A Reinvestigation of the Reaction of Salicylideneaniline with Potassium Cyanide

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Treatment of salicylidene-anils with potassium cyanide in acetic acid affords 1:1 adducts shown to be the hydrocyan derivative. When the reaction is conducted in alcohol, salicylidene derivatives of 2-amino-3-arylamino-benzofurans or α-arylamino-o-hydroxy-phenylacetamide are formed depending on the molar ratio of the reactants. The formation of the products and the previously reported structures are discussed.

Schiff bases are known to add hydrogen cyanide to give α-arylaminoarylacetonitriles. Treatment of salicylideneaniline (1a) with potassium cyanide in acetic acid was reported to yield the 1:1 adduct, hydrocyanosalicylideneaniline (2a). The reaction of 1 with potassium cyanide in ethanol depended on the molar ratios of the reactants. With 0.5 mole of potassium cyanide, the reaction afforded a yellow product, m.p. 155 °C for which the authors gave the metaxazine structure 3 rather than 4 as previously stated by Schwab. When more than one mole of potassium cyanide was used, another yellow product, m.p. 135–137 °C was obtained. This product was considered to be an isomer of 2a. We are now reporting a reinvestigation of the behaviour of 1 towards the action of potassium cyanide in both acidic and basic media.

Treatment of 1a with potassium cyanide in a rather larger volume of acetic acid than that reported by Walther and Hübner afforded the 1:1-adduct 2a in an excellent yield and in a purer state. The structure 2a was inferred from being almost colourless and not brown as previously described, its correct analytical data, its IR spectrum which revealed absorptions characteristic for –CN, –NH and OH groups, and the colour reaction with ferric chloride. Similar treatment of salicylidene-m-toluidine (1b) afforded the hydrocyan adduct 2b.

When the reaction of 1a and potassium cyanide was conducted in equimolar ratios in aqueous ethanol at room temperature, the crude product had the melting point reported by Rohde and Schärtle. However, on purification, the product which had m.p. 170 °C, proved to be the acid amide 6 and not an isomer of 2a as previously reported. The assignment of structure 6 was based on analytical and spectral data and colour reaction with ferric chloride. The same compound was also isolated upon treatment of 2a with alcoholic potassium cyanide, potassium carbonate or cold sodium ethoxide. Since the experimental conditions for converting 2a into 6 are not those that can effect the hydrolysis of a cyanide group, it is believed that this conversion takes place via a base-catalysed cy-clo-tautomerisation to an unisolable benzofuran.
intermediate 5 that affords 6 by further action of
the base. The base-catalysed cyclisation of 2a to the
aminobenzofuran intermediate (5), is in analogy
with the reported cyclisation of salicylaldehyde
cyano hydrin to 2-aminobenzofuran on treatment
with sodium ethoxide.

\[
\text{NHPh} \quad \text{CH} - \text{C}=\text{N} \\
\text{NHPh} \quad \text{CH} \quad \text{O} \quad \text{CONH} \\
\text{OH} \\
\text{Base} \\
\text{Salicylaldehyde} \\
\text{base} \\
\text{NHPh} \quad \text{CH} \quad \text{N}=\text{CH} \\
\text{NHPh} \quad \text{CH} \quad \text{O} \\
\text{Base} \\
\text{Salicylidene-aniline} \\
\text{2a} \\
\text{5} \\
\text{6}
\]

Treatment of an alcoholic solution of 1a with
0.5 mole of potassium cyanide at room temperature
afforded a yellow product, m.p. 157 °C, the analyti-
cal data of which are in accordance with that
reported by ROHDE and SCHÄRTEL and not with
that of SCHWAB. However the structure 3, proposed
for this product is not in agreement with the fact
that it is deeply yellow, the absence of absorption
characteristic of a cyano group in its IR, its NMR
spectrum and the ease of its hydrolytic fission with
cold concentrated hydrochloric acid to 2a and
salicylaldehyde. It is now believed that the product,
m.p. 157 °C is the Schiff base 7 arising from salicyl-
idene interchange between the unreacted salicyl-
idene aniline and the aminobenzofuran intermediate
(5). In confirmation of this view, compound 7 was
readily obtained by treatment of 2a with salicyl-
aldehyde in presence of catalytic amount of piperi-
dine. Similar treatment of 2a or 2b with aromatic
aldehydes afforded the Schiff bases 8a–d.

