CLI.—*Derivatives of Naphthacenequinone. Part II.*

By WILLIAM HENRY BENTLEY, ARTHUR FRIEDL, and CHARLES WEIZMANN.

IN a former paper (this vol., p. 417), we described an aminohydroxynaphthacenequinone containing both substituent groups in the naphthalene ring :

and having observed a marked difference between hydroxy-derivatives of 1-hydroxynaphthacenequinone substituted in the benzene and in the naphthalene rings, it appeared to be of interest to make the same comparison with the amino-derivatives of 1-hydroxynaphthacenequinone. In order to prepare aminohydroxynaphthacenequinones containing the amino-group in the benzene ring, we condensed the two nitrophthalic acids with α -naphthol by means of boric acid, reduced the resulting nitro- α -hydroxynaphthoylbenzoic acid to the amino-acid, and condensed

this to the aminohydroxynaphthacenequinone by warming with concentrated sulphuric acid :

Unfortunately, these reactions proceeded with very bad yields, and the aminohydroxynaphthacenequinones obtained were in such small quantity that no detailed investigation of their properties was possible. We were able to observe, however, that considerable difference exists between the aminohydroxynaphthacenequinones having the amino-group in the benzene and in the naphthalene rings. Thus, when the amino-group is contained in the benzene ring, the solution of the compound in concentrated sulphuric acid is very much bluer than that of the corresponding compound containing the amino-group in the naphthalene ring, and, further, the solution of the former compound in alcoholic potash is much yellower than that of the latter.

With the object of preparing a naphthacenequinone containing, like alizarin, two hydroxy-groups in the adjacent α - and β -positions, we condensed hemipinic acid with α -naphthol, thus obtaining hydroxy-dimethoxynaphthoylbenzoic acid, $(\text{OMe})_2\text{C}_6\text{H}_2(\text{CO}_2\text{H}) \cdot \text{CO} \cdot \text{C}_{10}\text{H}_6 \cdot \text{OH}$, but on treating this acid with concentrated sulphuric acid only a small yield of the condensation product resulted, and this on analysis gave numbers agreeing with a trihydroxymonomethoxynaphthacenequinone, indicating that partial hydrolysis and oxidation had occurred in the condensation.

In our former communication (*loc. cit.*), the condensation product of phthalic acid and 1:5-dihydroxynaphthalene was described. As 1:5-dihydroxynaphthalene has two hydroxyl groups in the α -position, we condensed two molecular proportions of phthalic acid with one of 1:5-dihydroxynaphthalene and succeeded in obtaining 2:6-dicarboxy-benzoyl-1:5-dihydroxynaphthalene :

On treating this acid, however, with fuming sulphuric acid, the corresponding diquinone was not obtained, but a substance giving analytical numbers agreeing with trihydroxynaphthacenequinone together with a sulphonic acid, probably derived from the same substance. In this case, the quinone ring has been closed only on one side, whilst, presumably, on the other side of the naphthalene nucleus the benzoyl has been replaced by a hydroxyl group.

As the condensation of phthalic acid and 1:5-dihydroxynaphthalene yielded chiefly the monobenzoyl acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_{10}\text{H}_5(\text{OH})_2$, we were in possession of a considerable quantity of this material, and therefore endeavoured to condense it to the quinone without sulphonation taking place, as had occurred in our former experiments (*loc. cit.*). This was found possible to some extent at least, the product being a mixture of the quinone and its sulphonic acid, from which the 1:5-dihydroxynaphthacenequinone was easily separated.

EXPERIMENTAL.

3(6)-Nitro-1'-hydroxy-2- β -naphthoylbenzoic Acid,
 $\text{NO}_2\cdot\text{C}_6\text{H}_3(\text{CO}_2\text{H})\cdot\text{CO}\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$.

—3-Nitrophthalic anhydride (50 grams) and boric acid (150 grams) are intimately mixed and heated to partial fusion. The cold mass is then powdered, mixed with α -naphthol (40 grams) and boric acid (75 grams), and heated to 180° for three hours. The product is extracted with boiling water to remove boric acid, and afterwards with dilute aqueous sodium hydroxide; the alkaline solution on acidification yields a resinous precipitate, which is collected and boiled with water and calcium carbonate for several hours. The liquid is filtered cold, and the filtrate on being acidified with hydrochloric acid yields a yellow precipitate which on crystallisation from dilute alcohol separates in orange prisms melting indefinitely at 200° :

0.2034 gave 7.6 c.c. nitrogen at 18° and 756 mm. $N = 4.29$.

