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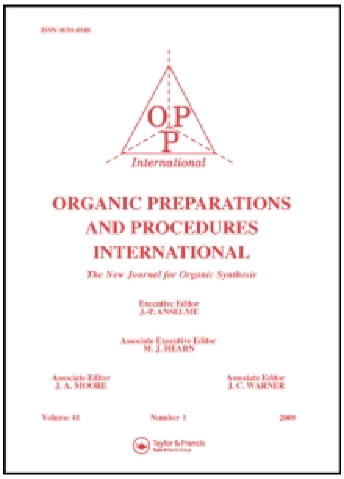

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THE COMPLETE N-ALKYLATION OF 1,4-DIAMINO-2,5-DIBROMOBENZENE AND OF 1,4-DIAMINO-2,5-DIMETHOXYBENZENE

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THE COMPLETE N-ALKYLATION OF 1,4-DIAMINO-2,5-DIBROMOBENZENE AND OF 1,4-DIAMINO-2,5-DIMETHOXYBENZENE

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The complete N-ethylation of 1,4-diamino-2,5-dibromobenzene using methods analogous to those described for p-diaminobenzene[2] did not succeed. Both IR spectra and TLC of the reaction products indicated that mixtures were formed.

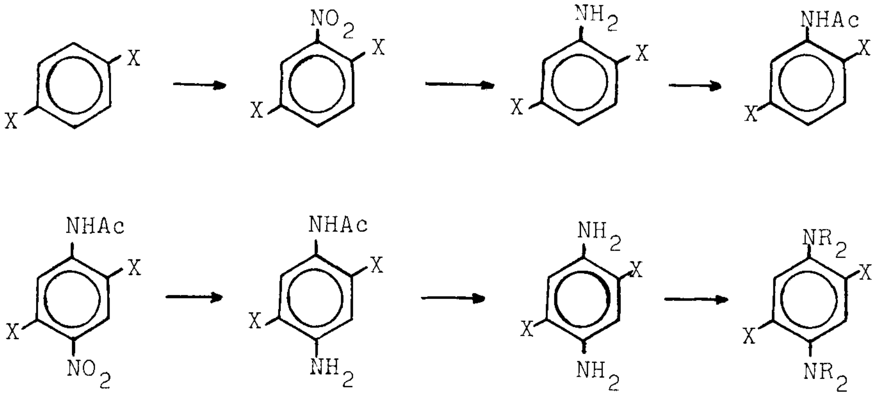
The preparation of pure N,N,N',N'-tetraethyl-1,4-diamino-2,5-dibromobenzene could, however, be effected by alkylation in DMSO using NaH as the base.

The corresponding tetramethyl compound could not be prepared in a pure state following the method of Eschweiler-Clarke,[3] a procedure which has been used for the preparation of tertiary amines which are otherwise difficult to obtain by methylation.[4]

The tetramethyl derivative could be obtained pure by application of the method of Torf and Khromov-Borisov[5] which leads, in our case, to the desired product (see Experimental Section) and not to the bis-methodides obtained in the cases investigated by Torf and Khromov-Borisov. The complete ethylation of 1,4-diamino-2,5-dimethoxybenzene was accomplished by alkylation with ethyl bromide and sodium hydroxide (see

Experimental Section), a procedure which failed for the ethylation of 1,4-diamino-2,5-dibromobenzene.

In addition, a number of derivatives of 1,4-diamino-2,5-dibromo and 1,4-diamino-2,5-dimethoxybenzenes (Scheme I) were prepared.



X = Br,OCH_3

Scheme I

EXPERIMENTAL

All melting points are uncorrected and were taken using an oil bath. Boiling points are uncorrected. UV spectra were obtained using a Zeiss spectrophotometer, model PMQ II except when otherwise indicated. Infrared spectra were recorded with a Perkin-Elmer model 125 grating spectrophotometer or with a Perkin-Elmer model 137 Infracord. PMR spectra were taken on a Varian model A-60 (w/v) with TMS as an internal standard (τ = 10.00) unless otherwise indicated. Elemental analyses were performed under the supervision of Mr. W. M. Hazenberg in our Microanalytical Department.

