LETTERS TO THE EDITOR

CONDENSATION OF QUINOLINE-5,6-DIAMINE WITH BENZALDEHYDE

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CONDENSATION of quinoline-5,6-diamine[1] with benzaldehyde in 1:2 molar proportions at room temperature in glacial acetic acid has been carried out to yield a yellow gummy material, which on elution through a neutral alumina column afforded two crystalline (TLC pure) products, I (m.p. 175° C) from pet-ether: benzene (1:3) fraction and II (m.p. 265° C) from benzene: ethylacetate (9:1) fraction.

The infrared spectrum of the compound I showed no $-NH$, $-NH_2$ or carbonyl functions. The molecular weight from mass spectrum (M^+ at m/z 335) and elemental analysis of compound I are corresponding to the molecular formula $C_{23}H_{17}N_3$, (found: C, 78·61, H, 4·60, N, 17·21; calculated: C 78·53, H 4·49, N 17·14%). The PMR spectrum ($CDCl_3$) of the compound showed signals at δ 5·5 (S, 2H,$-CH_2-Ph$), at δ 7–8 (m, 12H, aromatic) and at δ 9·2 (m, 3H, pyridine moiety of quinoline).
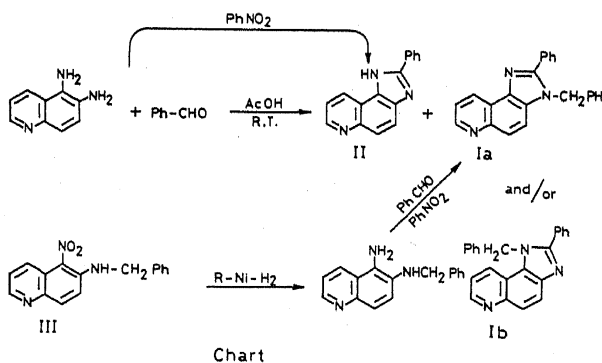
Chart

Based on these spectral and analytical data, compound I is shown to be 1:2 reaction product having either 3H-3-benzyl-2-phenyl imidazo- [4,5-f]-quinoline (I_a) or 1H-1-benzyl-2-phenyl imidazo-[4,5-f]-quinoline (I_b) structure (chart). It has been characterised as the 3H-3-benzyl-2-phenyl imidazo-[4,5-f] quinoline (I_a) by comparison with an authentic sample synthesised unambigously, starting from 6-benzyl amino-5-nitro quinoline[2] (III) by reduction with Raney nickel hydrazine and subsequent condensation with benzaldehyde in refluxing nitrobenzene. The synthetic sample and condensation product (I) have identical m.p., m.m.p. and i.r. spectra.

The i.r. spectrum of compound II showed a broad absorption at 3300–2900 cm^{-1}, assignable to tautomeric $-NH-$ function. The molecular weight from the mass spectrum M^+ at m/z 245) and elemental analysis are corresponding to molecular formula $C_{16}H_{11}N_3$, (found: C, 82·21; H, 5·10; N, 12·60; calculated: C 82·09, H, 5·08, N, 12·53%).

On the basis of these spectral and analytical data compound II is shown to be a 1:1 reaction product and characterised as 2-phenyl imidazo-[4,5-f]-quinoline. The structure has been confirmed by comparison with an authentic sample synthesised by the condensation of 5,6-quinoline diamine with benzaldehyde in 1:1 molar proportions in refluxing nitrobenzene for 1·5 h (identical m.p., m.m.p. and i.r. spectra).

Further details of the mechanism of formation of these products will be published elsewhere.

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SPECTROPHOTOMETRIC DETERMINATION OF TRACES OF FORMALDEHYDE WITH β-NAPHTHOL

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IN view of the importance of formaldehyde in industry, a systematic analytical method for its determination has been necessary. Polarographic[1,2], Gas chromatographic[3,4] and HPLC[5,6] methods have been proposed for the determination of formaldehyde. Among the colorimetric methods chromotropic acid[7], acetyl-acetone[8] and phenylhydrazine derivatives[9-11] are frequently employed, though these methods have their own drawbacks. During our investigations on the determination of formaldehyde in diesel exhausts it was found that β-naphthol reacted very sensitively with formaldehyde to give an orange-coloured product.

