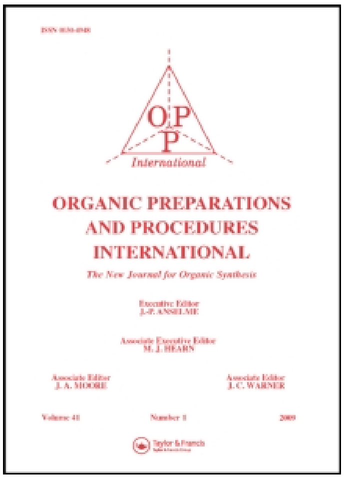

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N,N'-DIALKYL-*p*-PHENYLENEDIAMINES

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N,N'-DIALKYL-p-PHENYLENEDIAMINES

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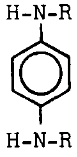
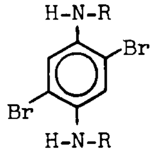
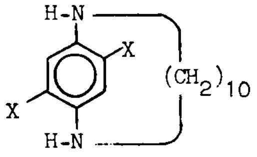
A previous paper[2] described the N-alkylation of a number of sulfonylamides derived from p-phenylenediamine and of some of its 2,5-disubstituted derivatives. The present work describes the scission of the SO_2-N bonds in these products, leading to the title compounds shown below.



I



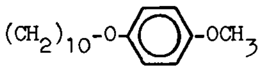
II



III

a. R = C_2H_5

b. R =



a. R = C_2H_5

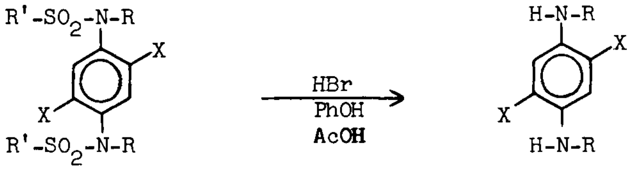
b. R = $(CH_2)_{10}Br$

a. X = H

b. X = Br

c. X = OCH_3

Various methods were tried; generally the best results were obtained by the method of Weisblat et al.[3], using phenol and HBr in acetic acid as the cleaving agent. Weisblat's procedure has the advantage that neither ether functions nor bromine atoms were attacked.



The compounds were characterized by their spectra and analyses. The monoansa compound IIIc could not be obtained in a pure state; it was therefore characterized as its N,N'-diacetyl derivative.

EXPERIMENTAL

General remarks: see general remarks in reference 2.

N,N'-Diethyl-p-phenylenediamine (Ia).

A mixture of 4.73 g (10.0 mmole) of N,N'-diethyl-N,N'-ditosyl-*p*-phenylenediamine,[2] 5.0 g of phenol and a solution of hydrogen bromide in acetic acid (40 ml; 27% by weight) was kept at room temperature for 18 hr. The suspension was poured into 225 ml of ether and the resulting white solid washed with ether (50 ml). The yield of N,N'-diethyl-*p*-phenylenediamine-*bis*-hydrobromide, mp 262° (dec.), was 3.25 g (100%); it was dissolved in water (nitrogen atmosphere) and the solution made slightly alkaline (pH 8) with 2 N potassium hydroxide. In this way was obtained 500 mg (30%) of N,N'-diethyl-*p*-diaminobenzene as a white substance with mp 49-50°. The low yield is probably due to the rather good solubility of N,N'-diethyl-*p*-phenylenediamine in water at pH 8. The same substance was reported by Hinsberg[4]; however no properties of the product were given.

IR spectrum (0.3 molar in CH_2Cl_2): N-H stretch vibration at 3390 cm^{-1}.

UV spectrum (96% ethanol), λ_{max}: 255 mμ (log ε 4.15) and 322 mμ (log ε 3.42).

PMR spectrum (20%, in $CDCl_3$): τ 3.52 (s), aromatic protons, τ 6.7-7.3 (broad signal) $N\underline{H}$, $NC\underline{H_2}$, τ 8.85 (t) $NCH_2C\underline{H_3}$, J = 7 cps.

Anal. Calc'd for $C_{10}H_{16}N_2$ (164.25): C 73.1; H 9.8; N 17.1.

Found: C 72.9; H 9.9; N 17.2.