Dimethylsulfoxide (DMSO; Fluka) was dried over calcium hydride and distilled from this material in vacuo; b.p. 75.5-76°/14 mm; n_D^{20} 1.4792, lit.[2d] b.p. 85-87°/25 mm; n_D^{21} 1.4787.

N,N,N',N'-Tetraethyl-1,4-diamino-3,5-dibromobenzene.

To a mixture of sodium hydride (3.84 g; 160 mmole; obtained from a suspension in oil by washing it 4x with ether and drying in vacuo) and 1,4-diamino-2,5-dibromobenzene (2.66 g; 10 mmole) was added DMSO (50 ml); the temperature rose to 28°. To this mixture stirred in a nitrogen atmosphere, was added a solution of ethyl bromide (5.45 g; 50 mmole) in DMSO (40 ml) over 15 min. (the temperature was maintained between 28 and 31° by cooling). The suspension was stirred for another $2\frac{1}{2}$ hr. at the same temperature; after standing one night at room temperature, the mixture was added slowly to 200 ml of water with stirring and cooling with ice. The solid was filtered, washed with 250 ml of water, dried, and recrystallized from petroleum ether (40-60°)-methanol mixture (3:5). This product was washed with methanol (30 ml) and recrystallized from methanol (45 ml). For the recrystallizations the solutions were cooled to 0°. In this way there was obtained 1.85 g (49%; no maximum yield) of N,N,N',N'-tetraethyl-1,4-diamino-2,5-dibromobenzene as pale yellow plates, m.p. 87-88°. For spectra and analysis, this product was again crystallized from methanol (25 ml) which resulted in the isolation of 1.65 g of compound, m.p. 87.5-88.5°. TLC (silica gel; eluent: petroleum ether (60-80°)-benzene 1:4) gave one spot. The product obtained in another way, viz. by reduction of N,N'-diacetyl-N,N'-diethyl-

1,4-diamino-2,5-dibromobenzene with $LiAlH_4$, had the same Rf value and a mixed m.p. was not depressed. IR spectrum (0.1 molar, in CH_2Cl_2): no absorption due to N-H stretch vibration. UV spectrum (cyclohexane), λ_{max}: 226 mμ (log ε 4.45) and 275 mμ (log ε 4.06). PMR spectrum (10%, in $CDCl_3$): τ 2.76 (s), arom. protons, τ 6.95 (q), $N\underline{CH_2}CH_3$, τ 8.98 (t), $NCH_2\underline{CH_3}$, J = 7 cps.

Anal. Calc'd for $C_{14}H_{22}Br_2N_2$: C, 44.5; H, 5.9; Br, 42.3; N, 7.4.

Found: C, 44.8; H, 6.0; Br, 42.0; N, 7.5.

N,N,N',N'-Tetramethyl-1,4-diamino-2,5-dibromobenzene.

A mixture of 1,4-diamino-2-5,dibromobenzene (8.87 g; 33.3 mmole), calcium carbonate (7.33 g; 73 mmole), methyl iodide (38.3 g; 0.270 mole), methanol (34 ml) and water (20 ml) was refluxed under a nitrogen atmosphere. After 21 hr. the carbonate had almost disappeared and white flakes had precipitated. Refluxing was continued for another 15 hr. The mixture was then cooled to 0°, the solid was collected, washed with water (75 ml) and dried. This product (7.17 g) was extracted three times by boiling it with 100 ml of petroleum ether (60-80°) each time. The combined solution was evaporated to dryness *in vacuo*; the residue (5.11 g) was recrystallized from 50 ml of petroleum ether (60-80°). Cooling to -5° gave 4.65 g (43%) of N,N,N',N'-tetramethyl-1,4-diamino-2,5-dibromobenzene, m.p. 121-122°. TLC (silica gel: eluent, benzene) showed only one spot. IR spectrum (0.1 molar solution in CH_2Cl_2): no absorption in the range of the N-H stretch vibration or N-H deformation vibration. *UV spectrum* (96% ethanol), λ_{max}: 223 m (log ε 4.33), 269 mμ (log ε 3.94) and 310 mμ (sh). *PMR spectrum* (about 15%, in $CDCl_3$): τ 2.79 (s), arom. protons and τ 7.28 (s), NCH_3.

