126. *The Reducing Action of Glycols in Alkali. Part II.*[1]

By Wadie Tadros, Moheb Sadek Ishak, and Edward Bassili.

Nitro-aromatic compounds are reduced by sodium 2-hydroxyethoxide in ethylene glycol to give the azo-compounds but, according to conditions, azoxy-compounds may be formed in addition and are, in fact, intermediate products. In the presence of a *para*-halogen atom, an ether or the azo- and azoxy-compound or a mixture may be obtained depending on the concentration of alkali.

Aromatic nitro-compounds are readily reduced by sodium 2-hydroxyethoxide in ethylene glycol, which had been shown[1] to convert substituted benzaldehydes into the corresponding stilbenes, alcohols, and acids. The glycol appears to be oxidised in the process.[2] Nitrobenzene was readily reduced by sodium 2-hydroxyethoxide in ethylene glycol, the

---

[1] Part I, Tadros, Ekladius, and Sakla, *J.*, 1954, 2351.

[2] Fry and Bowman, *J. Amer. Chem. Soc.*, 1930, **52**, 1531; B.P. 271818/9 (*Brit. Abs.*, 1928, 360), see Simons and Ratner, *J.*, 1944, 421.

reaction being vigorous. The main product was azobenzene, but some azoxybenzene was also produced according to the concentration of the reagent. The azobenzene was composed almost exclusively of the *trans*-isomer, the *cis*-isomer being formed only in traces, if at all (tested as by Badger *et al.*[3]). If formed however, it would be converted into the *trans*-isomer at the temperature of reaction (see Hartley [4]). With *p*-chloro- and *p*-bromonitrobenzene, the course of reaction was influenced by the concentration and the relative quantity of the reagent: (A) When the alkalinity was low, with one mol. of reagent, the main product was *p*-2-hydroxyethoxynitrobenzene, a small quantity of both the azoxy- and the azo-halogen compounds being also formed. (B) With a more concentrated solution or with 2 mol. of the reagent, 4 : 4′-dichloro(or dibromo)-azoxy- and -azo-benzene were formed, together with *p*-2-hydroxyethoxynitrobenzene; with 2 mol. of reagent a small quantity of 4 : 4′-di-2″-hydroxyethoxyazobenzene was also formed. Brand [5] similarly noted that the product obtained on treatment of *o*-chloronitrobenzene with alcoholic alkoxide varied with the alcohol and with the concentration of the reagent. The formation of *p*-2-hydroxyethoxynitrobenzene was evidently due to the activation induced by the presence of the nitro-group in the *para*-position. On the other hand, in conditions (B) the alkaline medium would alter the activating power of the nitro-group, probably with reversal of the electronic shift and hence the relative increase of the electron density round the carbon atom attached to the halogen. This would hinder the S_N reaction, but would evidently aid the oxidising power of the nitro-group, leading to the formation of the azoxy- and azo-compounds. Interference with the activating nitro-substituent by the alkali, even if not accompanied by reduction, should be borne in mind in interpreting results for the S_N mechanism involved.

Reduction of *m*-chloro- and *m*-bromo-nitrobenzene gave the corresponding azoxy-compounds which on further heating were converted into the azo-compounds. *o*- and *m*-Nitrotoluene gave the azo-compounds. A number of azoxy-compounds were readily converted into the corresponding azo-compounds. *p*-Nitrotoluene reacted very vigorously and the main product consisted of an orange-red substance which was sparingly soluble in most organic solvents (cf. products obtained by Fischer and Hepp,[6] Green, Davies, and Horsfall [7]).

EXPERIMENTAL

4 : 4′-*Dichloroazoxybenzene*.—This was prepared by a modification of the method used in the preparation of azoxybenzene.[8] *p*-Chloronitrobenzene (27 g.), dextrose (42 g.), and sodium hydroxide (30 g.) in water (100 c.c.) were heated to the b. p. for 5 hr., then diluted with water and steam-distilled. The product was filtered off, and recrystallised from acetic acid to give 4 : 4′-dichloroazoxybenzene (8 g.), m. p. and mixed m. p. with an authentic sample (prepared by Willgerodt's method [9]) 153—154°.

Reactions with Sodium 2-Hydroxyethoxide in Ethylene Glycol.—(*a*) *With anisaldehyde.* In repetition of the experiment previously reported,[1] but the solution being refluxed for 3—5 min. instead of 3·5—4 hr., the same products were obtained.

(*b*) *With nitro-compounds.* The reaction was vigorous. The nitro-compound and sodium 2-hydroxyethoxide in ethylene glycol were heated for a short time at the b. p., then diluted with water and steam-distilled. With nitrobenzene the main part of the azobenzene was also allowed to steam-distil. The alkaline solution was cooled and filtered, and the product was recrystallised or fractionated if it were a mixture. The products (Table; action of *p*-chloro- and *p*-bromo-nitrobenzene not included) were identified by analysis or mixed m. p. with an authentic sample. Azoxy- and azo-compounds were usually orange-red or reddish-brown.

