JOURNAL

OF

THE CHEMICAL SOCIETY.

TRANSACTIONS.

I.—*Azomethine Derivatives of the 2- and 4-Hydroxy- α -Naphthaldehydes.*

By GILBERT T. MORGAN and HARRY GORDON REEVES.

THE analogy between azo- and azomethine-compounds was first pointed out by Weil (*Ber.*, 1894, **27**, 3317) and afterwards further examined by Möhlau (*Ber.*, 1895, **28**, 324; 1898, **31**, 2250), who prepared, from *p*-nitrobenzaldehyde and three of the amino-naphthols, Schiff condensation products having the formula $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{N} \cdot \text{C}_{10}\text{H}_6 \cdot \text{OH}$, and corresponding with the benzene-azo- α - and - β -naphthols, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{N} \cdot \text{C}_{10}\text{H}_6 \cdot \text{OH}$.

On investigating the solubility of *p*-nitrobenzylidene-4-amino- α -naphthol, Möhlau found that this azomethine compound resembled *p*-nitrobenzeneazo- α -naphthol in dissolving readily in cold dilute aqueous sodium hydroxide; *p*-nitrobenzylidene-1-amino- β -naphthol dissolved rather more sparingly in aqueous sodium hydroxide, whereas *p*-nitrobenzylidene-2-amino- α -naphthol was almost insoluble in this reagent. The last azomethine derivative accordingly resembles in this respect *p*-nitrobenzeneazo- β -naphthol (para-red), which owes its technical application largely to its insolubility in aqueous alkalis.

From these experimental results, Möhlau inferred that the marked difference between the ortho- and para-series of azonaphthols subsists to a certain extent in the case of the corresponding azomethine compounds, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{N} \cdot \text{C}_{10}\text{H}_6 \cdot \text{OH}$. We have now carried this comparison between azo- and azomethine-compounds

a stage further by examining the reactions of a series of Schiff condensation products having the general formula

The members of the new series, which are isomeric with Möhlau's compounds, contain the azomethine chromophore reversed, as shown in formulæ I and II; they are prepared by condensing the nitroanilines with 2- and 4-hydroxy- α -naphthaldehydes, the products obtained from *p*-nitroaniline having the following constitutions:

(I)

(II)

4-Hydroxy- α -naphthylidene-*p*-nitroaniline (II) is very sparingly soluble in cold aqueous sodium hydroxide, but its isomerides from 4-hydroxy- α -naphthaldehyde and *o*- and *m*-nitroanilines dissolve readily in cold 10 per cent. sodium hydroxide, giving yellow solutions of the alkali salts, which slowly undergo hydrolysis into the generators of the azomethine compounds.

2-Hydroxy- α -naphthylidene-*p*-nitroaniline (I) and its two isomerides from *o*- and *m*-nitroanilines and 2-hydroxy- α -naphthaldehyde are insoluble in cold aqueous sodium hydroxide solution. As in the similar case of *p*-nitrobenzeneazo- β -naphthol, the acidic character of the hydroxyl group is diminished very appreciably by its proximity to the azo- or azomethine-chromophore. This analogy is not, however, very close, for under more drastic treatment with stronger aqueous or alcoholic alkali hydroxide the *o*-hydroxy-azomethine compounds undergo hydrolysis into their generators.

The diminution in acidic character of the *o*-hydroxy-azomethine compounds may result from a quinonoid rearrangement corresponding with that assumed to occur in the azo- β -naphthols in order to account for their insolubility in alkalis.

(V.)

It is noteworthy that with azomethines derived from *o*- and *p*-nitroanilines a double quinonoid change is possible. The latter configuration (V) would account for the more intense colorations developed by the *ortho*- and *para*-nitro-compounds in alcoholic sodium hydroxide solution or in concentrated sulphuric acid. Apart from these colour changes and the difference in solubility, the hydroxy-azomethine compounds have the general properties of Schiff bases in regard to the action of hydrolytic agents and in the formation of additive compounds.