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

Found: C, 37.4; H, 4.6; Br, 49.8; N, 8.6.

N,N,N',N'-Tetraethyl-1,4-diamino-2,5-dimethoxybenzene.

In a sealed Carius tube, a mixture of 1,4-diamino-2,5-dimethoxybenzene-*bis*-hydrochloride (7.23 g; 30.0 mmole), ethyl bromide (24.0 g; 0.220 mole) and a solution of sodium hydroxide (10.8 g; 0.270 mole, dissolved in 30 ml of water) under nitrogen, was shaken and heated at 125-135° for 18 hr. After cooling, the mixture was diluted with 150 ml of 0.2 N sodium hydroxide solution and 150 ml of ether. The water layer was extracted 3 times with 75 ml of ether. The combined ethereal solution was washed with water (2 x 50 ml) and dried over potassium carbonate. The ether was distilled and the residue gave upon distillation *in vacuo* 7.75 g of a colorless oil, b.p. 97.5-98.5°/0.2 mm, which crystallized upon standing. Two crystallizations under a nitrogen atmosphere from a mixture of 30 ml of petroleum ether (40-60°) and 5 ml of absolute ethanol (solutions were cooled to -40°) yielded 6.02 g (71%) of pure N,N,N',N'-tetraethyl-1,4-diamino-2,5-dimethoxybenzene as a white solid, m.p. 30.5-32.0°. *IR spectrum* (neat; Infracord): no absorption at 3500-3100 cm^{-1}. *UV spectrum* (cyclohexane), λ_{max} 215 mμ (log ε 3.96), 265 mμ (log ε 3.96) and 306 mμ (log ε 3.78)

Anal. Calc'd for $C_{16}H_{28}N_2O_2$: C, 68.5; H, 10.1; N, 10.0. Found: C, 68.8; H, 10.2; N, 10.1.

1,4-Dibromo-2-nitrobenzene. The procedure of Hammond and Modic[3] was modified in the following way. To 275 ml of nitric acid (s.g. 1.52, 97-100%) was added over 0.5 hr. with stirring 165 g (0.70 mole) of pure p-dibromobenzene; during the addition the temperature of the reaction mixture was kept between 15 and 22°. The mixture was then stirred for another 0.5 hr. at 15°, poured onto ice, the precipitate collected and washed with large amounts of water. The solid was dried and crystallized 3 times from ethanol (96%). The yield of pale yellow 1,4-dibromo-2-nitrobenzene was 161 g (82%), m.p. 83.5-84.5° (lit.[6] m.p. 82°, yield not stated).

2,5-Dibromoaniline. To a boiling stirred solution of 200 g of tin(II) chloride $2H_2O$ (90%), 0.80 mole) in 150 ml of conc. hydrochloric acid, a suspension of 56.2 g (0.200 mole) of 1,4-dibromo-2-nitrobenzene in 96% ethanol (150 ml) was added in small quantities over 15 min. This manner of addition prevents, as much as possible, the elimination of the ortho bromo atom. After the addition, the mixture was refluxed for 0.5 hr. and kept for one night at room temperature. The solid, consisting of a complex of the amine with tin salt, was dried. It was stirred with 96% ethanol (175 ml) and this suspension was treated with 50% sodium hydroxide solution (200 ml). The mixture was stirred for a few minutes and then, under continuous stirring, poured into water (1000 ml). The solid was collected, washed with 2 N sodium hydroxide solution and with water, then dried in a desiccator over potassium hydroxide. The yield of 2,5-dibromoaniline was 40.4 g (80%), m.p. 54.5-55° (lit.[7] m.p. 51-52°).

