

125. *Chemical Evidence of Chelation in the Sodium Salts of o-Hydroxybenzaldehydes.*

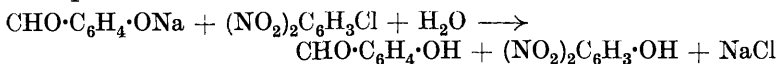
By OSCAR L. BRADY and WALTER H. BODGER.

THIS investigation arose from an attempt to prepare a dinitrophenyl ether of salicylaldehyde.

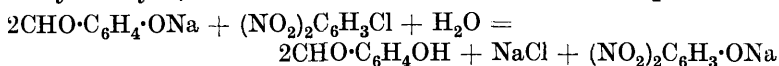
When warmed in alcohol with one equivalent each of sodium ethoxide and 2:4-dinitrochlorobenzene, both *m*- and *p*-hydroxybenzaldehyde readily yield dinitrophenyl ethers, but salicylaldehyde gives none. This failure does not seem to be due to steric hindrance by the aldehyde group, since *salicylaldehydemethylphenylhydrazone* and salicylaldoxime *O*-methyl ether, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{NOMe}$, both give excellent yields of the dinitrophenyl ethers under these conditions. Similarly, 3-ethoxysalicylaldehyde gives no dinitrophenyl ether, but its methylphenylhydrazone readily does so.

A number of other hydroxy-aldehydes have been investigated. 1-Naphthol-4-aldehyde gives a dinitrophenyl ether readily, but 5-nitro- and 5-bromo-salicylaldehyde and 2-naphthol-1-aldehyde fail to do so under similar conditions.

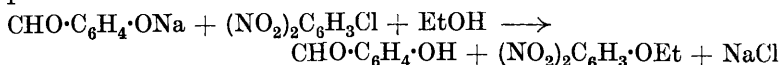
The reaction between 2 : 4-dinitrochlorobenzene and salicylaldehyde in 95% alcohol in the presence of one equivalent of sodium ethoxide takes place in the sense



but, since the dinitrophenol as formed decomposes the sodium salicylaldehyde, the stoichiometric relations are expressed as



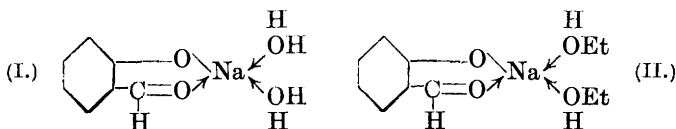
When special precautions are taken to eliminate water, dinitrophenetole is formed :



The most probable explanation of the above results is that, under the conditions of experiment, the sodium compound of salicylaldehyde in alcohol is co-ordinated and that the replacement of the aldehydic oxygen by the group :NOMe or :N·NMePh, which are less likely to favour co-ordination, enables the ONa group to function normally.

Sidgwick and Brewer (J., 1925, **127**, 2385) have shown that the compound of sodium salicylaldehyde with a further molecule of salicylaldehyde described by Hantzsch (*Ber.*, 1906, **39**, 3089) has some of the physical properties of a chelate compound, and lithium salicylaldehyde forms a dihydrate which is soluble in toluene and is probably chelated. Although Hantzsch says that even in the presence of an excess of base the salt $\text{C}_7\text{H}_5\text{O}_2\text{Na}$, $\text{C}_7\text{H}_6\text{O}_2$ is precipitated, under the conditions of our experiments, where equimolecular amounts of sodium ethoxide and salicylaldehyde were employed, this was not the case, as the sparingly soluble salt which separated was the compound $\text{C}_7\text{H}_5\text{O}_2\text{Na}$.

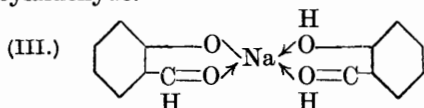
We suggest that the reaction proceeds between the dinitrochlorobenzene and the sodium compound in solution. It seems probable that the sodium salt has a chelate structure (I), analogous to Sidgwick and Brewer's lithium compound, in aqueous-alcoholic solution and a structure (II) in anhydrous alcoholic solution.



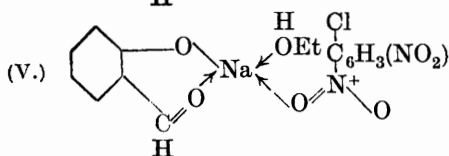
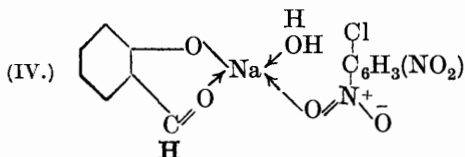
Some support is lent to this view by the fact that the dihydrate of lithium salicylaldehyde and Hantzsch's sodium compound are yellow, whereas sodium salicylaldehyde is almost colourless but the alcoholic mother-liquor from which it separates is deep yellow, and salicylaldehyde in excess of aqueous sodium hydroxide gives a bright yellow solution.

