115. *The Reduction of Nitro-compounds by Aldehydes in Ethyl-alcoholic Potassium Hydroxide Solution.*

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It has been shown by one of us (J., 1926, 522) that *p*-chloronitrobenzene is not reduced when heated at 60° in *N*/2-ethyl-alcoholic potash solution free from acetaldehyde, but that considerable reduction to *p*-dichloroazoxybenzene results when the alcohol contains acetaldehyde. Experiments have now been made with the object of discovering whether alcoholic potash at the same temperature and concentration would reduce nitrobenzene, the isomeric chloronitrobenzenes, nitrotoluenes, nitrophenols, nitroanilines, nitrobenzoic acids, and α-nitronaphthalene. In the absence of acetaldehyde azoxy-compounds were only obtained from *m*-chloronitrobenzene (50%), *o*-chloronitrobenzene (9·5%), *m*-nitrotoluene (3%), and α-nitronaphthalene (3%), the yields stated being isolated after 96 hours' heating at 60°. In the presence of acetaldehyde of *N*/2-concentration the amount of reduction to azoxy-compound was increased only in the case of the chloronitrobenzenes, which yielded respectively 74%, 28%, and 31% of *m*-, *o*-, and *p*-dichloroazoxybenzenes.

However, complex products, insoluble in ligroin and acetone, were obtained from *m*-(19%) and *o*-chloronitrobenzene (9%), *m*-(13%) and *p*-nitrotoluene (59%), *m*-(13%) and *p*-nitrobenzoic acid (68%), and nitronaphthalene (93%) with alcoholic potash free from acetaldehyde, and in the presence of acetaldehyde considerable yields of similar insoluble products were formed by all the nitro-compounds investigated.

p-Chloronitrobenzene gave an insoluble *product*, $C_{26}H_{24}O_4NCl$, and the yield was increased from 6% to 106% by weight as the concentration of acetaldehyde was raised from 0·25 to 2·0*N* in *N*/2-alcoholic potash solution at 60°.

On the other hand, a similar raising of the concentration of the potash in *N*/2-alcoholic acetaldehyde solution resulted in a greater increase in the yield of *pp*′-dichloroazoxybenzene (57% with 2*N*-potassium hydroxide) than in that of the insoluble product.

Although the constitution of this compound has not been elucidated, it is believed to be a condensation product of either *p*-chloronitrosobenzene or, more probably, β-*p*-chlorophenylhydroxylamine, for both these compounds yielded a similar product, together with *pp*′-dichloroazoxybenzene, when heated under similar conditions with alcoholic potash. *p*-Nitrophenetole was also formed from both *p*-chloronitrosobenzene and β-*p*-chlorophenylhydroxylamine.

Experiments were also made to discover whether other aldehydes will reduce *p*-chloronitrobenzene in *N*/2-ethyl-alcoholic potash solution at 60°. After 96 hours' heating, the yields of *pp*′-dichloroazoxybenzene or *pp*′-dichloroazobenzene were: with acetaldehyde, 31%, m. p. 154°; β-phenylpropaldehyde, 30%, m. p. 154°; piperonal, 30%, m. p. 183·5°; propaldehyde, 25%, m. p. 164·5°; heptaldehyde, 12%, m. p. 184°; butaldehyde, 9%, m. p. 175·5°; dextrose, 8%, m. p. 161·5°; benzaldehyde, 6%; formaldehyde, 3%; phenylacetaldehyde, 2·5%, at *N*/2-concentrations. Less than 1% of *pp*′-

dichloroazoxybenzene was formed in the presence of cinnamaldehyde, vanillin, anisaldehyde, salicylaldehyde, and protocatechualdehyde. Acetone also caused reduction to the extent of 5% (m. p. 169°). An insoluble product, similar to that formed in the presence of acetaldehyde, was obtained in large amount only in the presence of protocatechualdehyde.

From the results obtained it is not possible to assess the effect of the various substituent groups on the reducibility of the nitro-group, for the origin of the insoluble products is doubtful. However, in the case of the three chloronitrobenzenes it is clear that *mm'*-dichloroazoxybenzene is far more readily formed than the *o*- and *p*-isomerides, and it may be concluded that the reaction

$$C_6H_4Cl{\cdot}NO_2 \longrightarrow C_6H_4Cl{\cdot}NO \longrightarrow C_6H_4Cl{\cdot}NH{\cdot}OH$$

proceeds most rapidly with the chlorine in the meta-position, since Brand and Mahr (*J. pr. Chem.*, 1931, **131**, 97) have shown that *m*- and *p*-chloronitrosobenzenes condense with the corresponding β-chlorophenylhydroxylamines with approximately the same velocity.

EXPERIMENTAL.