This paper describes the development of a sensitive analytical procedure based on this reaction for the determination of formaldehyde at microgram levels.

Samples (1 ml) containing 0–30 μg of formaldehyde were taken in a series of 10 ml standard flasks to which were added 0·5 ml of 0·1% β-naphthol in acetic acid and 5 ml of conc. sulphuric acid. The contents were mixed thoroughly for 2 minutes. This was followed by the addition of acetic acid upto the mark and the contents were again mixed. Absorbance of the samples was measured at 497 nm against the reagent blanks using a Shimadzu 200 A spectrophotometer.

Unknown samples were treated in the same manner and the formaldehyde content was determined by referring to the calibration curve.
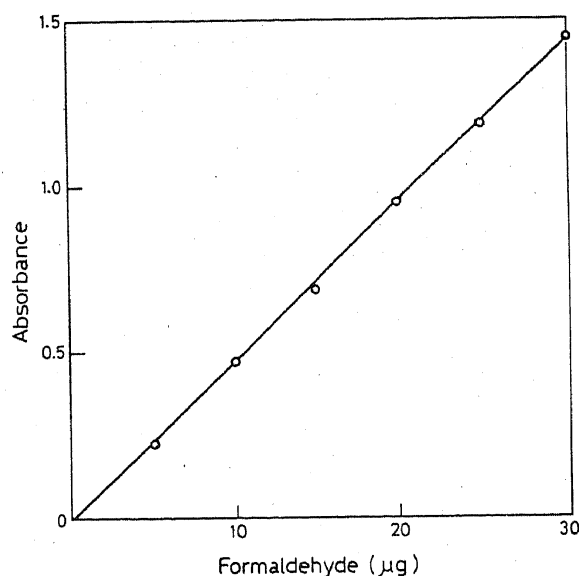
Formaldehyde (μg)

Preliminary investigations revealed that β-naphthol reacted with microgram quantities of formaldehyde in sulphuric acid medium with an absorbance maximum at 497 nm. The colour intensity was unaffected by other acids except acetic acid, which enhanced the absorbance maximally when present in equal proportions. Measurement of absorbance at different time intervals revealed that the complex was stable for more than 6 hours. Owing to the high viscocity of the medium, maximum colour development took place only after vigorous shaking for 2 minutes. Optimum reagent concentration was found to be 0·3 ml of 0·1% β-naphthol in acetic acid. However, a slight excess of the reagent (0·5 ml) was maintained in subsequent experiments. The reagents mixed in the order formaldehyde-β-naphthol-sulphuric acid-acetic acid gave maximum absorbance compared to other modes of addition. The absorbance was found to be linear upto 30 μg of formaldehyde, though the optimum working range up to 20 μg is recommended for routine experiments. The system was found to be remarkably free from interference from other aldehydes, ketones and glyoxal when present in equal quantities.

The composition of the complex was 1:2 and the relative standard deviation for 10 determinations of 7·5 μg of formaldehyde was 0·31%. The molar extinction coefficient and sandel sensitivity were determined to be $1·44 \times 10^4$ 1 mole^{-1} cm^{-1} and 0·002 μg/cm^2 which is considerably higher than chromotrophic acid method (0·003 μg/cm^2).

Exhaust emissions from a diesel engine were collected in a 500 ml separatory funnel with a side arm fitted with a wide inlet cone and a bulb containing anhydrous silica gel and glass wool to remove moisture and particulate matter. The exhaust was allowed to pass through the sampler for 5 minutes before the sample was collected. Then the side arm was removed, 10 ml of distilled water was introduced and equilibrated for 5 minutes. The aqueous solution was analysed by β-naphthol and chromotropic methods for formaldehyde content. Table I lists duplicate sampling and analysis data under different operating conditions, from which it is clear that β-naphthol method agrees closely with the standard method.