One very distinctive property of the aromatic azomethine compounds is their capacity for combining additively with anhydrous hydrogen cyanide (von Miller and Plöchl, *Ber.*, 1892, **25**, 2056; 1898, **31**, 2699). This tendency is diminished appreciably by the presence of acidic substituents in one or other of the two aromatic nuclei (Eibner, *Annalen*, 1898, **302**, 335), and sometimes the presence of nitro-groups inhibits the reaction completely (Morgan, T., 1900, **77**, 1210). In the present investigation, this addition of hydrogen cyanide was achieved in every instance, although it was found that the reaction occurred much more slowly with the *para*-nitro-compounds (I and II) than with their *o*- and *m*-isomerides. This difference in reactivity is probably due to more sparing solubility, which in turn would hinder the reversal of the dynamic changes indicated by formulæ III to V.

EXPERIMENTAL.

Preparation of 2- and 4-Hydroxy- α -naphthaldehydes (compare Gattermann, *Ber.*, 1899, **32**, 284; Morgan and Vining, T., 1921, **119**, 177).—One part of recrystallised α - or β -naphthol was added to a solution of freshly-prepared anhydrous zinc chloride (one part) in three parts of dry ether, hydrogen chloride was slowly introduced, and 10 c.c. of anhydrous hydrocyanic acid were added with continuous stirring. A clear, colourless solution was obtained which gradually assumed a greenish-yellow tint with α - or a clear yellow tint with β -naphthol, and ultimately became pasty owing to the separation of the aldimine hydrochloride. After twelve hours, this product was collected and hydrolysed with water, when the corresponding aldehyde was obtained; it was characterised by the formation of the Schiff base with aniline.

I. Azomethine Derivatives from 2-Hydroxy- α -naphthaldehyde.

An alcoholic solution containing 2-hydroxy- α -naphthaldehyde and the nitroaniline in molecular proportions, after heating in a

4 MORGAN AND REEVES : AZOMETHINE DERIVATIVES OF

reflux apparatus for an hour, deposited on cooling a crystalline precipitate of the azomethine derivative, which was purified by crystallisation from the same solvent.

$\text{HO}\cdot\text{C}_{10}\text{H}_6\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$.	Appearance.	M.p.	Requires N = 9.59 per cent.
2-Hydroxy- α -naphthylidene- o-nitroaniline	Lustrous, scarlet plates.	172°	Found : N = 9.70.
2-Hydroxy- α -naphthylidene- m-nitroaniline	Felted, orange needles.	165—166°	„ N = 9.65.
2-Hydroxy- α -naphthylidene- p-nitroaniline	Intensely crimson needles.	213°	„ N = 9.49.

Weighed quantities (0.02 to 0.05 gram) of the three isomerides were left in contact with 5 c.c. of cold 10 per cent. aqueous sodium hydroxide for one hour; the material in each case recovered unchanged without loss of weight gave the correct melting point, thus indicating an entire absence of solubility or of hydrolytic change. The three isomerides (*o*-, *m*-, and *p*-) dissolved in alcoholic sodium hydroxide, giving respectively yellow, orange-yellow, and crimson colorations which faded slowly to a pale yellow; they developed yellow colorations in concentrated sulphuric acid.

*Addition of Hydrogen Cyanide to the Azomethine Derivatives
of 2-Hydroxy- α -naphthaldehyde.*

Excess of anhydrous hydrogen cyanide was added to the powdered azomethine compound, and the mixture was left in a cooled stoppered bottle with occasional shaking.

Phenylamino-2-hydroxy- α -naphthylacetonitrile,
 $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{CH}(\text{CN})\cdot\text{C}_{10}\text{H}_6\cdot\text{OH},$

obtained in light yellow plates after a week, was crystallised from benzene and light petroleum in pale yellow, prismatic crystals melting at 117.5° (Found: N = 10.28. $\text{C}_{18}\text{H}_{14}\text{ON}_2$ requires N = 10.22 per cent.). It is noteworthy that the saturation of the chromophore by hydrogen cyanide has not in this instance destroyed the colour of the substance.

o-Nitrophenylamino-2-hydroxy- α -naphthylacetonitrile,
 $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}(\text{CN})\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}.$