\[
\begin{align*}
8a & : R = R' = H, \\
8b & : R = \text{OCH}_3; R' = H, \\
8c & : R = H, R' = \text{CH}_3, \\
8d & : R = \text{OH}-\text{O}; R' = \text{CH}_3, \\
8e & : R = \text{OCOC}_6\text{H}_5-\text{O}; R' = H, \\
8f & : R = \text{OSO}_2\text{C}_6\text{H}_5-\text{O}; R' = H.
\end{align*}
\]

Compound 8d was also obtained upon treatment
of salicylidene-\(m\)-toluidine with 0.5 mole of potas-
sium cyanide. We would like to report that the
substance, m.p. 126.5 °C isolated upon treatment
of Schiff base 7 with cold hydrochloric acid is not
the acid amide 6 as proposed by ROHDE and
SCHÄRTEL but the hydrocyano derivative (2a).

ROHDE and SCHÄRTEL prepared the benzoyl and
benzenesulphonyl derivatives of the compound,
m.p. 155 °C. The analytical data of these compounds
show that they are the monoacyl derivatives. These
derivatives are now given the O-acyl structure
(8e, f) based on their IR spectra, the negative
colour reaction with FeCl₃ and the recovery of 8a, b
unchanged upon attempted benzoylation.

**Experimental**

M.ps are uncorrected. The IR spectra were re-
corded on a Beckman IR 4-Spectrophotometer
(Nujol mulls).

*α-Arylamino-α-hydroxyphenylacetonitriles (2a, b)*

To a solution of salicylaldehyde (0.1 mole) and
aniline or \(m\)-toluidine (0.1 mole) in glacial acetic acid
(100 ml), potassium cyanide (0.1 mole) dissolved in
the least amount of water added, and the mixture
was kept aside at room temperature overnight. The
crystals that separated were filtered off and re-
crystallized from ethanol.
a-Phenylamino-o-hydroxyphenylacetonitrile (2a) formed almost colourless crystals, m.p. 126 °C, yield 85% and gave a violet colour with FeCl₃.

C₄₁H₁₅ON₂
Caled C 74.99 H 5.38 N 12.49
Found C 74.81 H 5.26 N 12.19
IR = 1620 cm⁻¹ (C = N), 2250 cm⁻¹ (C = N) and broad absorption at ~3300 cm⁻¹ (–NH and –OH).
a-m-Tolylamino-o-hydroxyphenylacetonitriles (2b) formed almost colourless crystals, m.p. 101 °C; yield 80%.

C₁₃H₁₄ON₂
Caled C 75.60 H 5.92 N 11.76
Found C 75.43 H 5.66 N 11.38.
a-Phenylamino-o-hydroxyphenylacetamide (6) formed deep yellow needles from ethanol, m.p. 151 °C, yield 70%-

The m.p. of the crude product was 135-137 °C but that separated were filtered off and recrystallized on twice recrystallisation from benzene, compound 6 was isolated as almost colourless prisms, m.p. 171 °C; yield 50% and gave violet colour with FeCl₃.

C₁₉H₁₄ON₂
Caled C 75.43 H 5.66 N 11.38.

An alcoholic solution of 1a was treated with equimolar amount of potassium cyanide following the procedure described by ROHDE and SCHÄRTEL. The m.p. of the crude product was 135-137 °C but on twice recrystallisation from benzene, compound 6 was isolated as almost colourless prisms, m.p. 171 °C; yield 50% and gave violet colour with FeCl₃.

C₁₉H₁₄O₂N₂
Caled C 69.40 H 5.83 N 11.56
Found C 68.22 H 5.66 N 11.40.
IR = 1690, 3360 and 3500 cm⁻¹ (primary amide group), 3400 cm⁻¹ (–NH) and broad absorption at 3200 cm⁻¹ (–OH).

