Syntheses of Some Hydroquinone Derivatives

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Work has been in progress in this laboratory for some time on the synthesis of a number of substituted phenyl- and benzoylalkanes. A Friedel-Crafts reaction on adipoyl chloride and hydroquinone dimethylether gave 1,4-bis(2,5-dimethoxybenzoyl)butane and δ-(2,5-dimethoxybenzoyl)valeric acid. The ratio of the two reaction products depended on the proportion of adipoyl chloride to hydroquinone dimethylether.

Reduction and demethylation of 1,4-bis(2,5-dimethoxybenzoyl)butane gave 1,6-bis(2,5-dihydroxyphenyl)hexane. Oxidation of this hydroquinone gave the corresponding quinone.

Until recently the only attempt that had been made to prepare these types of substances was that of Bruce *et al.* [1] who obtained δ-(2,5-dihydroxybenzoyl)valeric acid in poor yield from hydroquinone and adipic acid using an $AlCl_3$-NaCl melt. No other products were isolated. Okuma and Tamura [2] have now prepared some of these substances by other methods for use as antioxidants.

Experimental. (Melting points were determined with a Koefler apparatus.)

δ-(2,5-Dimethoxybenzoyl)valeric acid and 1,4-bis(2,5-dimethoxybenzoyl) butane. Hydroquinone dimethylether (70 g, 0.5 mole) and adipoyl chloride (183 g, 1.0 mole) were dissolved in dry carbondisulfide (300 g) and finely ground $AlCl_3$ (266 g, 2.0 mole) was added with stirring. The temperature was not allowed to exceed 10°C. After the addition of $AlCl_3$ was complete the solvent was decanted from the orange-red syrup, and this was decomposed with ice. The reaction products were shaken out with chloroform and the acid fraction was separated by shaking with $NaHCO_3$-solution. δ-(2,5-Dimethoxybenzoyl)valeric acid was precipitated with hydrochloric acid, dried and recrystallised from benzene-light petroleum, white prisms, m.p. 80.5—82°C (65 g). (Found: C 63.55; H 6.69; OCH_3 22.7. $C_{14}H_{18}O_5$ requires C 63.14; H 6.81; OCH_3 23.3.)

The neutral chloroform solution was dried and evaporated and the 1,4-bis (2,5-dimethoxybenzoyl) butane was recrystallised from 95 % ethanol, white needles, m.p. 112—113°C (10 g) (Found: C 68.50; H 6.63; $C_{22}H_{26}O_6$ requires C 68.37; H 6.78.)

δ-(2,5-Dihydroxybenzoyl)valeric acid. δ-(2,5-Dimethoxybenzoyl) valeric acid (5 g) was demethylated by refluxing for 1 h in a mixture of hydrobromic acid (48 %, 40 ml) and acetic acid (100 ml). The acetic acid was evaporated and the δ-(2,5-dihydroxybenzoyl) valeric acid was precipitated by cooling and recrystallised from water, yellow leaves m.p. 130—131.5°C (Bruce *et al.*[1]: 130°C) (3 g).

The crystalline acid chloride of δ-(2,5-dimethoxybenzoyl)valeric acid was prepared in good yield with oxalyl chloride in dry benzene at room temperature by the method of Adams[3]. It gave 1,4-bis (2,5-dimethoxybenzoyl) butane by reaction with hydroquinone dimethylether and aluminium chloride as above.

1,6-Bis (2,5-dimethoxyphenyl) hexane. 1,4-Bis(2,5-dimethoxybenzoyl)butane (10 g) suspended in absolute ethanol (300 ml) was hydrogenated over a 5 % Pd on charcoal catalyst (2 g) (Theilacker [4]). 2 400 ml of hydrogen (760 torr) was adsorbed in 120 min. The reduced product was soluble in ethanol; the catalyst was filtered off and the solvent evaporated giving 1,6-bis (2,5-dimethoxyphenyl) hexane (7.5 g) which was recrystallised from light petroleum, white needles, m.p. 55—56°C. (Found: C 73.38; H 8.33. $C_{22}H_{30}O_4$ requires C 73.71; H 8.44.)

1,6-Bis (2,5-dihydroxyphenyl) hexane. 1,6-Bis (2,5-dimethoxyphenyl)hexane (5 g) was mixed with pyridine hydrochloride (20 g) and heated to 200°C in oil bath for 2 h by the method of Prey [5]. After cooling, 150 ml of water was added to the reaction mixture. The oil which separated crystallised on standing and was recrystallised from acetonitrile, white needles, m.p. 160.5—162°C (3 g). (Found: C 70.61; H 7.18; $C_{18}H_{22}O_4$ requires C 71.50; H 7.34.)

