of *p,p'*-diaminostilbene obtained after removal of the solvent and dilution with water is dried at 100° for 30 minutes, boiled with chlorobenzene and 0.5 g. of activated carbon, filtered while hot, allowed to cool in an ice-bath for 6 hours, filtered and dried. A yield of 60% of *p,p'*-diaminostilbene, m.p. and mixture m.p. 227–228°,[25] is obtained.

The reaction mixture for each of the isomeric aminocinnamic acids is filtered while hot and the precipitate is extracted 3 times with a warm solution of 15 ml. of 3 *N* ammonium hydroxide. The acetone filtrate is concentrated on a water-bath to about 30 ml. and combined with the ammonium hydroxide solutions. *p*-Aminocinnamic acid is obtained by acidifying the ammonium hydroxide solution with excess acetic acid. The precipitate is filtered, washed once with cold dilute acetic acid and once with ice-cold water and dried. The crude product (74%), m.p. 172°, recrystallizes from boiling water with about 20% loss due to partial decomposition, m.p. 175–176° dec., (lit.[26] m.p. 175–176° dec.) The solution containing the *m*-isomer was acidified with 30 ml. of concentrated hydrochloric acid, cooled in an ice-bath for 3 hours, filtered, dissolved in boiling water and the amino acid, precipitated by addition of excess sodium acetate, appears as small yellow crystals which are filtered and washed with ice-cold water, boiled with 50 ml. of water, filtered while hot and cooled in an ice-bath. An additional portion from acidifying the filtrate from recrystallization with hydrochloric acid, filtering, boiling with water and precipitating with sodium acetate gives a total yield of 70% m.p. 181° (lit.[27] 181.5–183°). The *o*-isomer is obtained by acidifying the ammonium hydroxide solution and concentrating the solution to about half its volume. A stream of hydrogen chloride is then passed through the mixture until saturation. The mixture is stored overnight at 0–5°, filtered, the precipitate dissolved in boiling water and reprecipitated with sodium acetate. The product washed with ice-cold water, dried and recrystallized from toluene gives m.p. 157–158° (lit.[28] 157–158°), (63%).

Attempts to repeat Alway and Bonner's preparation[2] of *m*- and *p*-nitrosocinnamic acids were unsuccessful. In each case reduction of nitrocinnamic acids afforded amines and not hydroxylamines.

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