N,N'-bis[10-(p-Methoxyphenoxy)-decyl]-p-phenylenediamine(Ib).

To 1.88 g (2.0 mmole) of N,N'-bis[10-(p-methoxyphenoxy)-decyl]-N,N'-ditosyl-p-phenylenediamine[2] was added benzene (6 ml), phenol (1.5 g) and a 36% solution of HBr in acetic acid (15 ml). After 5 hr at room temperature, ether (50 ml) was added; the solid was collected after 1.5 hr and washed with benzene (10 ml) and ether (50 ml). The resulting bis-HBr salt of Ib weighed 1.56 g and melted from 230-237.5° (dec.). A suspension of this salt in 50 ml of ethanol was made alkaline with 2N potassium hydroxide solution.

After 1 hr at room temperature the solid was collected, washed with ethanol (10 ml) and with water (50 ml), recrystallized first from benzene (60 ml) and then from a mixture of chloroform (20 ml) and petroleum-ether (bp 40-60°, 15 ml). Yield 0.99 g (78%) of N,N'-bis-[10-(p-methoxyphenoxy)-decyl]-p-phenylenediamine, mp 124.5-125.5°.

A mixed melting point with the substance prepared according to the method of Lüttringhaus and Simon[5] gave no depression.

UV spectrum (dioxan), λ_{max}: 264 mμ (log ε 4.22), 335 mμ (log ε 3.41), sh at 291 mμ (log ε 3.96).

PMR spectrum (10%, in CF_3COOH): τ 2.15 (s), protons of the "central" benzene nucleus, τ 2.95, protons of the two other benzene nuclei, τ 5.5-6.5, NCH_2, OCH_2, OCH_3, τ 7.8-8.8 with a maximum at τ 8.59, CH_2 of the rest of the molecule.

N,N'-Decamethylene-p-phenylenediamine (IIIa).

A mixture of N,N'-ditosyl-N,N'-decamethylene-p-phenylenediamine[2] (2.57 g, 4.63 mmole), dry benzene (25 ml), phenol (4.0 g) and a 36% solution of HBr in acetic acid (40 ml) was kept at room temperature in a nitrogen atmosphere for 5 days. To the suspension was added dry ether (100 ml); the solid was filtered after a few hr, washed with ether (30 ml), benzene

(20 ml) and finally with ether (15 ml). The salt (1.79 g) was suspended in 1.5N potassium hydroxide solution (25 ml) under nitrogen. After 1 hr water (15 ml) was added, the solid filtered, washed with water (50 ml) and dried.

This material (0.973 g of a white product melting from 104-108°) was crystallized from petroleum ether (bp 60-80°) and then from a mixture of petroleum ether (12 ml) and ethanol (2 ml); the solutions were cooled to 0° and the filtered crystals washed with petroleum ether (20 ml). Yield 570 mg (50%) of N,N'-decamethylene-p-phenylenediamine, mp 106-107.5°. In the solid state the product is hardly oxidized when exposed to the air.

IR spectrum (0.25 molar in CH_2Cl_2): N-H stretch vibration at 3390 cm^{-1} (broad band).

UV spectrum (cyclohexane), λ_{max}: 266 mμ (log ε 4.12) and 328 mμ (log ε 3.30).

PMR spectrum (20%, in $CDCl_3$): τ 3.42 (s), arom. protons, multiplet probably consisting of triplet τ 6.81 ($N-CH_2$) and singlet τ 6.91 (NH), τ 8.3-9.4 with a maximum at τ 9.28 (remaining protons).

Anal. Calc'd for $C_{16}H_{26}N_2$ (246.40): C 77.9; H 10.6; N 11.4.

Found: C 77.7; H 10.8; N 11.3.

N,N'-Diethyl-1,4-diamino-2,5-dibromobenzene(IIa).

To a mixture of N,N'-diethyl-N,N'-ditosyl-1,4-diamino-2,5-dibromobenzene[2] (2.10 g, 3.33 mmole) and phenol (2.5 g) was added a 27% solution (by weight) of HBr in acetic acid (20 ml). The reaction mixture was kept at room temperature for 2.5 months. It was then diluted with dry ether (80 ml) and the solid material washed with ether (35 ml) and dried. This product (1.59 g) was treated under nitrogen with an excess of 10% $KHCO_3$ solution. The precipitate was filtered, washed with water (50 ml) and twice recrystallized from 12 ml of methanol (cooled to -25°). Yield 0.81 g (76%) of N,N'-diethyl-1,4-diamino-2,5-dibromobenzene, mp 104-105°.