---

[3] Badger, Buttery, and Lewis, *J.*, 1953, 2143.
[4] Hartley, *J.*, 1938, 633.
[5] Brand, *J. prakt. Chem.*, 1903, **67**, 145.
[6] Fischer and Hepp, *Ber.*, 1893, **26**, 2231.
[7] Green, Davies, and Horsfall, *J.*, 1907, 2076.
[8] Vogel, " A Text Book of Practical Organic Chemistry," Longmans, Green and Co., London, 1st Edn., 1948, p. 604.
[9] Willgerodt, *Ber.*, 1882, **15**, 1002.

(*c*) *Reaction with azoxy-compounds.* The azo-compounds obtained were recrystallised and identified as in (*b*) (Table).

Reduction of nitro-compounds $X{\cdot}C_6H_4{\cdot}NO_2$

X	Nitro-cpd. (mol.)	Sodium (g.-atom)	Ethylene glycol (c.c.)	Heating (min.)	Solv.	Products azo (g.; m. p.)	Products azoxy (g.; m. p.)
H	0·1	0·1	25	2—3	P	1·5; 67—68°[a]	6·5; 36°
,,	,,	,,	50	5	P	5·4; 67—68	
,,	,,	,,	,,	20	P	6·5; 67—68	
,,	,,	,,	,,	75	P	6·7; 67—68	
,,	,,	,,	,,	90	P	6·7; 67—68	
,,	,,	0·2	100	3—5	P	8·0; 67—68	
o-Me	,,	0·1	50	5	E	2·0; 51	
,,	,,	,,	,,	15	E	3·0; 51	
m-Me	,,	,,	,,	60	A	8·5; 51[b]	
o-Cl	,,	,,	,,	2	P	0·1; 136[c]	
m-Cl	,,	,,	,,	3—5	A	—	13·0; 95—96[d]
	0·05	,,	,,	20—25	A	4·9; 101[e]	
m-Br	0·1	,,	,,	2	A	—	17·4; 110—111
	0·05	,,	,,	10—15	A	7·0; 125	
p-$HO{\cdot}CH_2{\cdot}CH_2{\cdot}O$	0·1	,,	,,	3—5	A	3·0; 200[g]	

Reduction of azoxy-compounds $X{\cdot}C_6H_4{\cdot}N(O){:}N{\cdot}C_6H_4{\cdot}X$

H	0·05	0·1	50	3—5	P	8·0; 67—68
2-Me	,,	,,	,,	3—5	E	10·0; 53—54
4-Cl	,,	,,	,,	3—5	An or Ac	9·6; 184—185°[h]

Solvents: A = alcohol; Ac = acetic acid; An = acetone; E = ether; P = light petroleum (b. p. 50—70°). [a] Found: C, 78·5; H, 5·4; N, 15·4. Calc. for $C_{12}H_{10}N_2$: C, 79·1; H, 5·5; N, 15·4%. [b] Found: C, 79·9; H, 6·7; N, 13·0. Calc. for $C_{14}H_{14}N_2$: C, 80·0; H, 6·7; N, 13·3%. Goldschmidt (*Ber.*, 1878, **11**, 1624) also gave m. p. 51°; others gave 54—55°. [c] Found: C, 57·0; H, 3·3; N, 11·0. Calc. for $C_{12}H_8N_2Cl_2$: C, 57·4; H, 3·2; N, 11·2%. [d] Found: N, 10·0; Cl, 26·2. Calc. for $C_{12}H_8ON_2Cl_2$: N, 10·5; Cl, 26·6%. [e] Found: C, 57·2; H, 3·4; N, 11·0; Cl, 28·5. Calc. for $C_{12}H_8N_2Cl_2$: C, 57·4; H, 3·2; N, 11·2; Cl, 28·3%. [f] Found: C, 40·9; H, 2·3; N, 7·4; Br, 44·7. Calc. for $C_{12}H_8ON_2Br_2$: C, 40·4; H, 2·2; N, 7·9; Br, 44·9%. [g] Found: C, 63·5; H, 5·9; N, 9·5. $C_{16}H_{18}O_4N_2$ requires C, 63·6; H, 6·0; N, 9·3%. [h] Found: C, 57·2; H, 3·3; N, 11·0; Cl, 28·0. Calc. for $C_{12}H_8N_2Cl_2$: C, 57·4; H, 3·2; N, 11·2; Cl, 28·3%.

