[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

DERIVATIVES OF 2,5-DIBROMONITROBENZENE

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RECEIVED APRIL 8, 1929 PUBLISHED AUGUST 7, 1929

Of the dibromonitrobenzenes, the 2,5-isomeride[1] has been studied but little. Three derivatives were found on record, and of these only one was a reduction product, *viz.*, the aniline, which was prepared in the usual way.[2] The present report includes observations on the aniline and on products obtainable by reduction in alkaline mixtures.

Of the products theoretically possible by alkaline reduction the azoxy and azo compounds were obtained in small yields. Attempts to prepare the hydrazo compound and the isomeric benzidine by starting with the nitro compound were unsuccessful. When the azo compound was subjected to the action of stannous chloride and hydrochloric acid, as directed by Jacobson,[3] with the hope of converting it to the hydrazo compound and rearranging the latter to the benzidine, a yield of 42% of 2,5-dibromo-aniline was obtained and nothing else could be isolated from the mixture.

Following the directions of Knoevenagel,[4] 2,5-dibromo-aniline was diazotized with amyl nitrite and converted into a nearly colorless diazonium salt that decomposed explosively above 117°. Boiling this salt with water gave no phenol, but reduction of its alcoholic solution with stannous chloride and hydrochloric acid gave 2,5-dibromo-aniline and 59% of the ammonia required by the equation.[5] The diazonium salt readily reacts with

$$C_6H_3Br_2N_2X + 6(H) \longrightarrow C_6H_3Br_2NH_2 + NH_4X$$

the aniline, when the experiment is conducted by Noelting and Kopp's[6] method, to give a nearly quantitative yield of the diazoamino compound, which latter could not be rearranged to the aminoazo body. Reduction of this product with stannous chloride and hydrochloric acid gave 2,5-

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[1] Many derivatives of the 2,5-dichloro compound have been prepared by Noelting and Kopp [*Ber.*, **38**, 3506 (1905)] and by Crowell and Raiford [THIS JOURNAL, **42**, 145 (1920)].

[2] Meyer and Stüber [*Ann.*, **165**, 180 (1873)] obtained the aniline by reduction of the nitro compound with tin and hydrochloric acid, but recorded no yield. Meldola and Andrews [*Proc. Chem. Soc.*, 11, 110 (1895)] could not reduce with zinc dust and acetic acid, and found that the alcoholic solution must be boiled with tin and hydrochloric acid to give satisfactory results.

[3] Jacobson, *Ann.*, **287**, 147 (1895).

[4] Knoevenagel, *Ber.*, **23**, 2995 (1890).

[5] Fischer [*Ann.*, **190**, 78 (1878)] found that the diazonium salt from aniline is reduced by sodium sulfite to phenylhydrazine, while Meyer and Lecco [*Ber.*, **16**, 2976 (1883)] obtained the same results with stannous chloride and hydrochloric acid.

[6] Noelting and Kopp, *Ber.*, **38**, 3507 (1905).

dibromo-aniline and ammonia.[7] With β-naphthol the diazonium salt coupled to give an azo dye.

Derivatives of 2-Nitro-4-bromo-anisole.—This ether,[8] obtained here from the dibromonitrobenzene by Blom's[9] method, was converted to the corresponding azoxy compound in four different experiments. The methyl alcoholic solution was reduced (1) with metallic sodium as directed by Starke;[10] (2) with sodium amalgam by Kanonnikow's[11] method; (3) by Brand's[12] electrolytic method and (4) by treatment with aqueous sodium hydroxide and zinc dust at 45° or below. The corresponding azo compound was obtained by (1) reduction of the azoxy derivative with sodium amalgam at 70°; (2) by reduction of the nitro-anisole with sodium amalgam at 70°; (3) by electrolytic reduction of the nitro compound as directed by Elbs and Kopp,[13] and (4) by treatment of the alcoholic solution of the nitro compound with zinc dust and alkali, as recommended by Starke for reduction of *o*-nitro-anisole. Continued treatment with excess of zinc gave a small yield of what appeared to be the hydrazo compound.[14] This product was converted to the benzidine by the usual treatment with hydrochloric acid, while an attempt to benzoylate it caused rearrangement and the formation of the dibenzoylbenzidine.[15] The benzidine was further characterized by diazotization and coupling the product with β-naphthol to give an azo dye.

2-Nitro-4-bromophenetole obtained by Blom's method was converted into the azo compound by the various methods described above for the anisole. Attempts to reduce further with stannous chloride and hydrochloric acid did not give the hydrazo compound and the expected diphenetidine, but 4-bromo-*o*-phenetidine. However, the hydrazo compound was obtained in small yield directly from the nitro compound, by the method used with the anisole. It was readily oxidized to the azo compound as explained above.