IR spectrum (0.15 molar in CH_2Cl_2): N-H stretch vibration at 3390 cm^{-1}.

UV spectrum (96% ethanol), λ_{max}: 218 mμ (log ε 4.35), 257 mμ (log ε 4.21) and 344 mμ (log ε 3.62).

PMR spectrum (20%, in $CDCl_3$): τ 3.24 (s), arom. protons, τ 6.43 (broad band), NH, τ 6.93 (q), NCH_2CH_3, τ 8.76 (t), NCH_2CH_3, J = 7 cps.

Anal.Calc'd for $C_{10}H_{14}Br_2N_2$ (322.07): C 37.3; H 4.4; Br 49.6; N 8.7.

Found: C 37.5; H 4.6; Br 49.3; N 8.5.

Derivative:

N,N'-Diacetyl-N,N'-diethyl-1,4-diamino-2,5-dibromobenzene was prepared by refluxing for 1.5 hr under nitrogen a mixture of 685 mg (2.12 mmole) of N,N'-diethyl-1,4-diamino-2,5-dibromobenzene, acetic acid (3 ml) and acetic anhydride (3 ml). After cooling to room temperature, methanol (10 ml) was added and the mixture evaporated to dryness in vacuo. The residue gave, by recrystallization from a 1:5 mixture of absolute ethanol: petroleum ether (bp 60-80°), 682 mg (67%) of N,N'-diacetyl-N,N'-diethyl-1,4-diamino-2,5-dibromobenzene, mp 216-217°.

IR spectrum (0.1 molar in CH_2Cl_2): amide I band at 1662 cm^{-1}.

UV spectrum (96% ethanol), λ_{max}: 226 mμ (log ε 4.35), sh at 280 mμ (log ε 2.92).

PMR spectrum (10%, in $CDCl_3$): τ 2.35 (s), arom. protons, τ 5.6-7.0 (m), NCH_2CH_3, τ 7.68 (s) and τ 8.16 (s), $COCH_3$, τ 8.82 (q), NCH_2CH_3, J = 7 cps.

Anal. Calc'd for $C_{14}H_{18}Br_2N_2O_2$ (406.15): C 41.4; H 4.5; Br 39.4; N 6.9.

Found: C 41.6; H 4.6; Br 39.7; N 7.1.

N,N'-bis(10-Bromodecyl)-1,4-diamino-2,5-dibromobenzene(IIb)

N,N'-bis(10-Bromodecyl)-N,N'-ditosyl-1,4-diamino-2,5-dibromobenzene[2] (11.08 g,10.93 mmole) was dissolved in a mixture of benzene (90 ml) and phenol (20 g). To this solution was added a solution of HBr in acetic acid (225 ml; 31,5%). After 3 days at room temperature, 500 ml of dry ether was added. The suspension was cooled to 0° for 1 hr and the solid washed with ether(200 ml), benzene (75 ml) and ether (125 ml). The white product obtained (9.05 g) was suspended under nitrogen in 100 ml of 96% ethanol and made alkaline with 2N potassium hydroxide solution. The solid was washed with 120 ml of 50% ethanol and then with absolute ethanol (15 ml). Recrystallization from a mixture of dimethylformamide (600 ml) and absolute ethanol (400 ml) gave 6.63 g (86%) of N,N'-bis(10-bromodecyl)-1,4-diamino-2,5-dibromobenzene, mp 99-102.5°. For analysis and spectra 1.96 g was chromatographed over 47 g of alumina (Merck, neutral, Brockmann activity II-III). By elution with benzene 1.81 g of product was obtained which was subsequently recrystallized from petroleum ether (30 ml; bp 60-80°), from a mixture of methanol (50 ml), petroleum ether (50 ml; bp 60-80°), benzene (25 ml) and from a mixture of dimethylformamide (25 ml) and absolute ethanol (150 ml). The mp did not change by all these purifications.

In the solid state the product is stable for unlimited periods of time.

IR spectrum (0.15 molar in CH_2Cl_2): 3400 cm^{-1} (N-H stretch vibration).