There were prepared by heating equimolar amounts of 2a with potassium cyanide, potassium carbonate or sod. ethoxide as previously described for the presumed to be an isomer of 2a.

C₂₇H₂₀O₄N₂S
Found C 74.81 H 5.26 N 12.19.
Calcd C 74.99 H 5.38 N 12.49.

3-Arylamino-2-arylideneaminobenzofuran (8a-d)
The Schiff bases 8a-d were prepared by heating equimolar amounts of 2a or 2b and the aromatic aldehyde in presence of a trace of piperidine on a boiling water-bath for 15 minutes, trituration with dilute ethanol and crystallization from ethanol.

Treatment of an ethereal solution of compound 7 with conc. hydrochloric acid as described by ROHDE and SCHÄRTEL afforded the product, m.p. 126 °C which proved to be 2a (m.p. and mixed m.p. and IR spectra) and not compound 6 as previously reported.

The benzoyl derivative (8e) of compound 7 was prepared following the procedure of ROHDE and SCHÄRTEL and it formed deep yellow crystals from ethanol, m.p. 189 °C and gave no colour with FeCl₃.

C₂₈H₂₀O₃N₂S
Caled C 77.76 H 4.66 N 6.37
Found C 77.51 H 4.34 N 6.37.
IR = 1620 cm⁻¹ (C = N), 1735 cm⁻¹ (ester CO) and 3400 cm⁻¹ (–NH).

The benzensulphonyl derivative (8f) of compound 7 formed yellow lustrous needles, m.p. 162 °C.

C₃₇H₂ₐO₅N₂S
Caled C 69.22 H 4.30 N 5.98 S 6.83
Found C 69.01 H 4.18 N 5.69 S 6.72.

2-O-Hydroxybenzylideneamino-3-phenylaminobenzofuran (6)
To a solution of salicylideneaniline (10 g) in ethanol (30 ml), a solution of potassium cyanide (1.7 g) in water (5 ml) was added. The mixture was shaken for three hours, and the orange crystals (7) that separated were filtered off and recrystallized from ethanol as deep yellow needles, m.p. 157 °C; yield 80%.

C₂₃H₁₆O₂N₂
Caled C 67.81 H 4.91 N 8.53
Found C 67.64 H 4.65 N 8.33.
IR = 1625 cm⁻¹ (C = N), 3400 cm⁻¹ (–NH) and broad absorption at 3200 cm⁻¹ (–OH). The ¹H NMR spectrum revealed absorption at –2.20 τ (1 H; for –OH), 1.36 τ (singlet 1 H; for azomethene H), 2.87 τ (multiplet 13 H; for aromatic protons) and 4.30 τ (1 H; for –NH).

Compound 7 was also obtained in 70% yield by heating equimolar amounts of 2a and salicylidenealdehyde in the presence of a trace of piperidine on a boiling water-bath for 15 minutes, trituration with dilute ethanol and crystallization from ethanol.

2-p-Methoxybenzylideneamino-3-phenylaminobenzofuran (8b) formed deep yellow needles from ethanol, m.p. 132 °C, yield 65%.

C₂₉H₂₁O₂N₂
Caled C 80.75 H 5.16 N 8.97
Found C 80.33 H 5.12 N 8.63.

2-0-Hydroxybenzylideneamino-3-m-tolylaminobenzofuran (8d) formed deep yellow needles from ethanol, m.p. 181 °C, yield 70%.
C_{22}H_{18}O_2N_2
Calcd C 77.17 H 5.30 N 8.18,
Found C 76.84 H 5.16 N 8.01.
IR = 1620 cm\(^{-1}\) (C=N), 3400 cm\(^{-1}\) (–OH).

Compound 8d was also obtained in 80% yield by treatment of an ethanolic solution of salicylidene-m-toludine with potassium cyanide as described for compound 7.

Compounds 8a and 8b were recovered unchanged in an almost quantitative yield upon attempted benzylation.

4 W. Haarmann, Chem. Ber. 6, 338 [1873].
6 O. Schwab, Chem. Ber. 34, 839 [1901].