

## Reactions of 1,2-Dinitrophenylethanols. Intramolecular Participation by the Nitro Group

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The reaction of 1,2-di(*o*-nitrophenyl)ethanol (**1**) under acidic conditions gave *o,o'*-dinitrostilbene (7 %), 2-(*o*-nitrophenyl)isatogen (**2**) (8 %), and 3-(*o*-nitrobenzoyl)anthranil (**3**) (6 %). 1-(*o*-Nitrophenyl)-2-(*p*-nitrophenyl)ethanol under the same conditions gave *o,p'*-dinitrostilbene (2 %), 2-(*p*-nitrophenyl)isatogen (21 %) and 3-(*p*-nitrobenzoyl)anthranil (7 %). 2-(*o*-Nitrophenyl)-1-(*p*-nitrophenyl)ethanol gave its tosylate (trace) and *o,p'*-dinitrostilbene. *o*-Nitrotolan provided 3-benzoylanthranil (27 %) and 2-phenylisatogen (16 %) as products.

Some time ago, we reported the synthesis of 1,2-di(*o*-nitrophenyl)ethanol (**1**) from *o*-nitrotoluene.<sup>1</sup> In order to verify the structure of **1**, dehydration with *p*-toluenesulfonic acid was attempted. However, a rather complex reaction mixture was obtained, which contained only traces of *o,o'*-dinitrostilbene.

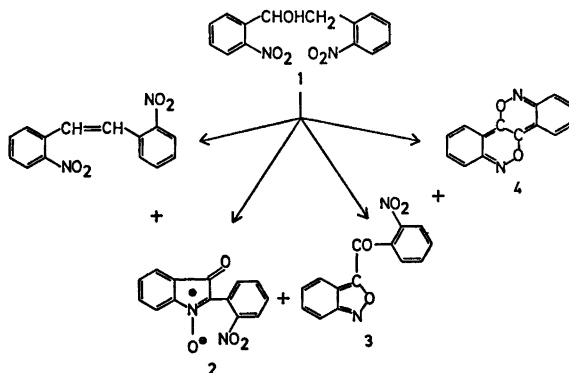
We recently reported the reactions of *o*-nitrobenzyl alcohol<sup>2</sup> and of 1-(*o*-nitrophenyl)-2-phenylethanol<sup>3</sup> under acidic conditions. The relationship between one of the nitro groups

and the hydroxyl group in 1,2-di(*o*-nitrophenyl)ethanol (**1**) is the same as in the former two substances, and **1** might be expected to react analogously. The dehydration of **1** was therefore reinvestigated and the results obtained, together with those for some related substances, are reported here.

The reaction of 1,2-di(*o*-nitrophenyl)ethanol was slow, and gave four major products, in addition to low yields of a number of unidentified substances.

The structure of one of the isolated substances, (C<sub>14</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub> by M.S.), (yield 5 %), has not yet been conclusively demonstrated. The spectral data are in accord with the compound **4**, but not with the isomeric 6*H*,12*H*-indazolo[2,1-*α*]indazole-6,12-dione. Non-identity with the latter compound was conclusively demonstrated by direct comparison of the present product with an authentic sample.<sup>4</sup>

The other isolated compounds were 2-(*o*-nitrophenyl)isatogen (**2**) (8 %), 3-(*o*-nitro-



benzoyl)anthranil (3) (6%), and *o,o'*-dinitrostilbene (7%). Compounds 2 and 3 were not interconverted on treatment with *p*-toluenesulfonic acid and were recovered unchanged.

The ratio of the yields of 2 to 3 probably reflects the influence of the nitro group in the 2-aryl ring of 1,2-di(*o*-nitrophenyl)ethanol. When 1-(*o*-nitrophenyl)-2-phenylethanol was reacted under the same conditions, only traces of 2-phenylisatogen were found.<sup>8</sup> A mechanism was discussed for that reaction where the enol form of the postulated intermediate *o*-nitrosophenyl benzyl ketone provided precursors for 2-phenylisatogen and 3-benzoylanthranil. It was suggested that the anthranil might have been formed by attack of the hydroxyl group of the enol compound on the nitroso nitrogen, and the isatogen by addition of the  $\pi$ -electrons to the nitroso group. According to that mechanism, the introduction of a nitro group into the 2-phenyl ring could be reflected in the ratio of the yield of isatogen to anthranil. The nitro group would increase the electron density around the carbon atom 2 in the chain, and also lower the electron density at the hydroxyl oxygen of the enol. Both these effects would increase the ratio of the yields of the isatogen to the anthranil, as observed in the present reaction of 1