2',5'-Dibromoacetanilide. To a mixture of 2,5-dibromoaniline (80.3 g; 0.320 mole) and glacial acid (100 ml) was added gradually acetic acid anhydride (75 ml). The mixture was refluxed for 15 min. and cooled to room temperature. The separation of white crystals was completed by adding 200 ml of water dropwise. The product was washed with water and, after being dried, crystallized from a mixture of benzene and petroleum ether (80-100°). For one gram of substance about 9 ml of benzene and 4 ml of petroleum ether was used. The crystals were collected, first washed with the above-mentioned mixture and then with 96% ethanol. The yield was 67.4 g (72%) 2',5'-dibromoacetanilide, m.p. 172.5-173.5° (lit.[8] m.p. 171-172°; no yield given). From the mother liquor another quantity of the compound can be obtained. Purification can also be achieved by crystallization from absolute ethanol (for 1 gram about 10 ml). IR spectrum (0.1 molar, in CH_2Cl_2): 3400 cm^{-1} (NH) and 1705 cm^{-1} (amide I). UV spectrum (cyclohexane), λ_{max}: 218 mμ (log ε 4.51), 243 mμ (log ε 4.13), 285 mμ (log ε 3.14) and 293 mμ (log ε 3.14).

2',5'-Dibromo-4'-nitroacetanilide. 2',5'-Dibromoacetanilide (100.0 g; 0.341 mole) was added in small quantities to conc. sulfuric acid (s.g. 1.86), stirred and cooled to -5°. To this slightly brownish mixture nitric acid (130 ml; s.g. 1.52; 97-100%) was added dropwise. The temperature was kept between -5° and -3°. After the addition, stirring at the same temperature was continued for another 30 min. The brownish-black mixture was poured onto a mixture of ice and water (about 10 l.). The precipitate was collected, washed with water (10 l.) until free from acid. After being dried, the solid was recrystallized from ethanol (2 l., 96%). The yield of the pale yellow needles of 2',5'-dibromo-4'-nitroacetanilide was 80-85%, m.p. 181-182°. Two additional crystallizations from ethanol (96%) raised the m.p. to 181.5-182.0°.

IR spectrum (0.2 molar solution in dichloromethane); a N-H band at 3400 cm^{-1} and an amide I band at 1715 cm^{-1}.

UV spectrum (cyclohexane), λ_{max}: 223 mμ (log ε 4.29), 246 mμ (log ε 4.14), 254 mμ (sh) and 287 mμ (log ε 3.91).

PMR spectrum (10%, CD_3COCD_3): τ 1.20 (s), 1.70 (s) and 7.70 (s), respectively H_3 and H_6 of the benzene ring and CH_3CO. The absence of coupling between the phenyl protons is in agreement with the accepted structure. In addition to the 3 singlets, the spectrum in $CDCl_3$, showed a broad signal at ∿ 2.25 (NH).

Anal. Calc'd for $C_8H_6Br_2N_2O_3$: C, 28.4; H, 1.8; Br, 47.3; N, 8.3.

Found: C, 28.6; H, 1.9; Br, 47.8; N, 8.3.

2,5-Dibromo-4-nitroaniline. This compound, already described by Jackson and Calhane,[9] was obtained by hydrolysis of 2',5'-dibromo-4'-nitroacetanilide (8.00 g; 23.7 mmole) in ethanol

(96%, 170 ml) was treated with conc. hydrochloric acid (10 ml). The solution was refluxed (1 hr), 15 ml of conc. hydrochloric acid was added and refluxing continued for 3 hr. Water (150 ml) was then added whereupon a yellow substance crystallized. The ethanol was removed by distillation and the residue made slightly alkaline. The precipitate was collected, washed with water, dried and crystallized from ethanol (96%, 110 ml). Yield 7.0 g (99%) yellow 2,5-dibromo-4-nitroaniline, m.p. 180.0-181.5° (lit.[9] m.p. 174-175°; yield very low). IR spectrum (KBr): 3480 and 3370 cm^{-1}, sharp (NH_2 stretch). UV spectrum (96% ethanol), λ_{max}: 217 mμ (log ε 4.25), 268 mμ (log ε 3.80) and 359 mμ (log ε 3.98). PMR spectrum (10% CD_3COCD_3) τ values: 1.79 (s) and 2.77 (s) (respectively H_3 and H_6 of benzene ring) and a broad band at 3.5-4.1 (NH_2).

Anal. Calc'd for $C_6H_4Br_2N_2O_2$: Br, 54.0; N, 9.5.
Found: Br, 53.8; N, 9.5.