Reduction of Nitro-compounds by N/2-*Ethyl-alcoholic Potassium Hydroxide* (a) *containing* N/2-*Acetaldehyde,* (b) *free from Acetaldehyde.*—Ethyl alcohol (68 O.P.) was refluxed with caustic soda (1—2%) for 8 hours, distilled off, and boiled with *m*-phenylenediamine hydrochloride (1%) for 8 hours. The final distillate, the first 50 c.c. being rejected, was used for preparing a *N*-solution of potassium hydroxide, which was filtered from potassium carbonate, and did not darken to more than a pale straw colour in a week, if kept in the dark. The absence of acetaldehyde was confirmed by heating the solution, diluted with an equal volume of the purified alcohol, with *p*-chloronitrobenzene (about 4%) at 60°. A trace of acetaldehyde was sufficient to cause the solution to become dark brown in a few hours, but it remained pale yellow even after 96 hours if free from aldehyde.

Each nitro-compound (0·05 g.-mol.) was heated at 60° for 96 hours in a solution made by diluting 100 c.c. of the *N*-alcoholic potash (*a*) with 100 c.c. of a *N*-solution of freshly distilled acetaldehyde in the purified alcohol, (*b*) with 100 c.c. of the purified alcohol. The solutions were then just acidified with *N*-sulphuric acid and the alcohol was distilled off. Volatile nitro-compounds were recovered by steam distillation, and estimated by extraction with ether and weighing of the dried and evaporated extract. Any insoluble reduction products were then filtered off, dried, and weighed, and azo- or azoxy-compounds extracted by ligroin in a Soxhlet apparatus.

The ligroin extract was weighed and its melting point determined after recrystallisation, as it was slightly contaminated with a resinous product. The latter was then removed from any residue insoluble in ligroin by extraction with acetone, leaving finally a dark brown solid practically insoluble in all solvents. Both resin and brown solid were weighed.

In the case of the nitroanilines the solution left after distillation of the alcohol was made strongly acid and filtered from any insoluble product, and unchanged nitroaniline was extracted with ether after precipitation with alkali. The nitrophenol solutions were filtered hot to remove insoluble products, and extracted with ether. The melting points and weights of the extracts showed that these nitro-compounds were practically unaffected by alcoholic potash at 60°.

The nitrobenzoic acids, precipitated with excess of mineral acid, were filtered off together with any other products, and extracted, the *o*-isomeride with chloroform, and the *m*- and *p*-isomerides with ether. No azoxy-compound or other product was dissolved by these solvents, for the extracts had the correct melting points for the pure nitro-acids. Any insoluble residue was weighed, and extracted with ligroin and acetone to separate azoxy-compounds and resin respectively. Table I shows the results obtained (*a*) in the presence, (*b*) in the absence of acetaldehyde, and Table II shows the effect of increasing either the aldehyde concentration or the potassium hydroxide concentration in the case of *p*-chloronitrobenzene.

TABLE I.

Showing the effect of *N*/2-potassium hydroxide in purified ethyl alcohol at 60° on various nitro-compounds.

(*a*) Acetaldehyde in *N*/2-concentration. (*b*) In the absence of acetaldehyde.

		Nitro-compound recovered, %.		Ligroin-soluble azoxy-compounds, %.		Product insoluble in ligroin.					
						Crude unextr., %.		Acetone-soluble, %.		Acetone-insoluble, %.	
Substance.	W., g.	(*a*).	(*b*).	(*a*).	(*b*).	(*a*).	(*b*).	(*a*).	(*b*).	(*a*).	(*b*).
m-Chloronitrobenzene ...	7·92	9·4	20·8	73·7	50·4	33·3	19·2	22·1	15·3	11·1	3·9
o-Chloronitrobenzene ...	7·92	41·7	72·7	27·8	9·5	38·8	9·4	33·4	5·8	5·4	3·6
p-Chloronitrobenzene ...	7·92	49·0	102·0	30·8	0·0	21·9	0·0	19·8	0·0	9·5	0·0
m-Nitrotoluene	6·85	82·1	78·6	0·8	3·0	17·5	12·8	16·6	11·3	0·9	1·5
o-Nitrotoluene	6·85	69·3	87·2	5·4	0·23	17·6	1·7	12·0	0·0	5·5	0·0
p-Nitrotoluene	22·82	—	43·2	—	0·0	—	58·9	—	0·0	—	0·0
m-Nitroaniline	6·40	—	93·6	—	0·18	—	4·7	—	1·2	—	3·5
o-Nitroaniline	4·28	—	99·8	—	0·0	—	0·0	—	0·0	0·0	0·0
p-Nitroaniline	6·40	—	99·9	—	0·0	—	0·0	—	0·0	0·0	0·0
m-Nitrophenol	6·95	88·4	99·2	0·0	0·0	24·0	0·3	—	0·0	—	0·0
o-Nitrophenol	6·95	85·2	100·0	2·2	0·0	13·1	0·0	12·3	0·0	0·8	0·0
p-Nitrophenol	6·95	—	100·0	—	0·0	—	0·0	—	0·0	—	0·0
m-Nitrobenzoic acid	8·35	53·8	83·3	0·1	0·15	41·6	12·7	7·5	1·6	34·1	11·1
o-Nitrobenzoic acid	8·35	57·0	100·0	1·0	0·0	35·6	0·0	29·6	0·0	6·0	0·0
p-Nitrobenzoic acid	8·35	16·7	13·5	0·3	0·0	75·1	68·4	13·8	7·0	61·3	61·4
a-Nitronaphthalene	8·65	2·9	3·2	4·2	3·4	107·6	92·5	79·1	70·0	28·5	22·3
Nitrobenzene	6·15	76·0	99·8	1·4	0·0	15·8	0·0	15·6	0·0	0·2	0·0

