440. *Dehalogenation during the Reduction of Halogenonitroarenes with Lithium Aluminium Hydride.*

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Lithium aluminium hydride removes iodine when reducing aromatic iodonitro-compounds; bromine is removed if adjacent to the nitro-group or to a chlorine atom. Chlorine is not eliminated.

According to Gaylord[1] and Mićović and Mihailović,[2] lithium aluminium hydride does not normally reduce aromatic halides, but Braithwaite, Holt, and Hughes[3] reported that iodine is eliminated when 4,4′-di-iodo-3,3′-dimethyl-4,4′-dinitrobiphenyl is so reduced. When 33 halogenonitroarenes were reduced with an excess of the hydride we found that chlorine was never eliminated, that iodine was always eliminated, and that bromine was eliminated when *ortho* to the nitro-group or to a chlorine atom; thus the 3-bromo-2-chloro-, 3-bromo-4-chloro-, and 4-bromo-3-chloro-nitroarenes were converted into dichloroazo-compounds. 1,2-Dibromo-3-methyl-5-nitrobenzene gave a complex mixture from which only 3,3′-dibromo-5,5′-dimethylazobenzene was isolated in small amount. 1-Bromo-2-nitronaphthalene gave good yields of 2,2′-azonaphthalene but 1-nitronaphthalene gave a tar from which no azonaphthalene could be isolated.

When less lithium aluminium hydride was used, azoxy-compounds were isolated (Table 1). Only in the case of 3-iodonitrobenzene which gave 3,3′-di-iodoazoxybenzene was a halogen retained which would have been eliminated with an excess of hydride.

Experimental

Halogenonitrobenzenes.—Most of the halogenonitroarenes were prepared from commercially available amines, or their bromination products, by Hodgson and Walker's modification of the Sandmeyer reaction. 1,5-*Dibromo*-2-*chloro*-3-*nitrobenzene* formed colourless needles, m. p. 61° (Found: C, 22·95; H, 0·6; N, 4·2; Hal., 60·55. $C_6H_2Br_2ClNO_2$ requires C, 22·65; H, 0·6; N, 4·4; Hal., 62·0%). 2-*Bromo*-1-*chloro*-3-*methyl*-5-*nitrobenzene* formed pale yellow rhombs, m. p. 97° (Found: C, 33·95; H, 2·0; N, 5·4. $C_7H_5BrClNO_2$ requires C, 33·6; H, 2·0; N, 5·6%).

1,3-Dibromo- and 1,3-dichloro-5-nitrobenzene were prepared by deamination of the 2,5-dihalogeno-4-nitroanilines.

1,3,5-*Tribromo*-2-*nitrobenzene*.—2,4,6-Tribromoaniline (1·0 g.) in acetic acid (10 ml.) was treated with 80% w/v hydrogen peroxide (1 ml.). The solution was heated on a water-bath for 4 hr. and then poured into water. The precipitate was filtered off and recrystallised from ethanol to give the nitro-compound (0·8 g.), m. p. 123—124° (lit., 125°).

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[1] Gaylord, "Reductions with Complex Metal Hydrides," Interscience Publ., Inc., New York, 1956.

[2] Mićović and Mihailović, "Lithium Aluminium Hydride in Organic Chemistry," Monograph 237, Serbian Acad. Science, Belgrade, 1955.

[3] Braithwaite, Holt, and Hughes, *J.*, 1958, 4073.

TABLE 1.

Reductions of halogenonitro-compounds (1 mol.) with lithium aluminium hydride (1 mol.).

Nitrobenzene deriv.	M. p. Found	M. p. Lit.	Azobenzene deriv.	M. p. Found	M. p. Lit.
2-Cl *	32°	32°	2,2′-Cl_2	134—136°	137°
2-Cl-5-Me	4—5	7	2,2′-Cl_2-5,5′-Me_2	164—165	†
2-Cl-5-MeO	32	32	2,2′-Cl_2-5,5′-$\mathrm{(MeO)}_2$	172	†
3-Cl	44	44	3,3′-Cl_2	101	101
4-Cl *	83	83	4,4′-Cl_2	184	184
4-Cl-3-Me	43—44	44	4,4′-Cl_2-3,3′-Me_2	166	162—163
2-Br *	40	41	(Azobenzene)	69 ‡	69
2-Br-5-Me	33	33—34	3,3′-Me_2	55 ‡	55
2-Br-5-MeO	45	45	3,3′-$\mathrm{(MeO)}_2$	76 ‡	76—77
2-Br-5-$\mathrm{CO_2Et}$ *	72—73	74	3,3′-$\mathrm{(CH_2{\cdot}OH)}_2$	105 ‡	106
3-Br	53	54	3,3′-Br_2	125	125
3-Br-5-Me	83	83	3,3′-Br_2-5,5′-Me_2	163	162—163
4-Br *	127	127	4,4′-Br_2	203	205
4-Br-3-Me	78	78	4,4′-Br_2-3,3′-Me_2	141	†
2-I	49	49	(Azobenzene)	69 ‡	69
3-I	33	38	(Azobenzene)	68—69 ‡	69
4-I	174	174	(Azobenzene)	69 ‡	69
2,5-Cl_2	54	56	2,5,2′,5′-Cl_4	187	188—189
3,4-Cl_2	41	43	3,4,3′,4′-Cl_4	158	195·5 ¶
3,5-Cl_2	65	65·4	3,5,3′,5′-Cl_4	196	158·5 ¶
2,3-Br_2-5-Me	65	63—65	3,3′-Br_2-5,5′-Me_2	162 ‡	162—163
2,5-Br_2 *	85	85	3,3′-Br_2	125 ‡	125
3,4-Br_2-5-Me	105—106	105—106	3,3′-Br_2-5,5′-Me_2	140 ‡	141
			+ Mixture ††	124—130	—
3,5-Br_2	104	106	3,5,3′,5′-Br_4	244	244—245
2,3,5-Br_3	81	§	3,5,3′,5′-Br_4	244 ‡	244—245
2,4,6-Br_3	123—124	125	4,4′-Br_2	205 ‡	205
2-Cl-3-Br-5-Me	60	60	2,2′-Cl_2-5,5′-Me_2	164 ‡	164—165
2-Cl-3,5-Br_2	61	†	2,2′-Cl_2-5,5′-Br_2	226 ‡	226
2-Cl-5-Br	72	72	2,2′-Cl_2-5,5′-Br_2	226	†
3-Cl-4-Br	61—62	62	3,3′-Cl_2	99 ‡	101
4-Cl-3-Br-5-Me	97	†	4,4′-Cl_2-3,3′-Br_2-5,5′-Me_2	260	†
			4,4′-Cl_2-3,3′-Me_2	154 ‡	166
5-Cl-2-Br	70	70	3,3′-Cl_2	97—98 ‡	101
3,5-Cl_2-4-Br	87—88	87—88	3,5,3′,5′-Cl_4	196 ‡	196
(1-Br-2-NO_2-naphthalene)	97	98	(2,2-′Azonaphthalene)	208	208