Experimental Part

The 2,5-dibromonitrobenzene used as starting material in this work was obtained by nitration of *p*-dibromobenzene, as outlined by Crowell and Raiford[16] for the chlorine compound. The derivatives were prepared by the standard methods indicated, the details of which will be omitted. The physical constants and analytical data for these products are shown in Tables IA and IB.

Summary

1. 2,5-Dibromo-aniline has been converted into a diazonium salt that did not give a phenol when boiled with water, but which coupled with β-

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[7] Fischer [*Ann.*, **190**, 78 (1878)] found that the unsubstituted compound gave aniline and phenylhydrazine.

[8] First prepared by Staedel [*ibid.*, **217**, 57 (1883)].

[9] Blom, *Helv. Chim. Acta*, **4**, 1029 (1921).

[10] Starke, *J. prakt. Chem.*, [2] **59**, 206 (1899).

[11] Kanonnikow, *Ber.*, **18** (Ref.) 611 (1885).

[12] Brand, *J. prakt. Chem.*, **67**, 145 (1903).

[13] Elbs and Kopp, *Z. Elektrochem.*, **5**, 108 (1898).

[14] The reactivity of the compound toward oxygen prevented the isolation of a pure product. When air was bubbled for 48 hours through a ligroin solution of this material at 50° it was converted into the azo compound.

[15] Stern, *Ber.*, **17**, 379 (1884).

[16] Crowell and Raiford, THIS JOURNAL, **42**, 147 (1920).

Table IA

Derivatives of 2,5-Dibromonitrobenzene

	Compound	Solvent	Crystal form	Yield, %
1	Tetrabromoazoxybenzene	Alcohol	....	15
2	Tetrabromoazobenzene	Alcohol	Red needles	13
3	Tetrabromodiazoaminobenzene	Alcohol	Yellow needles	Nearly quant.
4	Dibromophenyldiazonium chloride	Alc. and ether	Colorless granules	....
5	Dye	Alc. and ligroin	Red needles	....
6	5,5′-Dibromoazoxy-*o*-anisole	Alcohol	Straw - colored needles	60
7	5,5′-Dibromoazo-*o*-anisole	Pyridine	Red needles	81
8	5,5′-Dibromohydrazo-*o*-anisole	Ligroin	Nearly colorless needles	Very small
9	6,6′-Dibromodianisidine	Alcohol	Fawn-colored plates	60
10	Dibenzoyldianisidine	Ligroin	Granules	Nearly quant.
11	Dye	....	Amorphous red powder	....
12	5,5 - Dibromohydrazo - *o* - phenetole	Ligroin	Colorless needles	14

Table IB

Derivatives of 2,5-Dibromonitrobenzene

	Formula	M. p., °C.	Subs., g.	Ag hal., g.	Halogen, %	
					Calcd.	Found
1	$C_{12}H_6ON_2Br_4$	217	0.1027	0.1500	62.25	62.15
2	$C_{12}H_6N_2Br_4$	247	.0973	.1466	64.25	64.12
3	$C_{12}H_7N_3Br_4$	185[a]	.1028	.1463	62.38	61.97
4	$C_6H_3N_2ClBr_2$	...	.1103	.1194	65.49	65.32
5	$C_{16}H_{10}ON_2Br_2$	...	.1562	.1444	39.37	39.34
6	$C_{14}H_{12}O_3N_2Br_2$	121	.1014	.0914	38.46	38.37
7	$C_{14}H_{12}O_2N_2Br_2$	238	.1034	.0970	40.00	39.91
8	$C_{14}H_{14}O_2N_2Br_2$	120–121[b]	....	....	...	...
9	$C_{14}H_{14}O_2N_2Br_2$	168	.1089	.1017	39.80	39.74
10	$C_{28}H_{22}O_4N_2Br_2$	274	.1997	.1218	26.22	25.95
11	$C_{34}H_{24}O_4N_4Br_2$	...	.2972	.1561	22.47	22.35
12	$C_{16}H_{18}O_2N_2Br_2$	171–172	.1199	.1044	37.20	37.05

[a] A product which appeared to have this composition was reported by Meldola and Andrews, *Proc. Chem. Soc.*, 11, 110 (1895), to melt at 234–235°.

[b] Analytical data were not satisfactory.

naphthol to give an azo dye. It coupled with aniline to give a diazo-amino compound, but the latter could not be rearranged into the isomeric amino-azo compound. Treatment of the diazonium salt with stannous chloride and hydrochloric acid did not give the expected hydrazine, but regenerated the amine and split off ammonia.

2. Of the reduction products expected in alkaline mixtures, only the azoxy and the azo compounds were obtained.

3. The monobromo-anisole and phenetole prepared from the dibromonitrobenzene gave, in addition, the respective hydrazo compounds.

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