UV spectrum (96% ethanol), λ_{max}: 218 mμ (log ε 4.41), 258 mμ (log ε 4.27) and 345 mμ (log ε 3.67).

PMR spectrum (20%, in $CDCl_3$): τ 3.24 (s), arom. protons, τ 6.2-7.15 broad signal with a triplet at τ 6.63 (CH_2Br), τ 6.98 (t), NCH_2, τ 6.4 (broad band), NH, τ 7.9-8.8 (broad signal) with a sharp peak at τ 8.70 (remaining protons).

Anal. Calc'd for $C_{26}H_{44}Br_4N_2$ (704.32): C 44.3; H 6.3; Br 45.4; N 4.0.

Found: C 44.7; H 6.4; Br 45.0; N 4.2.

Derivative:

N,N'-bis(10-Bromodecyl)-N,N'-diacetyl-1,4-diamino-2,5-dibromobenzene was prepared by refluxing for 2 hr a mixture of N,N'-bis(10-bromodecyl)-1,4-diamino-2,5-dibromobenzene, mp 99-102.5° (330 mg; 0.47 mmole), acetic anhydride (2 ml) and acetic acid (2 ml). The crude product was first crystallized from 20 ml of petroleum ether (bp 60-80°) and then from 6 ml of methanol (the solution was cooled to -10°). Yield 205 mg (56%) of N,N'-bis(10-bromodecyl)-N,N'-diacetyl-1,4-diamino-2,5-dibromobenzene, mp 86.5-88.5°. TLC (silica, ether) showed only one spot.

IR spectrum (0.15 molar in CH_2Cl_2): amide I band at 1662 cm^{-1}.

UV spectrum (96% ethanol), λ_{max}: 227 mμ (log ε 4.36), sh at about 285 mμ.

Anal. Calc'd for $C_{30}H_{48}Br_4N_2O_2$ (788.39): C 45.7; H 6.1; Br 40.5; N 3.6.
Found: C 46.0; H 6.2; Br 40.8; N 3.6.

Molecular weight (determined with a Mechrolab osmometer, model 301 A, in benzene): 766, 773, calculated: 788.

N,N'-Decamethylene-1,4-diamino-2,5-dibromobenzene (IIIb).

To a solution of N,N'-ditosyl-N,N'-decamethylene-1,4-diamino-2,5-dibromobenzene[2] (5.34 g, 7.50 mmole) in a mixture of phenol (4 g) and benzene (15 ml), was added (nitrogen atmosphere) 50 ml of a 36% solution of HBr in acetic acid. After 6 days at room temperature, dry ether (150 ml) was added to the reaction mixture. The solid was filtered and washed with dry ether (100 ml), chloroform (40 ml), dry ether (15 ml) then dried at 0.5 mm over KOH. The residue (4.61 g of a white substance) was suspended in a mixture of chloroform (130 ml), methanol (65 ml) and water (200 ml) and made alkaline with 0.1N sodium hydroxide solution (phenolphthalein). The layers were separated, the water layer extracted with chloroform, the combined organic extracts washed with water, dried with $MgSO_4$ and evaporated to dryness *in vacuo* to give 3.03 g product. Recrystallization under nitrogen from a mixture of petroleum ether (bp 60-80°, 5 ml) and methanol (10 ml) yielded 2.38 g (79%) of pure N,N'-decamethylene-1,4-diamino-2,5-dibromobenzene, mp 94-95°. In the solid state the substance is stable in the air.

IR spectrum (0.1 molar in CH Cl): 3390 cm^{-1} (N-H stretch vibration).

UV spectrum (96% ethanol), λ_{max}: 263 mμ (log ε 4.14) and 339 mμ (log ε 3.53).

PMR spectrum (15%, in $CDCl_3$): τ 3.07 (s), arom. protons, τ 6.0-7.0 (broad band), with a maximum at τ 6.19 N<u>H</u>, and at τ 6.7 NC<u>H</u>$_2$, τ 8.2-9.4 broad signal with maxima at τ 8.87 and 9.23, remaining protons.

Anal. Calc'd for $C_{16}H_{24}Br_2N_2$ (404.22): C 47.5; H 6.0; Br 39.5; N 6.9.