TABLE I

Diesel exhaust analysis

| Operating conditions | | | Formaldehyde (PPM) | |
RPM	Load	Temp.	β-naphthol	Chromo- tropic acid
2000	82	550°C	18·07	18·7
			18·8	18·7
2000	52	350°C	16·0	15·5
			15·5	15·5
2000	—	100°C	15·5	15·0
			15·5	15·0

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KINETICS AND MECHANISM OF CHROMIC ACID OXIDATION OF LACTIC ACID

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ALL known chromic acid oxidations involve either Cr(IV) and/or Cr(V) as transient species[1]. Cr(V) closely parallels in the reactivity with Cr(VI) in affecting C–H cleavage in the oxidation of alcohols[2,3]. Cr(IV) is responsible for the C–C cleavage product in the oxidation of cyclobutanol[4]. Both C–H and C–C cleavage products have been reported in the Cr(VI) oxidation of glycolic[5] and mandelic[6] acids.

In our search for other closely related systems where there is a possibility of C–H and C–C bond breaking,

we found that previous work on the oxidation of lactic acid has been fragmentary[7-8]. In two of the authentic reviews on chromic acid oxidation by Westheimer[9] and Wiberg[1], lactic acid oxidation was shown to give quantitative yields of the C–C cleavage product *viz.* acetaldehyde.

$$3CH_3CHOH\ COOH + 2Cr(VI) \longrightarrow$$
$$3CH_3CHO + 3CO_2 + 2Cr(III) \qquad (1)$$
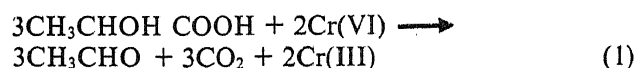
We have reexamined the oxidation of lactic acid by Cr(VI). The following new features emerged from our study.

1. In the concentration range LA $(5 \times 10^{-3} - 2 \cdot 0M)$, H^+ $(5 \times 10^{-4} - 5 \times 10^{-1}M)$ and Cr(VI) $(5 \times 10^{-4} - 2 \times 10^{-2}M)$, the rate expression has the form.

$$-\frac{[Cr(VI)]}{dt} = [HCrO_4^-][LA]\ (k_1 + k_2\ (H^+) + k_3\ (LA)) \qquad (2)$$

At 35° the least square values of the rate constants are:

$$k_1 = 2 \cdot 17 \times 10^{-4}\ M^{-1}\ s^{-1}$$
$$k_2 = 4 \cdot 44 \times 10^{-2}\ s^{-1}\ \text{and}\ k_3 = 5 \cdot 33 \times 10^{-3}\ M^{-2} s^{-1}.$$

The second order term in lactic acid (LA) is dominant at low $[H^+\ \delta]$ and is being reported for the first time.

2. Oxidation of lactic acid under conditions when the LA: Cr(VI) ratio is high yielded the C–H cleavage product, pyruvic acid.

Table I presents the product yields in the Cr(VI) oxidation of lactic acid.

In a typical experiment 10 ml of 5M LA, 5 ml of 10M $HClO_4$ was made to a total volume of 90 ml and was taken in a 250 ml 3-necked flash fitted with a nitrogen entry tube, a separatory funnel, a gas outlet tube with polythene tubing connecting to a gas inlet tube which dipped into a saturated solution of 2,4 dinitrophenylhydrazine in 2N HCl (50 ml). 10 ml of $0 \cdot 1M$ $Na_2Cr_2O_7$ solution was added while a slow stream of oxygen free nitrogen was bubbling. The reaction mixture was warmed (60°C) to sweep off any acetaldehyde by nitrogen into the 2,4-dinitrophenyl hydrazine solution. Negligibly small amounts of acetaldehyde-2,4-dinitrophenyl hydrazone formed mp 165° (lit. 168). The main reaction mixture was then treated with 100 ml of saturated solution of 2,4-dinitrophenyl hydrazine in 2N HCl and kept overnight. The precipitated 2,4 DNPH was filtered, dried and was characterised as pyruvic acid, 2,4 DNPH mp 218°C (lit. 218). The IR and ^{1}HNMR spectra was identical with that of an authentic sample indicating that it is essentially free from acetaldehyde-2,4 DNPH impurity.