To test this point further, and to confirm that only the nitro group of the 1-aryl ring of 1 directly participated in the reaction, two other compounds, 1-(*o*-nitrophenyl)-2-(*p*-nitrophenyl)ethanol and 2-(*o*-nitrophenyl)-1-(*p*-nitrophenyl)ethanol were subjected to the same reaction conditions.

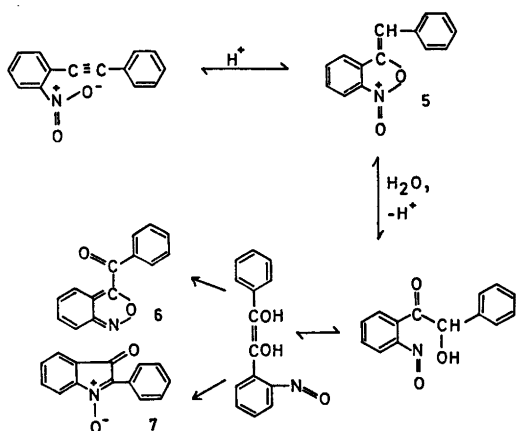
The reaction of 1-(*o*-nitrophenyl)-2-(*p*-nitrophenyl)ethanol under acidic conditions proved to be analogous to that of 1,2-di(*o*-nitrophenyl)ethanol: both 2-(*p*-nitrophenyl)isatogen (21%) and 3-(*p*-nitrobenzoyl)anthranil (7%) were formed. The ratio of isatogen to anthranil was higher than for the reaction of 1, in agreement with the known greater influence of a *para* as compared with an *ortho* nitro group. Further, this showed that both 2-(*o*-nitrophenyl)isatogen (2) and 3-(*o*-nitrobenzoyl)anthranil (3) were formed by reactions between the hydroxyl group and the nitro group of the 1-aryl ring, and that the nitro group of the 2-aryl ring was not directly involved in the reaction.

From these results, and those reported earlier,<sup>8</sup> 2-(*o*-nitrophenyl)-1-(*p*-nitrophenyl)ethanol was expected to yield *o,p'*-dinitrostilbene on reaction with *p*-toluenesulfonic acid. This indeed proved to be the case. Further, a low yield of 2-(*o*-nitrophenyl)-1-(*p*-nitrophenyl)ethyl *p*-toluenesulfonate was isolated, but neither 2-(*p*-nitrophenyl)isatogen nor 3-(*p*-nitrobenzoyl)anthranil were produced. This is further evidence that only the nitro group of the 1-aryl ring of 1,2-dinitrophenylethanol (1) participated in the reaction of 1, just as indicated by the reaction of 1-(*o*-nitrophenyl)-2-(*p*-nitrophenyl)ethanol.

In an attempt to obtain information about the mechanism discussed above, especially at which stage the oxidation took place, *o*-nitrotolan was treated with *p*-toluenesulfonic acid. Acetylenic bonds are susceptible to nucleophilic attack, a capacity increased by electro-negative substituents.<sup>8</sup> In *o*-nitrotolan this increase, combined with the proximity of the nitro group, would give opportunities for intramolecular reactions similar to those discussed above. Reactions of nitro groups with acetylenic bonds, both under acidic conditions<sup>7,8</sup> and by photochemical stimulation,<sup>9-11</sup> have been reported.

The main products from the present reaction of *o*-nitrotolan were 3-benzoylanthranil (6) (27%) and 2-phenylisatogen (7) (16%). The reactions of *o*-nitrotolan have previously been reported to yield 2-phenylisatogen,<sup>7-11</sup> and 3-benzoylanthranil was not then mentioned even as a by-product. This difference may stem from variation in the reaction conditions. Bayer<sup>7,8</sup> ran his reactions in aqueous sulfuric acid, and the photochemical reactions were mainly carried out in nucleophilic solvents, *e.g.* pyridine.<sup>9,11</sup> Due to the electrophilic nature of the acetylenic bond, the reactive species in these reactions may have been a complex between the solvent and *o*-nitrotolan. The addition of amines to acetylenes is well known.<sup>6,12</sup>

The formation of 6 and 7 may be explained by a mechanism similar to the one discussed above. An attack of the nitro group oxygen atoms on the acetylenic bond, together with proton addition would give the intermediate 5. From this, the anthranil 6 and the isatogen 7 could be obtained, *e.g.* by the reactions depicted below.