Found: C 47.5; H 6.0; Br 39.7; N 6.9.

Derivative:

N,N'-Diacetyl-N,N'-decamethylene-1,4-diamino-2,5-dibromobenzene was prepared by refluxing 440 mg (1.09 mmole) of IIIb with acetic acid (2.5 ml) and acetic anhydride (2.5 ml) for 2 hr. After cooling to room temperature 15 ml of water was added; the precipitate was collected, washed with water (20 ml) and dried. Yield 509 mg (96%) of N,N'-diacetyl-N,N'-decamethylene-1,4-diamino-2,5-dibromobenzene, mp 202-203.5°.

IR spectrum (0.1 molar in CH_2Cl_2): amide I band at 1658 cm^{-1}.

UV spectrum (96% ethanol), λ_{max}: 229 mμ (log ε 4.38).

PMR spectrum (20%, in $CDCl_3$): τ 2.23 (s) and τ 2.39 (s), arom. protons, τ 6.24 (t) NC<u>H</u>$_2$, τ 7.70 (s) and τ 8.04 (s), COC<u>H</u>$_3$, τ 8.3-9.1 (broad signal), remaining protons, the peak at the highest field is present at τ 8.98.

Anal. Calc'd for $C_{20}H_{28}Br_2N_2O_2$ (488.29): C 49.2; H 5.8; Br 32.7; N 5.7.

Found: C 48.9; H 5.8; Br 32.9; N 5.7.

N,N'-Diacetyl-N,N'-decamethylene-1,4-diamino-2,5-dimethoxybenzene, (diacetyl derivative of IIIc).

a. N,N'-Decamethylene-1,4-diamino-2,5-dimethoxybenzene-bis-hydrogen bromide.

A mixture of N,N'-dimesyl-N,N'-decamethylene-1,4-diamino-2,5-dimethoxybenzene^2 (26.47 g, 57.3 mmole), phenol (40 g) and a solution (31% by weight) of hydrogen bromide in 300 ml of acetic acid was kept at room temperature for 24 hr in a nitrogen atmosphere. Addition of dry ether (1.5 l) gave a white precipitate. After two days at 0°, the supernatant liquid was decanted.

The solid was washed with absolute ether (150 ml), dichloromethane (100 ml), ether (150 ml) then dried *in vacuo* (2 mm) for 6 hr at room temperature. The white product obtained (23.47 g) was impure N,N'-decamethylene-1,4-diamino-2,5-dimethoxybenzene-*bis*-hydrobromide as was shown by the equivalent weight of 257 and 253 [234.15 calculated for $C_{18}H_{32}Br_2N_2O_2$ (468.30)]. The titration was carried out in N_2 atmosphere with 0.1N NaOH (phenolphtalein indicator) while dichloromethane was added to dissolve the base generated.

b. N,N'-Diacetyl-N,N'-decamethylene-1,4-diamino-2,5-dimethoxybenzene was prepared by treating a solution of impure base as obtained above with a mixture of acetic anhydride and pyridine (24 hr). The impure product (4.22 g) was chromatographed over 130 g of alumina (Merck, neutral, Brockmann activity I; eluents:ether ethyl acetate mixtures). Two crystallizations from ethyl acetate (cooled to -40°) gave pure N,N'-diacetyl-N,N'-decamethylene-1,4-diamino-2,5-dimethoxybenzene (1.89 g) as a white product with mp 225-226°.

IR spectrum (0.1 molar in CCl_4): 1658 cm^{-1} (amide I band).

UV spectrum (cyclohexane), λ_{max}: 205 mμ (log ε 4.33), 254 mμ (log ε 3.74), 306 mμ (log ε 3.78) and sh 228 mμ (log ε 4.10).

PMR spectrum (10%, in $CDCl_3$): τ 3.15 (s), arom. protons, τ 6.14 (s), $OC\underline{H_3}$, τ 5.9-6.6 (m), $NC\underline{H_2}$, τ 7.71 (s) and 8.06 (s), $C\underline{H_3}CO$, τ 8.2-9.1 (broad signal with a sharp peak at τ 9.02), remaining protons.

Anal. Calc'd for $C_{22}H_{34}N_2O_4$ (390.53): C 67.7; H 8.8; N 7.2.

Found: C 67.5; H 9.1; N 7.1.

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