$\text{C}_{18}\text{H}_{11}\text{O}_6\text{N}$ requires $N = 4.15$ per cent.

When the acid is heated with concentrated sulphuric acid or treated in the cold with fuming sulphuric acid, it yields a small quantity of a naphthacenequinone derivative which dissolves in alcoholic potash with a cherry-red, and in sulphuric acid with a violet, colour.

3(6)-Amino-1'-hydroxy-2- β -naphthoylbenzoic Acid,
 $\text{NH}_2\cdot\text{C}_6\text{H}_3(\text{CO}_2\text{H})\cdot\text{CO}\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$.

—This acid is obtained by treating the sodium salt of the nitro-acid just described with an excess of ferrous sulphate and sodium carbonate. The mixture is filtered hot and the filtrate acidified with acetic acid; the resulting brown precipitate is dissolved in sodium carbonate and precipitated with sulphurous acid, being obtained as a grey powder melting at 167 — 170° :

0.1898 gave 7.2 c.c. nitrogen at 17° and 760 mm. $N = 4.40$.

$\text{C}_{18}\text{H}_{13}\text{O}_4\text{N}$ requires $N = 4.56$ per cent.

The alcoholic solution of this amino-acid gives a dark green coloration with ferric chloride.

When dissolved in concentrated sulphuric acid, it yields a red solution which, when treated with boric acid and fuming sulphuric

acid, changes to an intense violet solution. On pouring this into water, the corresponding 7(10)-amino-1-naphthacenequinone,

is precipitated, which, after filtration, washing with water and dilute ammonia, and drying on porous porcelain, is obtained as a black powder. The yield is extremely small, and in consequence no analytical data can be furnished.

The substance dissolves in concentrated sulphuric acid, yielding an intensely violet solution, which is much bluer than that given by 6-amino-1-hydroxynaphthacenequinone. Its cherry-red solution in alcoholic potash is much yellower than that of 6-amino-1-hydroxynaphthacenequinone.

4(5)-Nitro-1'-hydroxy-2-β-naphthoylbenzoic Acid.—This acid is prepared from 4-nitrophthalic acid in a similar manner to that just described from 3-nitrophthalic acid. It forms a yellow powder melting indefinitely at 130—140° :

0.2383 gave 8 c.c. nitrogen at 18° and 756 mm. $N = 3.85$.

$\text{C}_{18}\text{H}_{11}\text{O}_6\text{N}$ requires $N = 4.15$ per cent.

This nitro-acid is readily soluble in alcohol or acetic acid, but it is difficult to crystallise. With sulphuric acid, it behaves exactly like 3(6)-nitro-1'-hydroxy-2-β-naphthoylbenzoic acid. It is easily reduced with ferrous sulphate and sodium carbonate to

which, after isolation and purification like the foregoing amino-acid, is obtained as a yellow powder melting at 160—163° :

0.2446 gave 9.8 c.c. nitrogen at 17° and 760 mm. $N = 4.65$.

$\text{C}_{18}\text{H}_{13}\text{O}_4\text{N}$ requires $N = 4.56$ per cent.

The alcoholic solution of this acid gives a dark green coloration with ferric chloride.

When treated with fuming sulphuric acid in presence of boric acid, it behaves just like the 3(6)-amino-1'-hydroxy-2-β-naphthoylbenzoic acid, yielding a very small quantity of 8(9)-amino-1-hydroxynaphthacenequinone, which is a dark powder possessing properties exactly similar to those of 7(10)-amino-1-hydroxynaphthacenequinone.

—For the preparation of this acid, hemipinic anhydride (20 grams) and boric acid (60 grams) are intimately mixed and heated to partial fusion. The cold mass is powdered, mixed with α-naphthol (14 grams) and boric acid (40 grams), and heated to 180° for one and a half hours. The black, pasty mass is extracted with boiling water and the residue

with boiling dilute aqueous sodium hydroxide; the alkaline extract is acidified, the precipitated acid collected and repeatedly boiled with water and calcium carbonate as long as the filtrate yields a precipitate on acidification. The united filtrates are acidified with hydrochloric acid, the precipitate collected and crystallised from methyl alcohol, which deposits pale yellow prisms melting at 250—252°:

0.1076 gave 0.2690 CO₂ and 0.0461 H₂O. C = 68.18; H = 4.76.

