

**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<sup>1</sup> and Mićović and Mihailović,<sup>2</sup> lithium aluminium hydride does not normally reduce aromatic halides, but Braithwaite, Holt, and Hughes<sup>3</sup> 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°).

<sup>1</sup> Gaylord, "Reductions with Complex Metal Hydrides," Interscience Publ., Inc., New York, 1956.

<sup>2</sup> Mićović and Mihailović, "Lithium Aluminium Hydride in Organic Chemistry," Monograph 237, Serbian Acad. Science, Belgrade, 1955.

<sup>3</sup> Braithwaite, Holt, and Hughes, *J.*, 1958, 4073.

TABLE I.

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

Nitrobenzene deriv.	M. p.		Azobenzene deriv.	M. p.	
	Found	Lit.		Found	Lit.
2-Cl *	32°	32°	2,2'-Cl <sub>2</sub>	134—136°	137°
2-Cl-5-Me	4—5	7	2,2'-Cl <sub>2</sub> -5,5'-Me <sub>2</sub>	164—165	†
2-Cl-5-MeO	32	32	2,2'-Cl <sub>2</sub> -5,5'-(MeO) <sub>2</sub>	172	†
3-Cl	44	44	3,3'-Cl <sub>2</sub>	101	101
4-Cl *	83	83	4,4'-Cl <sub>2</sub>	184	184
4-Cl-3-Me	43—44	44	4,4'-Cl <sub>2</sub> -3,3'-Me <sub>2</sub>	166	162—163
2-Br *	40	41	(Azobenzene)	69 †	69
2-Br-5-Me	33	33—34	3,3'-Me <sub>2</sub>	55 †	55
2-Br-5-MeO	45	45	3,3'-(MeO) <sub>2</sub>	76 †	76—77
2-Br-5-CO <sub>2</sub> Et *	72—73	74	3,3'-(CH <sub>2</sub> OH) <sub>2</sub>	105 †	106
3-Br	53	54	3,3'-Br <sub>2</sub>	125	125
3-Br-5-Me	83	83	3,3'-Br <sub>2</sub> -5,5'-Me <sub>2</sub>	163	162—163
4-Br *	127	127	4,4'-Br <sub>2</sub>	203	205
4-Br-3-Me	78	78	4,4'-Br <sub>2</sub> -3,3'-Me <sub>2</sub>	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 <sub>2</sub>	54	56	2,5,2',5'-Cl <sub>4</sub>	187	188—189
3,4-Cl <sub>2</sub>	41	43	3,4,3',4'-Cl <sub>4</sub>	158	195-5 ¶
3,5-Cl <sub>2</sub>	65	65-4	3,5,3',5'-Cl <sub>4</sub>	196	158-5 ¶
2,3-Br <sub>2</sub> -5-Me	65	63—65	3,3'-Br <sub>2</sub> -5,5'-Me <sub>2</sub>	162 †	162—163
2,5-Br <sub>2</sub> *	85	85	3,3'-Br <sub>2</sub>	125 †	125
3,4-Br <sub>2</sub> -5-Me	105—106	105—106	3,3'-Br <sub>2</sub> -5,5'-Me <sub>2</sub>	140 †	141
3,5-Br <sub>2</sub>	104	106	{ 3,3'-Br <sub>2</sub> -5,5'-Me <sub>2</sub>	124—130	—
2,3,5-Br <sub>3</sub>	81	§	+ Mixture ††	244	244—245
2,4,6-Br <sub>3</sub>	123—124	125	3,5,3',5'-Br <sub>4</sub>	244 †	244—245
2-Cl-3-Br-5-Me	60	60	4,4'-Br <sub>2</sub>	205 †	205
2-Cl-3,5-Br <sub>2</sub>	61	†	2,2'-Cl <sub>2</sub> -5,5'-Me <sub>2</sub>	164 †	164—165
2-Cl-5-Br	72	72	2,2'-Cl <sub>2</sub> -5,5'-Br <sub>2</sub>	226 †	226
3-Cl-4-Br	61—62	62	2,2'-Cl <sub>2</sub> -5,5'-Br <sub>2</sub>	226	†
4-Cl-3-Br-5-Me	97	†	3,3'-Cl <sub>2</sub>	99 †	101
5-Cl-2-Br	70	70	{ 4,4'-Cl <sub>2</sub> -3,3'-Br <sub>2</sub> -5,5'-Me <sub>2</sub>	260	†
3,5-Cl <sub>2</sub> -4-Br	87—88	87—88	{ 4,4'-Cl <sub>2</sub> -3,3'-Me <sub>2</sub>	154 †	166
(1-Br-2-NO <sub>2</sub> -naphthalene)	97	98	3,3'-Cl <sub>2</sub>	97—98 †	101
			3,5,3',5'-Cl <sub>4</sub>	196 †	196
			(2,2'-Azonaphthalene)	208	208

Nitro-compound : LiAlH<sub>4</sub> = 4 : 1

	Azoxybenzene derivative	
	(Azoxybenzene)	
2-Br	36	36
3-I	115	118
2-Cl-5-Me	144 †	
2,5-Br <sub>2</sub>	109	111
2,4,6-Br <sub>3</sub>	176	175
2-Br-5-Cl	97	97
2-Br-5-MeO	70	73

\* Commercial samples. † New compound. ‡ Mixed m. p. with authentic sample within  $\pm 1^\circ$   
 § Körner (*Gazzetta*, 1874, **4**, 348) gave  $119.5^\circ$  (corr.), Claus and Wellbaum (*J. prakt. Chem.*, 1897, **56**, 58) gave  $81^\circ$ . ¶ 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 (%)				Required (%)			
	C	H	N	Hal	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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