1,4-Diamino-2,5-dibromobenzene. The reduction of 2',5'-dibromo-4'-nitroacetanilide was carried out as described for 1,4-dibromo-2-nitrobenzene. The reduction was accompanied by hydrolysis of the acetyl group resulting in the formation of 1,4-diamino-2,5-dibromobenzene. From 101.4 g (0.300 mole) of 2',5'-dibromo-4'-nitroacetanilide, 72.3 g of a white substance, m.p. 184-187°, was obtained. Crystallization from benzene (about 1.7 l.) gave 65.0 g (82%) of pure 1,4-diamino-2,5-dibromobenzene, m.p. 187-188° (dec.) (lit.[9] m.p. 183-184°, yield not given). The compound is also easily purified by sublimation at 140-150°/0.1 mm. IR spectrum (KBr): 3370 cm^{-1}, sharp, 3275 cm^{-1}, broad (w) and 3170 cm^{-1}, broad. UV spectrum (cyclohexane), λ_{max}: 217 mμ (log ε 4.32), 332 mμ (log ε 3.62) and a shoulder at 245 mμ. PMR spectrum (5%, CD_3COCD_3): τ values: 3.01 (s) (arom. protons) and a broad signal at 5.4-6.0 (NH_2).

Anal. Calc'd for $C_6H_6Br_2N_2$: C, 27.1; H, 2.3; Br, 60.1; N, 10.5.

Found: C, 27.2; H, 2.3; Br, 60.1; N, 10.6.

The pure dibenzylidene derivative (0.91 g; 28%) was obtained as yellow crystals, m.p. 215-215.5°. IR spectrum (Nujol): 1640 cm^{-1} (C=N). UV spectrum (96% ethanol), λ_{max}: 207 mμ (log ε 4.55), 264 mμ (log ε 4.59) and 355 mμ (log ε 4.26).

Anal. Calc'd for $C_{20}H_{14}Br_2N_2$: Br, 36.2; N, 6.3.
Found: Br, 36.5; N, 6.3.

N,N'-Diacetyl-1,4-diamino-2,5-dibromobenzene. To a mixture of 1,4-diamino-2,5-dibromobenzene (13.3 g; 0.050 mole)and acetic acid (60 ml) was added, in small portions, 20 ml of acetic acid anhydride. During the addition a precipitate formed. The mixture was refluxed for 45 minutes, cooled to room temperature and 75 ml of water was added. The solid was collected, washed with water, dried and crystallized twice from a mixture of N,N'-dimethylformamide and absolute ethanol; 100 ml of DMF and 33 ml of ethanol were used per gram substance and a temperature of 95° maintained when it was dissolved. N,N'-Diacetyl-1,4-diamino-2,5-dibromobenzene was obtained as white needles, m.p. 325-327° (65%). IR spectrum (KBr): 3280 cm^{-1}, broad; 1660 cm^{-1} (amide I). UV spectrum (dioxan), λ_{max}: 269 mμ (log ε 4.27) and 305 mμ (sh).

Anal. Calc'd for $C_{10}H_{10}Br_2N_2O_2$: C, 34.3; H, 2.9; Br, 45.7. Found: C, 34.5; H, 2.9; Br, 46.0.

N,N'-Ditosyl-1,4-diamino-2,5-dibromobenzene. Obtained as a white compound (yield 81%), m.p. 276.5-277.5°. The m.p. did not change after crystallization from a 1:3 mixture of DMF and methanol. IR spectrum (KBr): 3240 cm^{-1} (N-H), 1360, 1330 and 1157 cm^{-1} (SO_2). UV spectrum (96% ethanol), λ_{max}: 225 mμ (log ε 4.62) and 257 mμ (log ε 4.12) (sh).

Anal. Calc'c for $C_{20}H_{18}Br_2N_2O_4S_2$: C, 41.8; H, 3.2; Br, 27.8; N, 4.9; S, 11.2.
Found: C, 41.8; H, 3.2; Br, 27.7; N, 4.4; S, 10.7.

