The Action of Alkali on 2,4-Dinitrobenzaldehyde

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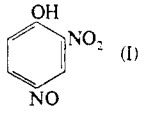
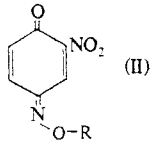
When 2,4-dinitrobenzaldehyde is treated with dilute sodium hydroxide it gives 2-nitro-4-nitrosophenol and formic acid. The phenol exists in hexane as the nitrosophenol, whilst its benzoate is obtained as a quinone oxime derivative. A mechanism for the reaction is postulated.

DURING the course of an investigation of the action of hydroxide ion on *ortho*-substituted benzaldehydes Lock [1] obtained formic acid from 2,4-dinitrobenzaldehyde, but did not identify the other products. This seemed a surprising omission and in view of our own studies in this field [2] we decided to re-investigate the reaction.

When 2,4-dinitrobenzaldehyde was treated with N-sodium hydroxide it gave as the sole isolable product a green crystalline solid, m. p. 65—66°. This was shown to be 2-nitro-4-nitrosophenol (I) from the following evidence. Elemental analysis and molecular weight determination indicated the formula, $C_6H_4N_2O_4$. The i.r. spectrum resembled that of 2,4-dinitrophenol showing a hydroxy-band at 3180 cm.$^{-1}$. The presence of an acidic group was indicated by its solubility in alkali. The u.v. spectrum showing (*inter alia*) bands at 738 and 743 mμ (ε 40 and 40) clearly indicated the presence of a nitroso-group. The n.m.r. spectrum indicated a 1,2,4-trisubstituted benzene containing one hydroxy-group. Treatment of the compound with dilute nitric acid gave a good yield of 2,4-dinitrophenol. The possibilities were thus limited to 4-nitro-2-nitroso- and 2-nitro-4-nitroso-phenols. Compound (I) was clearly shown to be the latter when it was smoothly reduced to 4-amino-2-nitrophenol with hydrogen using palladium on charcoal as catalyst. This reduction was also effected with hydriodic acid which has been shown to effective for reducing nitroso- but not nitro-groups.[3]



(I)



(II)

In non-polar solvents the compound exists as the nitrosophenol rather than the quinone oxime (II; R = H), as shown by the lack of a quinone band in the i.r. spectrum, and the weak absorption at 738 and 743 mμ in the visible spectrum. In ethanol however the compound probably exists as a quinone oxime. The solutions are yellow rather than green and the u.v. spectrum is markedly different showing bands at 244, 324, and 403 mμ (266 and 302 mμ). Attempts to isolate the quinone form by evaporating ethanolic solutions at low temperatures failed.†

Benzoylation of the phenol (I) with benzoyl chloride and potassium carbonate in benzene gave a single compound, a cream-coloured solid, m. p. 196—198°. Elemental analysis and spectral data are consistent with its formulation as the benzoate of the quinone oxime (II; R = Bz). The i.r. spectrum shows bands at 1772 (*N*-benzoate) and 1668 (quinone) cm.$^{-1}$. Its u.v.

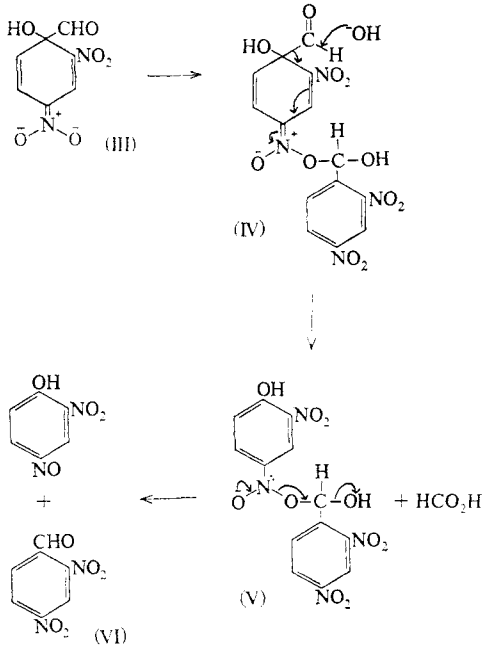
† *p*-Nitrosophenol exists in a solvent-dependent equilibrium with the quinone monoxime, the latter form predominating. The less polar the solvent the higher the concentration of the nitroso-form (A. Schors, A. Kraaijevel, and E. Havinga, *Rec. Trav. chim.*, 1955, **74**, 1243).

[1] G. Lock, *Ber.*, 1933, **66***B*, 1527, 1759.
[2] E. J. Forbes and M. J. Gregory, preceding paper.
[3] J. H. Boyer and W. Schoen, *J. Amer. Chem. Soc.*, 1956, **78**, 423.

spectrum more closely resembles that of the phenol in ethanol showing a maximum at 289 mμ.