C₂₀H₁₆O₆ requires C = 68.18; H = 4.54 per cent.

The acid dissolves in sulphuric acid forming an orange solution which on heating or treating with fuming sulphuric acid turns violet.

The solution, when poured into water, deposits a reddish-brown solid, which is purified by washing on a filter with hot water, drying on porous porcelain, and crystallising from nitrobenzene. The analysis indicates that the substance is a trihydroxymonomethoxynaphthacenequinone:

0.1091 gave 0.2710 CO₂ and 0.0380 H₂O. C = 67.74; H = 3.87.

0.0798 „ 0.1985 CO₂ „ 0.0270 H₂O. C = 67.84; H = 3.76.

C₁₉H₁₂O₆ requires C = 67.85; H = 3.57 per cent.

This *trihydroxymonomethoxynaphthacenequinone* forms a dark red powder which melts indefinitely at 260°. It dissolves in alkalis with a bluish-red colour.

2 : 6-Dicarboxybenzoyl-1 : 5-dihydroxynaphthalene,

CO₂H·C₆H₄·CO·C₁₀H₄(OH)₂·CO·C₆H₄·CO₂H.

—This acid is obtained, although only in small yield, by heating 1 : 5-dihydroxynaphthalene (12 grams) with an excess of phthalic anhydride (50 grams) in presence of boric acid (100 grams). The boric and excess of phthalic acids are extracted from the product with boiling water and the residue boiled with sodium carbonate. On acidifying the alkaline extract, a yellow precipitate is obtained, which is a mixture of the mono- and di-benzoyl acids. The former is removed by repeated digestion with methyl alcohol, and the residue is purified by converting it into the calcium salt by boiling with water and calcium carbonate. The acid is then reprecipitated with hydrochloric acid, well washed with hot water on a filter, and dried on porous porcelain:

0.1298 gave 0.3240 CO₂ and 0.0443 H₂O. C = 68.07; H = 3.79.

C₂₆H₁₆O₈ requires C = 68.44; H = 3.51 per cent.

This acid forms a yellow powder which decomposes above 300° without melting. It dissolves in sulphuric acid to a violet solution which on heating becomes first green and finally blue. It dissolves in alkalis with an orange colour.

1 : 4 : 5-Trihydroxynaphthacenequinone (?).—This substance is

apparently produced when the foregoing acid is condensed by means of boric acid and fuming sulphuric acid. The product is poured into water, the red precipitate washed on a filter with hot water, dried, and extracted with methyl alcohol in a Soxhlet apparatus in order to remove some sulphonie acid which is formed. The residue is crystallised from nitrobenzene, from which it separates as an orange powder which does not melt below 360° :

0.1123 gave 0.2888 CO_2 and 0.0358 H_2O . $\text{C} = 70.13$; $\text{H} = 3.54$.

$\text{C}_{18}\text{H}_{10}\text{O}_5$ requires $\text{C} = 70.58$; $\text{H} = 3.26$ per cent.

This *trihydroxynaphthacenequinone* dissolves in concentrated sulphuric acid and in cold sodium carbonate, yielding cornflower-blue solutions.

1:5-*Dihydroxynaphthacenequinone*.—This quinone is prepared by dissolving 1':5'-dihydroxy-2- β -naphthoylbenzoic acid together with twice its weight of boric acid in concentrated sulphuric acid and carefully adding fuming sulphuric acid until a sample of the mixture on pouring into water and making alkaline gives a cornflower-blue solution.

The product is poured into water, the precipitate washed with hot water on a filter, dried, and extracted with methyl alcohol in a Soxhlet apparatus. The residue is then crystallised from nitrobenzene:

0.1576 gave 0.4248 CO_2 and 0.0504 H_2O . $\text{C} = 73.51$; $\text{H} = 3.58$.

$\text{C}_{18}\text{H}_{10}\text{O}_4$ requires $\text{C} = 74.48$; $\text{H} = 3.44$ per cent.

1:5-*Dihydroxynaphthacenequinone* forms a brick-red powder which does not melt, but sublimes, below 300° . It dissolves in hot sodium carbonate with a cornflower-blue, and in concentrated sulphuric acid with a bluish-green, colour.

MANCHESTER UNIVERSITY.