Reduction of Nitrobenzene by the Sodium Derivative of Propylene Glycol.—Nitrobenzene (12·3 g.) and the sodium derivative (2·3 g.) in propylene glycol (50 c.c.) were heated at the b. p. for 3—5 min., then diluted with water and steam-distilled. Azobenzene (8·2 g.) passed over, and on recrystallisation from alcohol or light petroleum (b. p. 50—70°) formed orange-red crystals, m. p. and mixed m. p. 67—68°.

Influence of Concentration and Proportion of Reagent on the Course of the Reaction with p-*Halogeno-nitrobenzenes.* (A) (1). A solution of sodium hydroxide (4 g., 0·1 mol.) in water (10 c.c.) was added dropwise to a boiling solution of *p*-chloronitrobenzene (15·8 g., 0·1 mol.) in ethylene glycol (50 c.c.) with stirring, boiling being continued for a further 5 min. after complete addition. The colour of the solution changed to pale orange, red, and finally dark red. The product was diluted with water and steam-distilled to remove unchanged *p*-chloronitrobenzene (2·25 g.). The alkaline solution was filtered while hot, and the residue recrystallised from alcohol or acetic acid to give 4 : 4′-dichloroazoxybenzene (0·85 g.), m. p. and mixed m. p. 154—155°. The alkaline filtrate gave on cooling and further concentration *p*-2-hydroxyethoxynitrobenzene which recrystallised from water as crystals (overall yield, 9·9 g.), m. p. 83—84° (Found: C, 52·5; H, 4·9; N, 7·7. Calc. for $C_8H_9O_4N$: C, 52·5; H, 4·9; N, 7·7%). (2) A solution of sodium 2-hydroxyethoxide (from 2·3 g. of sodium; 0·1 g.-atom) in ethylene glycol (25 c.c.) was added dropwise to a boiling solution of *p*-chloronitrobenzene (15·8 g.; 0·1 mol.) in ethylene glycol (25 c.c.) as above. Steam-distillation gave unchanged material (1·5 g.). The residue was filtered off and treated with the minimum of hot alcohol. 4 : 4′-Dichloroazoxybenzene (0·75 g.), m. p. and mixed m. p. 154—155°, separated. The alcohol-insoluble fraction was recrystallised from acetone to give 4 : 4′-dichloroazobenzene (1·2 g.) as brownish-yellow crystals, m. p. and mixed m. p. 185°. The alkaline filtrate gave on cooling and concentration *p*-2-hydroxyethoxynitrobenzene (overall yield, 8·7 g.). (3) A relatively dilute solution of *p*-chloronitrobenzene (15·8 g.; 0·1 mol.) in a solution of sodium 2-hydroxyethoxide (from

2·3 g. of sodium; 0·1 g.-atom) in ethylene glycol (100 c.c.) was refluxed for 3—5 min., and the product was treated as above (unchanged *p*-chloronitrobenzene, 0·8 g.; 4 : 4′-dichloroazobenzene, 1·2 g.; and *p*-2-hydroxyethoxynitrobenzene, 12·0 g., were obtained).

(B) (i) When only 50 c.c. of ethylene glycol were used in experiment (A, 3) above, unchanged *p*-chloronitrobenzene (0·82 g.), 4 : 4′-dichloroazobenzene (3·73 g.), and *p*-2-hydroxyethoxynitrobenzene (5·54 g.) were obtained. (ii) Under similar conditions *p*-bromonitrobenzene (20·2 g.; 0·1 mol.) afforded unchanged *p*-bromonitrobenzene (0·2 g.), 4 : 4′-dibromoazobenzene [6·0 g.; orange-red crystals from benzene, m. p. 205° (Found: C, 42·4; H, 2·4; N, 8·0; Br, 46·2. Calc. for $C_{12}H_8N_2Br_2$: C, 42·4; H, 2·4; N, 8·2; Br, 47·1%)], and *p*-2-hydroxyethoxynitrobenzene (5·0 g.). (iii) Repetition of experiment (A, 3) but with 4·6 g. of sodium, gave *p*-chloronitrobenzene (0·05 g.), recovered by steam-distillation, and the residue obtained on cooling the alkaline solution was filtered off and washed with little acetone. Recrystallisation of the residue from acetone gave 4 : 4′-dichloroazobenzene (3·6 g.). The acetone mother-liquor was evaporated to dryness, and the residue treated with hot benzene. The insoluble fraction was recrystallised from alcohol, 4 : 4′-dihydroxyethoxyazobenzene (0·55 g.) separating as golden-yellow crystals, m. p. and mixed m. p. 200°. The benzene mother-liquor gave on cooling a yellow substance (0·95 g.), m. p. 145°, which is being investigated.

CHEMISTRY DEPARTMENT, FACULTY OF SCIENCE,
CAIRO UNIVERSITY, EGYPT.

[*Received, May 22nd*, 1958.]