The resemblance in the product composition of the reactions of 1-(*o*-nitrophenyl)-2-phenylethanol<sup>3</sup> and of *o*-nitrotolan may indicate a common intermediate. In the reaction of *o*-nitrotolan, no oxidation step is necessary to obtain the anthranil (6) and isatogen (7). The results from this reaction may thus indicate the oxidation steps in the reactions of 2-aryl-1-(*o*-nitrophenyl)ethanols to take place earlier than discussed in Ref. 3, and before the ring closure steps. Nevertheless, the higher ratio of isatogen (7) to anthranil (6) in the reaction of *o*-nitrotolan than in the case of 1-(*o*-nitrophenyl)-2-phenylethanol also indicates the reactions not to proceed entirely by common intermediates.

It seems unlikely that *o*-nitrotolan itself was an intermediate in the reaction of 1-(*o*-nitrophenyl)-2-phenylethanol, especially as both *o*-nitrostilbene and benzyl *o*-nitrophenyl ketone were stable under the reaction conditions.<sup>3</sup> Neither did *o*-nitrobenzyl *o*-nitrophenyl ketone react under these conditions.

The results of the present study and of previous work<sup>2,3</sup> indicate alcohols of the *o*-nitrobenzyl-type to react *via* analogous intermediates, originating from intramolecular expulsion of the hydroxyl group. The reaction of *o*-nitrotolan seems to proceed *via* similar intermediates.

## EXPERIMENTAL

The general instrumentation used in the experiments has been described earlier.<sup>3</sup>

### Reactions of 1,2-di(*o*-nitrophenyl)ethanol (1).

(a) *In p*-xylene. 1,2-Di(*o*-nitrophenyl)ethanol

(2 g), *p*-toluene sulfonic acid (4 g) and *p*-xylene (200 ml) were refluxed for 2.5 h. The solution, after neutralisation, gave 1.2 g of a mixture which yielded 63 mg of a crystalline substance (m.p. 215–218°C) from ethyl acetate solution. Recrystallisation gave 10 mg with m.p. 220–221°C, IR (KBr): 1630, 1515, 1450, 1370, 1165, 1155, 1145  $cm^{-1}$ . NMR:  $\delta$  8.30 (1 H), 8.15 (1 H), 7.85–7.0 (6 H, m). Mass spectrum: *m/e* 336 (100%,  $C_{14}H_9N_2O_2$ ), 208 (13%,  $C_{13}H_8NO$ ), 179 (64%,  $C_{13}H_7N_2$ ). UV: (96% EtOH)  $\lambda_{max}$  330 nm ( $\epsilon_{max}$  = 686  $m^2 mol^{-1}$ ), 229 (1275). A tentative structure for the crystalline compound is 4.

(b) *In toluene*. The analogous reaction in toluene gave three products in addition to 4 (5%), *o,o'*-dinitrostilbene (7%, identified by IR and NMR); 3-(*o*-nitrobenzoyl)anthranil (6%) m.p. 230–236°C. IR (KBr): 3100, 1670, 1630, 1560, 1530, 1450, 1445, 1360, 1300, 1230, 940  $cm^{-1}$ . NMR:  $\delta$  7.25–8.4 m. Mass spectrum: *m/e* 268 (10%,  $C_{14}H_9N_2O_4$ ), 150 (15%,  $C_7H_4NO_3$ ), 134 (100%,  $C_7H_4NO_2$ ); 2-(*o*-nitrophenyl) isatogen (8%), m.p. 201–203°C (lit.<sup>9</sup> 202–203°C). IR (KBr): 3080, 1710, 1610, 1570, 1520, 1470, 1385, 1350, 1290, 1190, 1180  $cm^{-1}$ . NMR:  $\delta$  8.05–8.3 (1 H, m),  $\delta$  7.5–8.0 (7 H, m). Mass spectrum: *m/e* 268 (4%,  $C_{14}H_9N_2O_4$ ), 134 (100%,  $C_7H_4NO_2$ ). The experiment was repeated several times with essentially the same result.