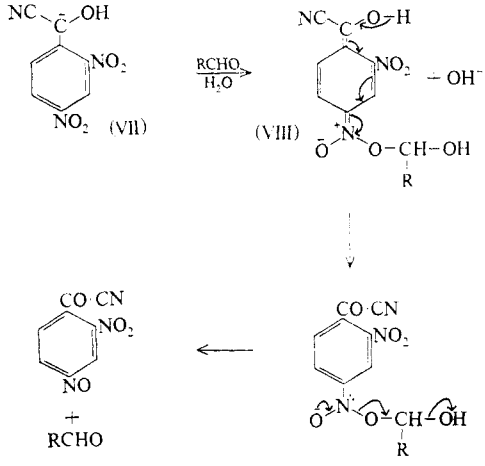
The ability of 2-nitro-4-nitrosophenol to exist in the phenolic form is attributed to hydrogen bonding between the hydroxy-group and the *ortho*-nitro-group. Ionisation of the hydroxy-group during esterification leads to a stabilised ion in which the nucleophilicity of the phenate oxygen is reduced to the point where the nitroso-oxygen effectively competes as a nucleophile. In this connection it may be recalled that *o*-nitrophenol can not be benzoylated in sodium hydroxide.

This new reaction represents a third mode of reaction between *o*-nitrobenzaldehydes and alkali.* It may obviously be viewed as an attack by hydroxide ion at C-1 or C-5, and with a view to distinguishing between these two possibilities the reaction was carried out with sodium deuteroxide in deuterium oxide. Attack at C-5 would require the incorporation of deuterium at C-1 in place of the cleaved formyl group. In practice the phenol (I) formed under these circumstances had an identical n.m.r. spectrum with that of the compound obtained under the usual conditions. The non-incorporation of deuterium implies hydroxide attack at C-1 leading to an intermediate (III).



Utilisation of the *para*- rather than the *ortho*-nitro-group as an electron sink is understandable on steric grounds, since the *aci*-nitro-group so formed needs to be coplanar with the benzene ring. Removal of an oxygen from the nitro-group requires its conversion into a leaving group. Protonation of the *aci*-nitro-group can probably be ruled out as its pK_a would be too low. Utilisation of another molecule of aldehyde acting as a Lewis acid is an attractive alternative since the intermediate (IV) will have a pK_a of 11 + and thus stability in its protonated form. The remaining steps are unexceptional. Attack by hydroxide ion on the aldehyde carbon of the intermediate (IV) leads to the intermediate (V) and formic acid. The latter has been observed to be a product of the reaction. Cleavage of the intermediate (V) then leads to the products (VI). The failure to observe this reaction with 2,6-disubstituted aldehydes may be due to the lower accessibility of the carbonyl carbon to the nucleophilic attack by what is in effect a large nucleophile [see (IV)].

A similar reaction of 2,4-dinitrobenzaldehyde has been reported by Heller.[4] Treatment of the aldehyde with aqueous potassium cyanide yielded 2-nitro-4-nitrosobenzoic acid. Attack by cyanide ion leads to the carbanion (VII) which reacts with another molecule of aldehyde (RCHO) to give (VIII). This may then break



down to give the acyl cyanide in the manner depicted. Acyl cyanides are known to cleave readily to give acids in the presence of mild alkali.[5] This would lead to the product obtained, and in a manner analogous to that advanced for our reaction.

The pH in this reaction will be much lower than in our reaction with hydroxide ion. Protonation, rather than reaction with a second molecule of aldehyde, might then serve to stabilise the *aci*-nitro-group.

Treatment of 2,6-dinitrobenzaldehyde with sodium methoxide in methanol gave a green solid similar to the nitroso-compound obtained above. However difficulties in obtaining starting material precluded its further investigation.

EXPERIMENTAL

Reaction between Sodium Hydroxide and 2,4-Dinitrobenzaldehyde.—2,4-Dinitrobenzaldehyde (5·0 g., 0·025 mole) was added to a solution of sodium hydroxide (5% w/v., 250 ml.). After 1 hr. the deep red solution was poured into a mixture of ice (100 g.) and conc. hydrochloric acid (25 ml.). The mixture was extracted with chloroform

* 2-Nitrobenzaldehyde undergoes a normal Cannizzaro reaction when treated with 35% sodium hydroxide (G. Lock, *Ber.*, 1930, **63**, 855).

[4] G. Heller, *J. prakt. Chem.*, 1923, **106**, 1.
[5] F. Hibbert and D. P. N. Satchell, *Chem. Comm.*, 1966, 516.

(5 × 100 ml.) and the combined extracts were washed with water (2 × 100 ml.) and dried ($MgSO_4$). Removal of the chloroform left an oil (2·4 g.) which was extracted with boiling benzene. The benzene extract was filtered, concentrated, and passed through a column of silica gel. Elution with benzene gave an oil which on treatment with n-hexane afforded 2-*nitro*-4-*nitrosophenol* (1·36 g., 32%) as emerald green needles, m. p. 65—66° [Found: C, 42·6; H, 2·3; N, 15·9%; *M* (thermistor at 37°), 173. $C_6H_4N_2O_4$ requires C, 42·9; H, 2·4; N, 16·7%; *M*, 168]; $\nu_{max.}$ (CS_2) 3180, 1330, 1263, 1124, and 1044 cm.$^{-1}$; $\lambda_{max.}$ (n-hexane) 216, 266, 302, 337, 738, and 743 mμ (ε 6400, 8700, 7700, 40, and 40); $\lambda_{max.}$ (EtOH) 219, 244, 324, and 403 (ε 9400, 5700, 13,200, and 15,600); τ (CH_3CN) −0·4 (singlet), 1·4 (doublet, J = 2·5 c./sec.), 3·1 (doublet, J = 9 c./sec.), and 2·5 (doublet of doublets, J = 9 and 2·5 c./sec.).