—After ten days in anhydrous hydrogen cyanide, the red, crystalline *ortho*-nitrated azomethine compound was replaced by yellow, glistening leaflets, which separated from benzene in pale yellow plates melting and decomposing at 153° (Found: N = 13.2. $\text{C}_{18}\text{H}_{13}\text{O}_3\text{N}_3$ requires N = 13.16 per cent.).

m-Nitrophenylamino-2-hydroxy- α -naphthylacetonitrile.—The addition of hydrogen cyanide was complete after ten days; the product crystallised from benzene in pale yellow needles melting at 127.5° (Found: N = 13.28 per cent.).

p-Nitrophenylamino-2-hydroxy- α -naphthylacetonitrile.—2-Hydroxy- α -naphthylidene-*p*-nitroaniline reacted with extreme slowness; it was suspended in ether and agitated daily with excess of anhydrous hydrogen cyanide for a period of three weeks, when the product had assumed a brownish-orange tint. This material was washed with water and extracted with benzene to remove any unaltered azomethine; the residue, when crystallised from alcohol, separated in orange-brown plates melting at 242° (Found: N = 13.42 per cent.).

II. Azomethine Derivatives from 4-Hydroxy- α -naphthaldehyde.

The reagents were heated under reflux for one to six hours in the minimum amount of alcohol required for solution. The products were not so readily crystallisable from alcohol as their isomerides from 2-hydroxy- α -naphthaldehyde. The *ortho*-compound, the most soluble of the series, was obtained after evaporating off the alcohol, and was crystallised from 50 per cent. acetic acid.

HO·C ₁₀ H ₆ ·CH:N·C ₆ H ₄ ·NO ₂ .	Appearance.	M.p.	Requires N = 9.59 per cent.
4-Hydroxy- α -naphthylidene- <i>o</i> -nitroaniline	Reddish-brown powder.	150—151°	Found: N = 9.38.
4-Hydroxy- α -naphthylidene- <i>m</i> -nitroaniline	Reddish-brown powder.	188°	„ N = 9.66.
4-Hydroxy- α -naphthylidene- <i>p</i> -nitroaniline	Dark crimson, granular powder.	238°	„ N = 9.75.

Weighed quantities (0.02 to 0.05 gram) of the foregoing isomerides were placed in 5 c.c. of cold 10 per cent. aqueous sodium hydroxide. The *ortho*- and *meta*-nitro-compounds dissolved within four minutes to an orange solution. When left over-night, the dissolved azomethine derivatives underwent hydrolysis with liberation of the corresponding nitroaniline, the acidified filtrate giving 4-hydroxy- α -naphthaldehyde. 4-Hydroxy- α -naphthylidene-*p*-nitroaniline was far less soluble than its isomerides, and under the foregoing experimental conditions the greater part remained unchanged; the dissolved portion, which gave a yellow solution, underwent hydrolysis into its generators.

In alcoholic sodium hydroxide solution the *o*-, *m*-, and *p*-nitro-compounds dissolved, giving respectively transient deep orange, orange-yellow, and orange-red colorations which faded to pale

6 DERIVATIVES OF 2- AND 4-HYDROXY- α -NAPHTHALDEHYDES.

yellow tints. The *o*- and *m*-compounds gave intense yellow solutions with concentrated sulphuric acid, whereas the *p*-isomeride developed a deep orange coloration.

*Addition of Hydrogen Cyanide to Azomethine Derivatives
of 4-Hydroxy- α -naphthaldehyde.*

Phenylamino-4-hydroxy- α -naphthylacetonitrile,
 $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{CH}(\text{CN})\cdot\text{C}_{10}\text{H}_6\cdot\text{OH},$

produced as a brownish-yellow powder, crystallised from benzene in colourless, silky needles melting at 122.5° and becoming pink on exposure to air (Found: N = 10.24. $\text{C}_{18}\text{H}_{14}\text{ON}_2$ requires N = 10.22 per cent.).