(c) *In benzene*. The reaction was run analogously with the preceding one, and gave similar results, except that only 54% of the 1,2-di(*o*-nitrophenyl)ethanol had reacted.

Several attempts were made to improve the yields. The reaction was run with the addition of water or with a water eliminator attached, without any noticeable difference. Further, the reaction was run in the exclusion of air (five freeze-thaw cycles under vacuum) or with air bubbled through the reaction mixture without affecting the result. The addition of nitrobenzene as an oxidant (24 mol nitrobenzene per mol of 1) produced no noticeable effect.

*Stability of 2-(o-nitrophenyl)isatogen (2) and 3-(o-nitrobenzoyl)anthranil (3)*. Both these compounds were stable to the reaction conditions applied to 1,2-di(*o*-nitrophenyl)ethanol (see above).

*3-(o-Nitrobenzoyl)anthranil (3)*. 2-(*o*-Nitrophenyl)isatogen (2) (75 mg) was dissolved in ethanol (15 ml) and conc. sulfuric acid (0.8 ml) added.<sup>5</sup> After reflux for 20 h, the reaction mixture was neutralised with sodium bicarbonate, filtered, and evaporated. 50 mg of a substance identical to 3-(*o*-nitrobenzoyl)anthranil from the reaction of 1 was isolated.

*1-(o-Nitrophenyl)-2-(p-nitrophenyl)ethanol*. *p*-Nitrotoluene (16 g), *o*-nitrobenzaldehyde (18 g), dimethylsulfoxide (100 ml), and KOH (0.2 g) were stirred overnight at 22°C. After work-up and removal of excess reactants by vacuum distillation, the residue was chromatographed on a silica gel column. Recrystal-

lisation gave 3.2 g of 1-(*o*-nitrophenyl)-2-(*p*-nitrophenyl)ethanol, m.p. 145–145.5°C. IR (KBr): 3510, 3110, 2940, 1610, 1600, 1520, 1350, 1110, 1040 cm<sup>-1</sup>. NMR (acetone-*d*<sub>6</sub>): δ 7.4–8.3 (8 H, m, signals due to AA'XX' from *p*-nitrophenyl could be recognized), 5.35–5.75 (1 H, X part of ABX), 4.75 (1 H, OH, disappeared on addition of D<sub>2</sub>O), 2.9–3.3 (2 H, AB part of ABX). Mass spectrum: *m/e* 152 (23%), 137 (100%), 120 (8%), 104 (19%).

2-(*o*-Nitrophenyl)-1-(*p*-nitrophenyl)ethanol. *o*-Nitrotoluene (40 g), *p*-nitrobenzaldehyde (12 g), dimethylsulfoxide (100 ml) and KOH (2 g) were stirred at 22°C overnight. After work-up, 2-(*o*-nitrophenyl)-1-(*p*-nitrophenyl)ethanol (1.1 g) was obtained, m.p. 118–121°C. IR (KBr): 3560, 3190, 2950, 1610, 1520, 1350, 1060 cm<sup>-1</sup>. NMR (CDCl<sub>3</sub>): δ 7.1–8.4 (8 H, m), 5.0–5.4 (1 H), 3.1–3.5 (2 H), 2.7–3.0 (1 H, disappeared on addition of D<sub>2</sub>O). Mass spectrum: *m/e* 152 (9%), 137 (78%), 120 (100%), 107 (12%), 92 (31%).