Oxidation of 2-*Nitro*-4-*nitrosophenol*.—The phenol (0·041 g.) in glacial acetic acid (1 ml.) was treated with conc. nitric acid (0·5 ml.). The solution developed a red colour and nitrous fumes were evolved. After 15 min. the solution was diluted with water and extracted with chloroform (5 × 10 ml.). The combined chloroform extracts were dried ($MgSO_4$) and evaporated to a small volume. Benzene (50 ml.) was added and the liquid evaporated. The residual solid was recrystallised from benzene–light petroleum to afford 2,4-dinitrophenol (0·017 g.) as buff needles, m. p. and mixed m. p. 112—113°.

Reduction of 2-*Nitro*-4-*nitrosophenol*.—(a) *Catalytic*. The phenol (0·05 g.) in benzene (5 ml.) was shaken under an atmosphere of hydrogen with 5% palladium on charcoal (0·01 g.) as catalyst. The reaction was stopped after the uptake of 45 ml. of hydrogen, and the solution was filtered. Evaporation of the filtrate left a red solid which was recrystallised from carbon tetrachloride. 4-Amino-2-nitrophenol (5 mg.) was thereby obtained as red needles, m. p. and mixed [6] m. p. 125—128°.

(b) *Using hydrogen iodide*. To the phenol (560 mg.) in dioxan (5 ml.) was added aqueous hydrogen iodide (6 ml., 48% w/v). After 15 min. at room temperature the precipitated iodine was removed by adding sodium sulphite. The solution was diluted with water (40 ml.), brought to pH 7 by the addition of sodium hydrogen carbonate and dil. hydrochloric acid, and extracted with ether (5 × 50 ml.). The combined ether extracts were dried ($MgSO_4$) and evaporated. Recrystallisation of the residue from carbon tetrachloride afforded 4-amino-2-nitrophenol (283 mg.) as red needles, m. p. and mixed m. p. 127—128°.

4-*Acetamido*-2-*nitrophenyl Acetate and* 4-*Acetamido*-2-*nitrophenol*.—Treatment of 4-amino-2-nitrophenol (obtained from 2,4-dinitrobenzaldehyde) with acetic anhydride afforded 4-acetamido-2-nitrophenyl acetate, m. p. 145—146°, which on hydrolysis with N-sodium hydroxide gave 4-acetamido-2-nitrophenol, m. p. 161—162°. Both compounds were identical with specimens obtained from authentic 4-amino-2-nitrophenol.[6]

3-*Nitro*-p-*benzoquinone* 1-O-*Benzoyloxime*.—To 2-nitro-4-nitrosophenol (121 mg.) in benzene (10 ml.) was added benzoyl chloride (0·217 g.) and anhydrous potassium carbonate (0·30 g.). The mixture was heated under reflux for 10 min. and filtered. The residue was washed with hot benzene (20 ml.) and the combined benzene solution evaporated. The residual semi-solid was extracted with hot benzene (10 ml.). Concentration of the extract afforded colourless needles (0·037 g.) of 3-*nitro*-p-*benzoquinone* 1-O-*benzoyloxime*, m. p. 196—198° (Found: C, 50·4; H, 4·2; N, 11·8. $C_{13}H_8N_2O_5$ requires C, 50·4; H, 4·5; N, 11·7%); $\nu_{max.}$ (CH_2Cl_2) 1772, 1668, 1600, 1032, 1004, and 990 cm.$^{-1}$; $\lambda_{max.}$ (CH_2Cl_2) 289 mμ (ε 8700).

Reaction of 2,4-*Dinitrobenzaldehyde with Sodium Deuteroxide*.—A solution of sodium deuteroxide was prepared by adding sodium–lead alloy (5·3 g., 8·8% Na) to deuterium oxide (20 ml.). When dissolution of sodium was complete the lead was removed and 2,4-dinitrobenzaldehyde (0·505 g.) added. After 1 hr. the solution was acidified with 4N-hydrochloric acid and extracted with chloroform (8 × 25 ml.). The combined extracts were dried ($MgSO_4$) and evaporated. The residue was extracted with benzene (5 ml.) and the solution chromatographed on silica gel. Elution with benzene afforded a green oil, which on further chromatography (silica gel) afforded the pure 2-nitro-4-nitrosophenol (75 mg.) as green needles. Its n.m.r. (CH_3CN) and i.r. (CS_2) spectra were identical to those of 2-nitro-4-nitrosophenol obtained earlier.

[7/1127 *Received, August 25th*, 1967]

[6] A. Girard, *Bull. Soc. chim. France*, 1924, **35**, 772.