453. *The Reduction and Hydrolysis of* o-, m-, *and* p-*Nitrophenetoles.*

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THE views of Lapworth, Robinson, and Ingold have provided a satisfactory explanation of the effect of the nitro-group on the mobility of an atom or radical ortho or para to it in the benzene ring, but the complementary effect of this radical on the reducibility of the nitro-group does not appear to have been investigated from a similar standpoint. Bacon and Richardson (this vol., p. 884) have shown that *m*-chloronitrobenzene is reduced in $N/2$-ethyl-alcoholic potassium hydroxide solution free from acetaldehyde to the extent of 50% after 96 hours' heating at 60°, the *o*-isomeride gives only 9·5% of reduction product, and the *p*-compound none at all.

The experiments to be described show that the reducibility of the nitrophenetoles is in the same order, the yields of *m*-, *o*-, and *p*-reduction products (azoxyphenetoles + phenetidines) being respectively 92%, 50%, and 10% after 96 hours' heating at 60° in 1·6N-alcoholic potash free from acetaldehyde. Electrolytic reduction of the three nitrophenetoles in alcoholic sodium acetate solution in exactly similar cells arranged in series gave 61%, 41%, and 17% respectively of the *m*-, *o*-, and *p*-azoxyphenetoles. It is therefore concluded that the order of reducibility, meta > ortho > para, is not dependent on the particular conditions of reduction in the experiments with alcoholic potash. In these the three nitrophenetoles were heated at 60° in aldehyde-free ethyl-alcoholic potash of concentrations varying from 0·125*N* to 2·9*N*, and the yields of azoxyphenetoles, phenetidines, nitrophenols, and unchanged nitrophenetoles determined. The results show that little reduction occurs when the concentration of the potash is below 1·4*N*, but that a small increase above this figure causes a large increase in the yields of azoxyphenetoles and phenetidines, particularly in the case of *m*-nitrophenetole.

The order of ease of hydrolysis is the reverse of the order of reducibility : after 96 hours' heating at 60° with 1·4*N*-alcoholic potash the yields of nitrophenols are : *p*-, 24% ; *o*-, 12% ; *m*-, 7%. That this order does not depend on the alkaline medium is shown by refluxing the three nitrophenetoles with 20% hydrochloric acid : 10%, 8%, and 6% respectively of *p*-, *o*-, and *m*-nitrophenol are obtained after 72 hours' boiling.

EXPERIMENTAL.

Reduction and Hydrolysis with Alcoholic Potassium Hydroxide.—*o*- and *p*-Nitrophenetoles were prepared by the method of Richardson (*J. Soc. Chem. Ind.*, 1926, **55**, 200T) and redistilled and recrystallised respectively. *m*-Nitrophenetole was prepared from silver *m*-nitrophenoxide and ethyl iodide and recrystallised. EtOH (95%) was freed as far as possible from acetaldehyde by refluxing with *m*-phenylenediamine hydrochloride and redistilled, and a standard solution of alc. KOH prepared. 100 C.c. of this solution were heated with 1·67 g. (0·01 mol.) of nitrophenetole for 96 hr. in a thermostat at 60°. Excess alkali was then neutralised with dil. H_2SO_4, and the EtOH distilled off on the water-bath. Unchanged nitrophenetole was recovered by steam distillation and filtration or ether extraction of the distillate, sufficient Na_2CO_3 to dissolve all nitrophenol being added before steam distillation in order to prevent the formation of globules of a low-melting eutectic of azoxyphenetole and nitrophenol which tenaciously retained the steam-volatile nitrophenetole. A negligible quantity of phenetidine was volatilised with the nitrophenetole in the steam distillation.

The insol. reduction product—crude azoxyphenetole—was washed, dried, and weighed without purification. The *o*- and *p*-isomerides, recryst. from ligroin, melted at 102° and 134° respectively. Phenetidine was extracted by Et_2O from the filtrate, dried, recovered, and weighed. The product was identified by acetylation with AcCl : the recryst. *o*-, *m*-, and *p*-acetphenetidides melted respectively at 79°, 95°, and 135°. The mother-liquors were finally acidified with dil. H_2SO_4 and filtered from any tarry matter which separated, and the nitrophenol was recovered by ether extraction, dried, and weighed. *m*-Azoxyphenetole was identified by combustion : m. p. 49° after repeated recrystn. from ligroin and EtOH (Found : C, 67·3 ; H, 6·05 ; N, 9·7. Calc. : C, 67·1 ; H, 6·3 ; N, 9·8%). When distilled with excess of Fe powder, it gave *m*-azophenetole, m. p. 88° after recrystn. from EtOH and ligroin.

The following table shows the yields obtained from *p*-, *o*-, and *m*-nitrophenetoles when the concn. of the KOH was varied between 0·125 and 2·9*N*.