Nitro-compound : $\mathrm{LiAlH}_4 = 4 : 1$

			Azoxybenzene derivative		
2-Br			(Azoxybenzene)	36	36
3-I			3,3′-I_2	115	118
2-Cl-5-Me			2,2′-Cl_2-5,5′-Me_2	144 †	
2,5-Br_2			3,3′-Br_2	109	111
2,4,6-Br_3			4,4′-Br_2	176	175
2-Br-5-Cl			3,3′-Cl_2	97	97
2-Br-5-MeO			3,3′-$\mathrm{(MeO)}_2$	70	73

* Commercial samples. † New compound. ‡ Mixed m. p. with authentic sample within ±1° § Körner (*Gazzetta*, 1874, **4**, 348) gave 119·5° (corr.), Claus and Wellbaum (*J. prakt. Chem.*, 1897, **56**, 58) gave 81°. ¶ The m. p. for the two isomers were evidently transposed in the paper by Kremer and Bendich (*J. Amer. Chem. Soc.*, 1940, **62**, 1279). †† See text.

TABLE 2.

Azobenzene	Found (%) C	H	N	Hal	Required (%) C	H	N	Hal
2,2′-Dichloro-5,5′-dimethyl-	59·3	4·3	10·4	—	60·1	4·3	10·1	—
2,2′-Dichloro-5,5′-dimethoxy-	54·1	4·1	8·9	22·5	54·0	3·9	9·0	22·8
4,4′-Dibromo-3,3′-dimethyl-	45·5	3·4	7·4	43·1	45·6	3·3	7·6	43·5
2,2′-Dichloro-5,5′-dibromo-	35·0	1·5	6·6	—	35·1	1·5	6·8	—
4,4′-Dichloro-3,3′-dibromo-5,5′-dimethyl-	39·5	2·4	6·9	—	38·4	2·3	6·4	—
4,4′-Dichloro-3,3′-dimethyl-	60·4	4·5	10·1	25·4	60·3	4·3	10·0	25·2

Reduction with an Excess of Lithium Aluminium Hydride.—The nitro-compound (0·2 g.) in dry ether was treated with lithium aluminium hydride (0·2 g.) in dry ether. The mixture was kept for 1 hr. at room temperature and then heated on a water-bath for 15 min. After cooling, water was added, the mixture was filtered and evaporated to dryness, and the residue recrystallised. The yields of azo-compound were 75—95% except from the reduction of *o*-chloronitrobenzene (40%) and *o*-bromonitrobenzene (35%), where the reaction was very vigorous and much tar was formed. The m. p. of the products are in Table 1. Analyses of new compounds are in Table 2.

Reduction with Less Lithium Aluminium Hydride.—Only 0·05 g. of hydride was added and the reaction was stopped by addition of water after 10 min. The products were separated on alumina. Light petroleum eluted the unchanged nitro-compound, and benzene eluted the azoxybenzene and azobenzene, in that order. The azoxybenzenes so obtained are listed in Table 1. 3,3′-Di-iodoazoxybenzene formed yellow needles from acetic anhydride (Found: C, 32·7; H, 1·8; I, 55·6. $C_{12}H_8I_2N_2O$ requires C, 32·2; H, 1·8; I, 56·4%). 2,2′-*Dichloro-5,5′-dimethylazoxybenzene* formed yellow feathery needles from ethanol (Found: C, 57·0; H, 3·94; N, 9·1. $C_{14}H_{12}Cl_2N_2O$ requires C, 57·0; H, 4·07; N, 9·5%).

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