o-Nitrophenylamino-4-hydroxy- α -naphthylacetonitrile,
 $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}(\text{CN})\cdot\text{C}_{10}\text{H}_6\cdot\text{OH},$

was obtained by leaving the *o*-nitro-azomethine compound in contact with hydrogen cyanide for ten days; it crystallised from benzene in pale brown needles melting at 167° (Found: N = 13.32. $\text{C}_{18}\text{H}_{13}\text{O}_3\text{N}_3$ requires N = 13.16 per cent.).

m-Nitrophenylamino-4-hydroxy- α -naphthylacetonitrile crystallised from benzene in very pale yellow, silky needles melting at 124 — 125° (Found: N = 13.22 per cent.).

p-Nitrophenylamino-4-hydroxy- α -naphthylacetonitrile.—4-Hydroxy- α -naphthylidene-*p*-nitroaniline was suspended in dry ether and agitated daily with excess of hydrogen cyanide over a period of four weeks, when the dark crimson colour had changed to deep orange. The product crystallised from benzene in yellowish-brown needles melting at 202° (Found: N = 13.30 per cent.).

III. Nitration of 2-Hydroxy- α -naphthaldehyde and
 β -Naphthacoumarin.

Nitro-2-hydroxy- α -naphthaldehyde, $\text{NO}_2\cdot\text{C}_{10}\text{H}_5(\text{OH})\cdot\text{CHO}$, was produced by adding 2 c.c. of nitric acid ($d = 1.52$) diluted with 3 c.c. of glacial acetic acid to 5 grams of 2-hydroxy- α -naphthaldehyde dissolved in 100 c.c. of the same solvent, the solution being subsequently heated at 100° . The nitro-derivative crystallised on cooling, and more was obtained on diluting with ice-water.

After crystallisation from benzene or aqueous alcohol, the nitro-aldehyde separated in pale yellow needles melting at 186 — 187° (Found: N = 6.49. $\text{C}_{11}\text{H}_7\text{O}_4\text{N}$ requires N = 6.45 per cent.).

This nitro-2-hydroxy- α -naphthaldehyde gave a sparingly soluble, orange-yellow *sodium* salt, and the *azomethine* derivative, $\text{HO}\cdot\text{C}_{10}\text{H}_5(\text{NO}_2)\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_5$, with hot alcoholic aniline; the latter

product separating in well-defined, orange-red needles melting at 252—253° (Found : N = 9.71. $C_{17}H_{12}O_3N_2$ requires N = 9.59 per cent.). This azomethine compound was insoluble in cold and sparingly soluble in hot aqueous sodium hydroxide, and dissolved to a red solution in alcoholic soda.

Nitro-β-naphthacoumarin, $NO_2 \cdot C_{10}H_5 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{CH} : \text{CH} \end{smallmatrix} \text{CO} \cdot \beta\text{-Naphtha-}$ coumarin, obtained in a 60 per cent. yield by heating equal parts of 2-hydroxy-α-naphthaldehyde and anhydrous sodium acetate with 50 parts of acetic anhydride (95 per cent.) in the rotating autoclave at 180° for three hours (pressure = 3 atm.), was crystallised from 50 per cent. acetic acid. Nitration was effected with two parts of nitric acid ($d = 1.42$) added to one part of naphthacoumarin in ten parts of glacial acetic acid. The solution set to a pale yellow mass, probably consisting of β-naphthacoumarin nitrate. Concentrated sulphuric acid was added until this substance entirely redissolved, when the solution was heated at 100° for two hours and poured on to ice. The nitration product crystallised from pyridine in bright yellow needles melting at 242° (Found : N = 6.09. $C_{13}H_7O_4N$ requires N = 5.81 per cent.).

The reduction of the foregoing nitro-compounds led to the production of somewhat oxidisable bases; the amino-β-naphthacoumarin, m. p. 180—182°, furnished acetyl, benzylidene, and azo-β-naphthol derivatives.

The authors desire to express their thanks to the Advisory Council of the Department of Scientific and Industrial Research for grants which have partly defrayed the expense of this investigation.

CHEMICAL DEPARTMENT,
UNIVERSITY OF BIRMINGHAM,
EDGBASTON.

[Received, December 14th, 1921.]