1,4-Dimethoxy-2-nitrobenzene. Prepared according to Blackhall and Thomson.[10]

The crude product was used for the preparation of 2',5'-dimethoxyacetanilide. IR spectrum (KBr): 1520 cm^{-1}(NO_2). UV spectrum (96% ethanol), λ_{max}: 219 mμ (log ε 4.23), 256 mμ (log ε 3.41) and shoulders at 242 and 268 mμ.

2',5'-Dimethoxyacetanilide. 1,4-Dimethoxy-2-nitrobenzene (36.6 g; 0.200 mole) and platinum oxide (150 mg) in absolute ethanol (200 ml) was hydrogenated in a Parr apparatus at about 3 atm. pressure. The temperature was kept below 45° by cooling. After the theoretical quantity of hydrogen was taken up, the reaction mixture was filtered and the filtrate evaporated to dryness under diminished pressure.

The residue, a nearly white solid, was refluxed for 1 hr with acetic acid (100 ml) and acetic anhydride (60 ml) in a nitrogen atmosphere. The solution was evaporated to dryness _in vacuo_. The crude 2',5'-dimethoxyacetanilide could be purified by crystallization from a mixture of acetone and water. The yield was 28.0 g (72%), m.p. 90-91° (lit.[11] m.p. 91°). _IR spectrum_ (0.25 molar, CH_2Cl_2): 3415 cm^{-1} (N-H) and 1688 cm^{-1} (amide I). _UV spectrum_ (96% ethanol), λ_{max}: 245 mμ (log ε 4.01) and 299 mμ (log ε 3.79).

2',5'-Dimethoxy-4'-nitroacetanilide. This compound was prepared according to Rubenstein.[12] Yellow needles (methanol) m.p. 167-168°. _IR spectrum_ (0.25 molar, CH_2Cl_2): 3410 cm^{-1} (N-H) and 1700 cm^{-1} (CO-NH). _UV spectrum_ (96% ethanol), λ_{max}: 258 mμ (log ε 3.91), 296 mμ (log ε 3.77), 369 mμ (log ε 3.90) and 226 mμ (log ε 4.12) (sh). _PMR spectrum_ (10% $CDCl_3$), τ values: 1.60 (s), hydrogen at 3 position of benzene ring, 2.49 (s) hydrogen at 6 position of benzene nucleus, 6.05 and 6.09 (OCH_3), 7.74 (CH_3CO) and a broad band at ∿ 2.0 (NH).

Anal. Calc'd for $C_{10}H_{12}N_2O_5$: N, 11.7.
Found: N, 11.7.

1,4-Diamino-2,5-dimethoxybenzene. 2',5'-Dimethoxy-4'-nitroacetanilide (30.0 g; 0.125 mole), 350 ml of absolute ethanol and 175 mg of platinum oxide were shaken at 40-50° with hydrogen at a pressure of about 3 atmospheres in a Parr apparatus. The original solid material dissolved slowly during the reaction and after some time a white product precipitated. The end of the reaction (after abour 4 hr) was characterized by a change of the suspension from yellow to nearly colorless, and this dissolved when treated with 200 ml of conc. hydrochloric acid. The catalyst was filtered and the solution was refluxed for 0.5 hr (N_2-atmosphere) while stirring and after 5 minutes a white precipitate formed. The mixture was stored at 0° overnight, filtered, and the solid consisting of crude 1,4-diamino-2,5-dimethoxybenzene-bis-hydrochloride was washed first with a cold mixture of absolute ethanol (50 ml) and ether (100 ml), then with ether (150 ml). The yield was 94-100%. The crude salt (30.0 g; 124.4 mmole) was dissolved in 440 ml of water, and under nitrogen, was made slightly alkaline. The precipitate was filtered, washed with water and after drying, sublimed at 140°/0.1 mm to give pure 1,4-diamino-2,5-dimethoxybenzene (19.36 g; 93%) as a white substance, m.p. 212.5-214° (N_2-atmosphere). In the solid state, the product can be stored unchanged for months when exposed to the air. This is in striking contrast to the statement of Lane and Williams[13] who observed a quick oxidation of the corresponding diethoxy compound under these circumstances. Solutions of the compound in air become red-brown in color. IR spectrum (KBr): 3375 cm^{-1} (sharp), 3280 cm^{-1} and 3170 cm^{-1}. UV spectrum (96% ethanol), λ_{max}: 241 mμ (log ε 3.87), 282 mμ (log ε 3.79), 310 mμ (log ε 3.71) and 352 mμ (sh).

