

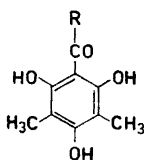
Phenol Dehydrogenations

12.* Oxidative Coupling of
3,5-Dimethyl-2,4,6-trihydroxy-
benzophenone

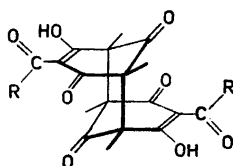
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It has recently been shown in this laboratory that some fully substituted phloroglucinol derivatives (Ia and Ib) couple oxidatively to give a novel type of dimer¹ (IIa and IIb, respectively). Somewhat similar dimerisations of pyrogallol and several other compounds have been reported by Teuber *et al.*^{2,3}



- I a, R = H
I b, R = CH₃
I c, R = C₆H₅



- II a, R = H
II b, R = CH₃
II c, R = C₆H₅

It was of interest to see whether suitably substituted benzophenones undergo similar oxidative dimerisations and therefore 3,5-dimethyl-2,4,6-trihydroxybenzophenone (Ic) was prepared and oxidised with ferric chloride. This gave a compound C₃₀H₂₄O₈ in about 70% yield.

Spectroscopic investigation showed the new dimer to be IIc. The IR spectrum

(CHCl₃) showed the presence of an enolised, strongly chelated 2-benzoylcyclohexane-1,3-dione grouping by bands at 1664 cm⁻¹ (conjugated carbonyl), 1540 cm⁻¹ (chelated carbonyl) and 1725 cm⁻¹ (non-conjugated carbonyl). (Corresponding figures¹ for compound IIb: 1665 cm⁻¹, 1545 cm⁻¹ and 1725 cm⁻¹, respectively.)

The NMR spectrum in deuterodimethylsulphoxide at 120° showed a signal corresponding to four methyl groups (12 protons) at 1.37 ppm and another corresponding to two phenyl groups (10 protons) at 7.65 ppm.

Experimental. 3,5-Dimethyl-2,4,6-trihydroxybenzophenone. Zinc chloride (2 g) was added to a solution of dimethylphloroglucinol (5 g) and benzonitrile (5 g) in dry ether (40 ml). Dry hydrogen chloride was passed through the mixture for 3 h and the sticky product was kept at 0° for 12 h. Dilute hydrochloric acid (1:1) was then added dropwise followed by a little water. The mixture was stirred and cooled in the refrigerator giving a fine yellow precipitate of the imine hydrochloride. This was collected and washed with a little water and then with ether. The dried product was dissolved in water (500 ml) and boiled for 30 min. The 3,5-dimethyl-2,4,6-trihydroxybenzophenone obtained on cooling was crystallised from water (or chloroform-light petroleum) giving yellow crystals, m.p. 134°. Yield 3.6 g (42%). (Found: C 68.6; H 5.5. Calc. for C₁₅H₁₄O₄: C 69.8; H 5.5).

Dehydrogenation of 3,5-dimethyl-2,4,6-trihydroxybenzophenone. Iron (III) chloride (2.5 g) in water (25 ml) was added to 3,5-dimethyl-2,4,6-trihydroxybenzophenone (1 g) in ethanol (20 ml). The mixture was boiled under reflux (1 h). Hydrochloric acid (1:1) (10 ml) was then added with stirring and the mixture kept at 0° when a brownish product was obtained. This was collected, washed with dilute hydrochloric acid and water and dried. The product was dissolved in pyridine (6 ml) and acetic acid (6 ml) was added followed by conc. hydrochloric acid (9 ml). The pale brownish precipitate obtained on cooling was washed with water, dried and recrystallised from glacial acetic acid giving slightly tan-coloured crystals, m.p. 284–286°. Yield 0.67 g (68%). (Found: C 70.15; H 4.6%. M.wt. (Rast) 506. Calc. for C₃₀H₂₄O₈: C 70.3; H 4.7%. M.wt. 512).

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Note on the Crystal Structure of Potassium Pentacyanonitrosylvanadate(I), $K_3V(CN)_5NO \cdot 2H_2O$

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Potassium pentacyanonitrosylvanadate was first prepared in 1958 by Griffith, Lewis and Wilkinson¹ who formulated the compound as $K_3V(CN)_5NO \cdot H_2O$. The crystal structure of the isoelectronic pentacyanonitrosylmanganate, $K_3Mn(CN)_5NO \cdot 2H_2O$ ² and the structures of the related chromium and molybdenum complexes, $K_3Cr(CN)_5NO$ ³ and $K_3Mo(CN)_5NO$ ⁴ have been determined at this department as part of a series of structural investigations of the transition metal pentacyanonitrosyls. The crystal structure of potassium pentacyanonitrosylvanadate, which should perhaps be reformulated as $K_3V(CN)_5NO \cdot 2H_2O$, has now also been investigated and a preliminary report will be given in this note.

Potassium pentacyanonitrosylvanadate was prepared according to the method of Griffith, Lewis and Wilkinson¹ whereby an alkaline solution of ammonium vanadate was first treated with a solution of potassium cyanide and then with hydroxylammonium chloride. The orange oily liquid phase which separated when the solution was subsequently poured on to alcohol was washed several times with alcohol, dissolved in water, re-separated with alcohol and then allowed to stand under alcohol. After several days bright orange plate-like

crystals separated from the oil. A suitable crystal was picked out under the microscope, dried between filter papers and mounted in a glass capillary. Rotation photographs and Weissenberg photographs of the layers $h0l-h4l$, inclusive, were recorded using multiple film equi-inclination Weissenberg techniques and $CuK\alpha$ radiation. The relative intensities of the 463 reflections thus registered were estimated by visual comparison with a standard scale.

The crystal was found to be orthorhombic with the approximate cell dimensions:

$$a = 15.6 \text{ \AA}, b = 7.2 \text{ \AA}, c = 11.7 \text{ \AA}$$

The observed conditions of reflection,

$$\begin{aligned} 0kl:l &= 2n \\ h0l:l &= 2n \\ hk0:h+k &= 2n \end{aligned}$$

are in accordance only with space group No. 56, *Pccn*. The calculated density based on four formula units of $K_3V(CN)_5NO \cdot H_2O$ in the unit cell is $2.15 \text{ g}\cdot\text{cm}^{-3}$ ($1.84 \text{ g}\cdot\text{cm}^{-3}$ for four formula units of $K_3V(CN)_5NO \cdot 2H_2O$). The experimental density was determined by the method of flotation using mixtures of bromoform and carbon tetrachloride to be $1.83 \text{ g}\cdot\text{cm}^{-3}$.

Three potassium atoms and the vanadium atom could be located from a "three-dimensional" Patterson synthesis of the reflection data. There were, however, no peaks which could be attributed to the two additional potassium atoms required by the formula $K_3V(CN)_5NO \cdot H_2O$. Successive Fourier syntheses based on the vanadium and the two preliminary potassium positions revealed the positions of all light atoms, including the oxygen atom O(1) of a water molecule situated in $8e$, the *R*-value being 0.151. The arrangement of the six ligand groups around vanadium was approximately octahedral and all groups were at this stage treated as cyanide. After five cycles of isotropic least squares refinement the *R*-value dropped to 0.117. The preliminary atomic parameters and isotropic temperature coefficients obtained after the last cycle are given in Table 1.

It was obvious that since vanadium occupies the position $4c$ and no ligands are aligned along the diad axis, the structure must be disordered, and, as expected, there are two shorter V-C distances (1.79 \AA) corresponding to V-C(2) and four longer V-C distances, two of 2.20 \AA (V-C(1)) and two of 2.16 \AA (V-C(3)). The nitrosyl