*Reaction of 1-(o-nitrophenyl)-2-(p-nitrophenyl)ethanol.* *p*-Toluenesulfonic acid (3.0 g) and 1-(*o*-nitrophenyl)-2-(*p*-nitrophenyl)ethanol (1.5 g) in toluene (150 ml) were refluxed for 25 h. The toluene solution contained 1.25 g of a mixture which was chromatographed (silica gel, chloroform), giving four fractions: F<sub>3</sub> (0.81 g) consisted mainly of the starting material and gave 0.45 g crystals (30%) identical with this. F<sub>1</sub> (0.51 g) was rechromatographed (silica gel, toluene) giving four fractions: F<sub>1-1</sub> (0.024 g) consisted of *o,p'*-dinitrostilbene (2%). F<sub>1-2</sub> (0.056 g) gave 30 mg of 3-(*p*-nitrobenzoyl)anthranil, m.p. 188.5–189.5°C. IR (KBr): 3140, 1650, 1600, 1550, 1520, 1450, 1350, 1290, 1220 cm<sup>-1</sup>. Mass spectrum: *m/e* 268 (100%), 224 (13%). F<sub>1-4</sub> (0.262 g) gave 0.18 g of 2-(*p*-nitrophenyl)isatogen m.p. 253–255°C, (lit<sup>13</sup> for 2-(*p*-nitrophenyl)isatogen: 250–254°C). The crystals had IR (KBr): 3140, 1720, 1600, 1520, 1490, 1390, 1450 cm<sup>-1</sup>. Mass spectrum: *m/e* 268 (100%), 251 (38%), 76 (26%), 59 (20%). Because of low solubility, no NMR spectrum was obtained. F<sub>1-3</sub> was a mixture of these two compounds. By inspection of TLC of F<sub>1-2</sub> to F<sub>1-4</sub>, the total yield of 3-(*p*-nitrobenzoyl)anthranil was estimated to be 0.1 g (7%) and of 2-(*p*-nitrophenyl)isatogen 0.3 g (21%). Reactions were also run in benzene and *p*-xylene with the same result, the only difference being the required reaction time. The presence or absence of oxygen was without effect on the reaction. The isatogen was transformed to the anthranil when refluxed with sulfuric acid in ethanol.<sup>5</sup>

*Reaction of 2-(o-nitrophenyl)-1-(p-nitrophenyl)ethanol.* *p*-Toluenesulfonic acid (0.5 g) and 2-(*o*-nitrophenyl)-1-(*p*-nitrophenyl)ethanol (0.25 g) in toluene (25 ml) were refluxed for 2 h. TLC then indicated complete reaction, and a single product to have been formed. However, TLC at earlier stages indicated the presence of a substance which slowly disappeared from

the reaction mixture. The product (0.25 g) gave crystals (0.12 g), m.p. 141–142°C. IR (KBr) 3130, 1600, 1515, 1345, 1110, 970, 960 cm<sup>-1</sup>. NMR (CDCl<sub>3</sub>): δ 6.85–8.3 (m). The AA'XX' signal of the *p*-nitrophenyl system, and a doublet (1 H) at δ 7.10, *J* = 15 Hz, probably due to *trans* protons of the double bond, were recognized.

The reaction was repeated in benzene: *p*-Toluenesulfonic acid (40 mg) and 2-(*o*-nitrophenyl)-1-(*p*-nitrophenyl)ethanol (40 mg) in benzene (4 ml) were refluxed for 3 h. Yield: 30 mg which was chromatographed (silica gel, chloroform). One of the fractions contained a substance with *R<sub>F</sub>* on TLC identical to the one that disappeared in the toluene reaction above. Recrystallisation of this fraction gave a substance (12 mg) with IR (KBr): 3110, 1610, 1520, 1370, 1345, 1180, 1170 cm<sup>-1</sup>. NMR (CDCl<sub>3</sub>): δ 6.9–8.3 (12 H, m), 5.8–6.0 (1 H), 3.1–3.6 (2 H), 2.35 (3 H). Mass spectrum: *m/e* 306 (17%), C<sub>14</sub>H<sub>12</sub>NO<sub>5</sub>S, 291 (8%), C<sub>14</sub>H<sub>13</sub>NO<sub>4</sub>S, 155 (100%), C<sub>7</sub>H<sub>7</sub>O<sub>2</sub>S, 136 (62%), C<sub>7</sub>H<sub>8</sub>NO<sub>2</sub>, 91 (70%).

*Reaction of o-nitrotolan* (2 g) and *p*-toluenesulfonic acid (4 g) in toluene (200 ml) at reflux for 3 h gave 2.0 g of product. Chromatographic separation (silica gel, chloroform) of this gave 3-benzoylanthranil (0.51 g, 27%) and 2-phenylisatogen (0.30 g, 16%), in addition to recovered *o*-nitrotolan (0.16 g, 8%).

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