PMR spectrum (10%, CF_3COOH): singlet τ 2.56 (protons of benzene ring) and τ 5.97 (OCH_3).

Anal. Calc'd for $C_8H_{12}N_2O_2$: C, 57.1; H, 7.2; N, 16.7. Found: C, 57.2; H, 7.3; N, 16.7.

Derivatives

Bis-hydrochloride. The above mentioned crude salt was crystallized (0.5 g from a mixture of methanol (90 ml) and 7.5 ml of conc. hydrochloric acid in a nitrogen atmosphere), yielding 82% of pure salt as a colorless substance melting with decomposition at about 328°.

Anal. Calc'd for $C_8H_{14}Cl_2N_2O_2$: C, 29.4; N, 11.6. Found: C, 29.4; N, 11.4.

4'-Amino-2',5'-dimethoxyacetanilide. This compound could be isolated if after the reduction of 2',5'-dimethoxy-4'-nitroacetanilide the reaction product was not hydrolyzed, but dissolved in benzene. The catalyst was then filtered and the filtrate evaporated to dryness *in vacuo*.

The residue, consisting of a silver colored solid was crystallized under nitrogen successively from benzene and from a mixture of benzene and ethanol (10:1). The 4'-amino-2',5'-dimethoxyacetanilide was obtained in a yield of 70%, m.p. 148-149°. IR spectrum (0.2 molar, CH_2Cl_2): 3420 and 3375 cm^{-1} and at 1670 cm^{-1} (amide). UV spectrum (cyclohexane), λ_{max}: 261 mμ (log ε 4.15) and 313 mμ (log ε 3.94).

Anal. Calc'd for $C_{10}H_{14}N_2O_3$: C, 57.1; H, 6.7; N, 13.3.
Found: C, 57.4; H, 6.8; N, 13.6.

N,N'-Diacetyl-1,4-diamino-2,5-dimethoxybenzene. Colorless crystals, m.p. 290-291° (dec). IR spectrum (KBr): Bands at 3255 and 3150 cm^{-1} (N-H) and 1660 cm^{-1} (amide).

Anal. Calc'd for $C_{12}H_6N_2O_4$: N, 11.1.
Found: N, 10.9.

N,N'-Dimesyl-1,4-diamino-2,5-dimethoxybenzene. Crude 1,4-diamino-2,5-dimethoxybenzene-bis-hydrochloride (33.0 g; 0.137 mole) was treated (N_2-atmosphere) with pure pyridine (300 ml). To this mixture was added with stirring, a solution of mesyl chloride (78 g; 0.68 mole) in purified pyridine (300 ml). The reaction mixture became red and a precipitate formed. The suspension was (under nitrogen) stirred for another 5 hr. and then acidified with 2 l. of 6 N hydrochloric acid. After standing for one night at room temperature the solid was filtered, washed with water (1.5 l.) and dried. The crude product (41.0 g) was dissolved in a mixture of 0.6 N potassium hydroxide solution (850 ml) and methanol (7,5 ml), stirred for 1 hr. with decolorizing coal, filtered and the filtrate acidified with 4 N hydrochloric acid. The precipitate was collected, washed with water (until free from acid), then with methanol (150 ml) and crystallized from a mixture of DMF (300 ml) and methanol (150 ml). The product N,N'-dimesyl-1,4-diamino-2,5-dimethoxybenzene was obtained as a white crystalline substance, m.p. 245-246° in a yield of 37.2 g (84%).

IR spectrum (KBr): 1322 and 1146 cm^{-1} (SO_2 vibrations).

UV spectrum (96% ethanol), λ_{max}: 210 mμ (log ε 4.49), 238 mμ (log ε 4.08) and 300 mμ (log ε 3.84).

Anal. Calc'd for $C_{10}H_{16}N_2O_6S_2$: C, 37.0; H, 5.0; N, 8.6; S, 19.8.

Found: C, 37.2; H, 5.0; N, 8.7; S, 19.6.

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