The mechanism of the reaction with dinitrochlorobenzene is obscure, but probably an addition compound is formed in the first place, leading to the production of dinitrophenol from (I) in 95% alcohol and of dinitrophenetole from (II) in anhydrous alcohol. There seems reason to suppose that the production of dinitrophenol in 95% alcohol is not due to sodium hydroxide formed by hydrolytic dissociation of the sodium salicylaldehyde, since even with low concentrations of sodium hydroxide and dinitrochlorobenzene in alcohol of this strength the main product of the reaction is dinitrophenetole.

An alternative explanation is that the reactive material in the alcoholic solution is a small quantity of Hantzsch's compound (III), more being formed as this is decomposed by the dinitrochlorobenzene by the action of the liberated salicylaldehyde on the suspended sodium salicylaldehyde.



This seems less likely, as it is not obvious here why the presence or otherwise of small amounts of water determines the formation of dinitrophenol or dinitrophenetole, since the latter is produced in the absence of salicylaldehyde even when relatively large quantities of water are present. If the first suggestion be adopted, one might tentatively suggest that the dinitrochlorobenzene displaces one molecule of the solvent in (I) and (II), giving (IV) and (V), which decompose with the production of sodium chloride and dinitrophenol and dinitrophenetole respectively.



EXPERIMENTAL.

p-2 : 4 - *Dinitrophenoxybenzaldehyde*.—*p* - Hydroxybenzaldehyde (6 g.) in alcohol (20 c.c.) was mixed with a solution of sodium (1.15 g.) in alcohol (20 c.c.), and a hot concentrated alcoholic solution of 2 : 4-dinitrochlorobenzene (12 g.) added. The deep red solution was boiled under reflux for 1 hour; a pale yellow precipitate then appeared. The solution was cooled in a freezing mixture, and the precipitate collected, washed with water to remove sodium chloride, and crystallised from alcohol-acetone, *p*-2 : 4-*dinitrophenoxybenzaldehyde* being obtained in good yield in stout white needles, m. p. 105° (Found : N, 10.3. $C_{13}H_8O_6N_2$ requires N, 10.3%). Only a trace of dinitrophenol was obtained from the mother-liquors.

m-2 : 4-*Dinitrophenoxybenzaldehyde*, similarly prepared from *m*-hydroxybenzaldehyde, crystallised in white needles, m. p. 125° (Found : N, 10.3%).

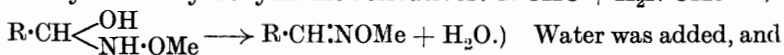
2 : 4-*Dinitrophenyl-4-aldehydo-1-naphthyl ether*, prepared analogously from 1-naphthol-4-aldehyde, crystallised in lemon-yellow needles, m. p. 158° (Found : N, 8.6. $C_{17}H_{10}O_6N_2$ requires N, 8.3%).

o-2 : 4 - *Dinitrophenoxybenzaldehydemethylphenylhydrazone*.—*Salicylaldehydemethylphenylhydrazone*, prepared by heating salicylaldehyde (10 g.), methylphenylhydrazine (10 g.), and alcohol (30 c.c.) on the water-bath until a solid began to separate, crystallised from alcohol in white leaflets, m. p. 69° (Found : N, 12.5. $C_{14}H_{14}ON_2$ requires N, 12.6%). This compound, boiled with sodium ethoxide (1 mol.) and 2 : 4-dinitrochlorobenzene (1 mol.) in alcohol for 1 hour, gave a sparingly soluble precipitate which, crystallised from alcohol-acetone, yielded *o*-2 : 4-*dinitrophenoxybenzaldehydemethylphenylhydrazone* in deep red cubes, m. p. 117° (Found : N, 14.5. $C_{20}H_{16}O_6N_4$ requires N, 14.3%). Yield, 60%.

2-(2' : 4' - *Dinitrophenoxy*)-3-*ethoxybenzaldehydemethylphenylhydrazone*.—2-Hydroxy-3-ethoxybenzaldehyde (2.8 g.), methylphenylhydrazine (2.5 g.), and alcohol (10 c.c.) were heated for some time on the water-bath. The precipitate obtained on cooling, when crystallised from alcohol, gave 2-*hydroxy-3-ethoxybenzaldehydemethylphenylhydrazone* in colourless leaflets, m. p. 72° (Found : N, 10.6. $C_{16}H_{18}O_2N_2$ requires N, 10.4%). This compound, treated with sodium ethoxide and 2 : 4-dinitrochlorobenzene in alcohol as before, gave 2-(2' : 4'-*dinitrophenoxy*)-3-*ethoxybenzaldehydemethylphenylhydrazone*, which crystallised from alcohol-acetone in orange cubes, m. p. 164° (Found : N, 12.9. $C_{22}H_{20}O_6N_4$ requires N, 12.8%).

o-2 : 4 - *Dinitrophenoxybenzaldoxime O-Methyl Ether*.—When salicylaldehyde (12 g.) and *O*-methylhydroxylamine (5 g.) were mixed, the temperature rose to 85°, but the liquid remained clear

until after 60 seconds it suddenly became opaque and in another few seconds had separated into two layers. (This behaviour seems the first direct evidence of the two stages in the reaction between aldehydes and hydroxylamine derivatives: $R \cdot CHO + H_2N \cdot OMe \longrightarrow$