TABLE II.

Showing the effects of varying acetaldehyde and potassium hydroxide concentrations on the reduction of *p*-chloronitrobenzene in ethyl alcohol at 60°.

$CH_3\cdot CHO$, conc., *N*.	KOH, conc., *N*.	Nitro-compound recovered.		Azo- and azoxy-compound.			Acetone-soluble.		Acetone-insoluble.	
		W.	W., %.	W.	Theory, %.	M. p.	W.	W., %.	W.	W., %.
0·00	0·50	8·04	102·0	0·00	0·0	—	0·00	0·0	0·00	0·0
0·25	0·50	5·20	66·0	1·47	22·0	154°	0·57	6·2	0·49	6·3
0·50	0·50	3·86	49·0	2·06	30·8	154	1·56	19·8	0·74	9·4
1·00	0·50	1·98	25·2	2·20	32·9	153·5	2·31	29·3	3·52	47·9
2·00	0·50	1·08	13·7	1·18	17·6	161	3·07	38·9	8·34	105·8
0·50	0·00	7·88	100·0	0·00	0·0	—	0·00	0·0	0·00	0·0
0·50	0·25	5·36	68·0	0·84	12·6	154	1·23	15·6	0·56	7·1
0·50	0·50	3·86	49·0	2·06	30·8	154	1·56	19·8	0·74	9·4
0·50	1·00	2·36	30·0	3·03	45·4	154	1·73	22·0	1·05	13·4
0·50	2·00	1·19	15·1	3·83	57·4	154	1·98	25·1	1·23	15·6

The Insoluble Product from p-*Chloronitrobenzene*.—Several specimens of this compound were prepared by heating *p*-chloronitrobenzene at 60° in a *N*-solution of potassium hydroxide in ethyl alcohol containing 44 g. of acetaldehyde per litre. The product was washed and thoroughly extracted with acetone to remove all azoxy- or azo-compounds and aldehyde-resin. The brown residue, decomp. 200°, was insoluble in benzene, ligroin, tetrachloroethylene and carbon tetrachloride and practically insoluble in methyl alcohol and acetone (Found in three separate specimens: C, 69·7, 69·3, 69·5; H, 5·1, 5·2, 5·3; N, 3·1, 3·0, 3·1; Cl, 7·7, 7·6, —. $C_{26}H_{24}O_4NCl$ requires C, 69·4; H, 5·3; N, 3·1; Cl, 7·9%).

Reduction of p-*Chloronitrobenzene by Other Aldehydes or Acetone in Ethyl-alcoholic Potassium Hydroxide Solution*.—Sufficient of the aldehyde, or acetone, was dissolved in 100 c.c. of purified alcohol to give a *N*-solution, *p*-chloronitrobenzene (0·05 g.-mol.) added, and the solution mixed with 100 c.c. of the *N*-alcoholic potash. After 96 hours' heating at 60°, chloronitrobenzene and nitrophenetole were recovered by steam distillation as before, but were not separated from any unchanged aldehyde, or acids derived from them which were also volatile in steam. Non-volatile solids were then filtered off after the addition of sufficient sodium carbonate to dissolve any acids formed from the aldehyde.

The washed and dried residues were extracted with ligroin to isolate any *pp'*-dichloroazoxybenzene or *pp'*-dichloroazobenzene, and the approximate percentage of each was determined from the melting points of the products by means of the following melting points of prepared mixtures of the pure substances:

pp'-Dichloroazobenzene, %	0·0	12·5	25·0	37·5	50·0	62·5	75·0	87·5	100·0
M. p. of mixture	154°	160·5°	165°	169°	172°	175°	178°	181°	183·5°

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