	Nitrophenetole.		Products, %.			
KOH, *N*.	Initial, g.	Recovered, %.	Nitrophenol.	Azoxyphenetole.	Phenetidine.	Total reduction products.
0·125	1·670 *p*-	96·2	1·7	0·0	0·0	0·0
0·50	1·670	92·8	5·5	0·0	0·0	0·0
0·64	1·670	84·4	8·5	0·0	0·0	0·0
0·75	1·670	86·2	10·8	0·0	0·0	0·0
1·21	1·670	82·0	18·6	1·5	0·0	1·5
1·40	1·670	78·8	23·7	3·5	0·0	3·5
1·60	1·670	70·9	24·6	7·3	0·4	7·7
1·60	1·670	70·6	23·9	9·8	1·1	10·9
1·75	1·670	60·6	23·7	22·9	2·0	24·9
1·79	1·670	22·6	18·6	39·2	19·7	58·9
1·86	1·670	17·1	17·3	57·5	—	—
1·86	1·670	17·8	19·2	56·2	16·8	73·0
2·10	1·670	6·0	13·5	67·1	10·7	77·8
2·90	1·670	0·0	12·8	72·0	15·0	87·0
0·50	1·670 *o*-	89·1	0·6	0·0	0·0	0·0
1·00	1·670	89·0	5·3	0·0	0·0	0·0
1·17	1·563	86·8	10·1	2·6	0·2	2·8
1·38	1·170	85·5	11·7	2·0	0·5	2·5
1·49	1·685	70·3	10·0	7·6	12·1	19·7
1·59	1·735	45·0	11·4	27·6	15·0	42·6
1·64	1·670	13·2	11·3	52·2	19·0	71·2
1·68	1·890	7·7	9·6	50·0	20·3	70·3
1·75	1·670	4·0	8·3	62·7	21·3	84·0
1·96	1·670	1·6	1·3	67·3	21·1	88·4
2·54	2·000	0·0	0·6	76·3	23·0	99·3
0·79	1·670 *m*-	90·4	0·7	0·0	0·0	0·0
0·86	1·670	82·9	1·9	1·9	0·0	1·9
0·97	1·670	84·8	3·2	1·0	0·0	1·0
0·99	1·670	81·0	1·4	2·4	0·0	2·4
1·11	1·670	83·6	3·1	2·5	0·0	2·5
1·22	1·670	82·4	4·5	3·8	0·0	3·8
1·32	1·670	79·1	4·5	4·5	0·0	4·5
1·38	1·670	77·7	4·5	4·9	0·0	4·9
1·40	1·670	26·7	7·7	39·2	15·5	54·7
1·43	1·670	12·0	6·0	50·4	18·6	69·0
1·47	10·020	1·2	5·5	59·4	21·8	81·2
1·50	1·670	7·8	7·4	60·2	22·6	82·8
1·90	4·175	0·0	6·6	71·6	27·3	98·9

Electrolytic Reduction.—*m*-, *p*- (1·67 g.), and *o*- (1·788 g.) Nitrophenetoles, dissolved in 35 c.c. of 95% EtOH containing 15 c.c. of 5% NaOAc aq., were reduced in cells, as described by Elbs (" Electrolytic Preparations "), arranged in series, by a current of 2·7 amp. at 100 v. for 1·5 hr.; the current was then 1·5 amp. Unchanged nitrophenetoles were recovered by steam distillation, and azoxyphenetoles filtered off and weighed. The yields were as follows :

	Meta.	Ortho.	Para.
Azoxyphenetole:	m. p. 45°	m. p. 78°	m. p. 145°
	0·880 g. (61·5%)	0·640 g. (41·8%)	0·251 g. (17·6%)
Nitrophenetole:	0·371 g. (22·2%)	0·765 g. (42·8%)	1·153 g. (69·0%)

The results were not greatly affected by interchanging the porous pots and electrodes, and reducing with a current of 5—6 amp. for 30 min.

Acid Hydrolysis.—The nitrophenetoles were refluxed for 72 hr. with 20% HCl (120 c.c.), and the products made alkaline. Unchanged nitrophenetoles were removed in steam, and nitrophenols extracted from the acidified mother-liquors with Et_2O.

	Meta.			Ortho.			Para.		
	Initial,	Recovered,		Initial,	Recovered,		Initial,	Recovered,	
	g.	g.	%.	g.	g.	%.	g.	g.	%.
Nitrophenetole :									
(I)	1·67	1·23	73·6	2·20	1·885	85·7	1·67	1·36	81·4
(II)	1·28	1·17	91·4	2·10	1·77	84·3	1·67	1·35	80·8
Nitrophenol :									
(I)	—	0·09	6·5	—	0·16	8·7	—	0·135	9·8
(II)	—	0·065	6·2	—	0·14	8·0	—	0·14	10·2

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