Water was added, and the mixture extracted with chloroform; after removal of the solvent salicylaldoxime *O*-methyl ether was obtained as a faintly yellow oil. This oil (3 g.) was mixed with a solution of sodium (0.5 g.) in alcohol (10 c.c.), and a boiling solution of 2 : 4-dinitrochlorobenzene (4 g.) in alcohol (25 c.c.) added. A deep red colour developed immediately, which rapidly faded and a crystalline precipitate separated: this, crystallised from alcohol, gave *o*-2 : 4-dinitrophenoxybenzaldoxime *O*-methyl ether in very pale yellow needles, m. p. 106° (Found: C, 53.0; H, 3.4; N, 13.5. $C_{14}H_{11}O_6N_3$ requires C, 53.0; H, 3.5; N, 13.3%).

Action of Sodium Salicylaldehyde on Dinitrochlorobenzene.—Sodium (1.1 g.) was dissolved in 95% alcohol (25 c.c.), and a solution of salicylaldehyde (6 g.) in alcohol (25 c.c.) slowly added with vigorous shaking, the sodium salt being precipitated; a solution of 2 : 4-dinitrochlorobenzene (11 g.) in hot alcohol (50 c.c.) was then rapidly poured in and the mixture boiled under reflux for 30 minutes. The very pale yellow sodium salicylaldehyde had now been replaced by a mass of long orange needles having the appearance of sodium dinitrophenoxide. After cooling, these were collected, washed with a little alcohol, suspended in water (10 c.c.), and acidified with concentrated hydrochloric acid; the dinitrophenol formed was collected and identified in the usual way (yield, 3.4 g., corresponding to 34% of the dinitrochlorobenzene employed, but some sodium dinitrophenoxide remained in the alcohol).

The alcohol was removed from the filtrate from the sodium dinitrophenoxide on the water-bath and water and ether were added to the residue. By repeated shaking with 2*N*-sodium hydroxide, the salicylaldehyde was removed from the ethereal extract which then gave on evaporation 6.2 g. of an oil: this solidified to a pasty mass, which when pressed on porous tile gave dinitrochlorobenzene. The sodium hydroxide solution on acidification and distillation in steam gave salicylaldehyde.

When alcohol which had been dried over calcium oxide and distilled over aluminium ethoxide was used in the above reaction, the solid obtained by filtration of the reaction mixture after 30 minutes' refluxing was found to be sodium chloride, the yield corresponding to 73% of the sodium employed in the reaction. The alcohol was removed from the mother-liquor on the water-bath, water added to

the residue, and the product shaken with ether; after separation, the aqueous layer on acidification gave 2 g. of dinitrophenol. This amount would be formed if, owing to incomplete dehydration or to absorption of water during manipulation, 0.2 g. of water was present during the reaction; although care was taken to avoid this, the amount is not surprising, since 100 c.c. of alcohol were used and several transfers of solutions were necessary. The ethereal layer, after repeated extraction with 2*N*-sodium hydroxide, gave on evaporation 8 g. of an oil which slowly solidified and was identified as dinitrophenetole; the amount corresponds to 73% of the theoretical yield. The sodium hydroxide solution on acidification yielded salicylaldehyde.

To test the action of sodium hydroxide on dinitrochlorobenzene in alcohol, 0.5 g. of the latter was dissolved in hot 95% alcohol (100 c.c.) and 1.3 c.c. of 2*N*-sodium hydroxide mixed with 200 c.c. of alcohol were added. After being heated for 2 minutes, the whole was poured into 500 c.c. of water; 56% of the theoretical yield of dinitrophenetole was then obtained.

In order to decide the composition of the sodium salt precipitated in the above reactions the first stage of the operation was repeated, the same quantities being used. The precipitated sodium salt was collected and washed with a very small quantity of alcohol and then with ether (compare Sidgwick and Brewer, *loc. cit.*). It was found to contain 15.2% of sodium ($C_7H_5O_2Na$ requires Na, 16.0%. $C_7H_5O_2Na, C_7H_6O_2$ requires Na, 8.6%). The filtrate from the sodium salt, excluding the washings, was acidified with concentrated hydrochloric acid and two volumes of anhydrous ether were added; the precipitated sodium chloride weighed 0.22 g. This result eliminates the possibility that the washing of the sodium salt had removed salicylaldehyde from the compound $C_7H_5O_2Na, C_7H_6O_2$, since had only half the sodium present been used in salt formation the yield of sodium chloride from the alcoholic solution should have been 1.18 g. The sodium chloride actually obtained from the alcoholic solution was probably produced to a great extent from the sodium salicylaldehyde in solution.

The other *o*-hydroxyaldehydes mentioned in the introduction gave similar results when treated in alcoholic solution with 1 equivalent each of sodium ethoxide and dinitrochlorobenzene.