1,6-Bis(p-benzoquinoyl)hexane. 1,6-Bis (2,5-dihydroxyphenyl) hexane (400 mg) dissolved in acetic acid (50 ml) was heated to about 50°C, and a 10 % solution of CrO_3 in water (2 ml) was added. The quinone which separated was filtered after cooling and recrystallised from acetonitrile, yellow leaves m.p. 153.5—155.5°C. (Found: C 72.15; H 6.10. $C_{18}H_{18}O_4$ requires C 72.47; H 6.08.)

ε-(2,5-Dimethoxyphenyl)hexanoic acid. δ-(2,5-Dimethoxybenzoyl)valeric acid was reduced in the same way as the 1,4-bis (2,5-dimethoxybenzoyl)butane; white crystals, m.p. approx. 40°C. It was difficult to purify and was characterised by its *p*-toluidide: ε-(2,5-

Dimethoxyphenyl) hexanoyl chloride (1 g), prepared with oxalyl chloride in the same way as δ-(2,5-dimethoxybenzoyl)valeroyl chloride, was refluxed with *p*-toluidine (2 g) in dry benzene (50 ml) for 15 min. After cooling the solution was washed with water, dilute hydrochloric acid and bicarbonate solution. The solution was dried and evaporated and the residue was recrystallised from benzene--light petroleum and gave white needles m.p. 103.5—105°C. (Found: C 73.26; H 7.98; N N 3.79. $C_{21}H_{27}O_3N$ requires C 73.86; H 7.97; N 4.10.)

1,4-Bis(2-hydroxy-5-methoxybenzoyl) butane. 1,4-Bis(2,5-dimethoxybenzoyl)butane (3 g) was dissolved in a cooled solution of $AlCl_3$ (12 g) in nitrobenzene (150 ml). After 45 h at room temperature the mixture was decomposed with ice and the nitrobenzene was removed by steam distillation. The solid product was dissolved in chloroform and shaken with sodium hydroxide solution (1 N). The alkaline solution was acidified with hydrochloric acid and the crystals which separated were dissolved in chloroform. After drying the chloroform solution was run through a silica gel column and evaporated. A small amount of pure 1,4-bis(2-hydroxy-5-methoxybenzoyl)butane was obtained. It was recrystallised from ethanol-benzene, yellow prisms, m.p. 157—158°C. It gave a violet colour with $FeCl_3$ in methanol. (Found: C 66.49; H 6.22; OCH_3 15.9. $C_{20}H_{22}O_6$ requires C 67.03; H 6.19; OCH_3 16.1.)

An attempt to prepare this substance from adipoyl chloride, hydroquinone monomethylether and aluminium chloride using the same conditions as in the preparation of 1,4-bis (2,5-dimethoxybenzoyl)butane gave the bis-*p*-methoxyphenylester of adipic acid, white needles from ethanol, m.p. 126—127°C. (Found: C 67.13; H 6.04. $C_{20}H_{22}O_6$ requires C 67.02, H 6.19.)

Infrared spectrum of 1,4-bis(2-hydroxy-5-methoxybenzoyl)butane indicated that the demethylation took place in the *ortho* positions to the carbonylgroups. There was no absorption attributable to a hydroxyl group in the 3 500—2 500 cm^{-1} region. The same is true for *o*-hydroxyacetophenone which is attributed to intramolecular hydrogen bonding by Hergert [6].

The carbonyl frequency of 1,4-bis(2,5-dimethoxybenzoyl) butane was measured to 1 665 cm^{-1} and that of 1,4-bis(2-hydroxy-5-methoxybenzoyl) butane to 1 650 cm^{-1}. The difference is 15 cm^{-1}. The difference between the carbonyl frequencies of *o*-methoxyacetophenone and *o*-hydroxyacetophenone [6] is 14 cm^{-1}, from 1 649 cm^{-1} to 1 635 cm^{-1}.

The low carbonyl frequency of 1,4-bis(2-hydroxy-5-methoxybenzoyl)butane may be explained if a conjugated chelate system as in *o*-hydroxyacetophenone [6] is assumed.

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Metal-Metal Bonding in a Mixed Chromium Molybdenum Oxide Phase of Rutile Structure

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Mixed chromium molybdenum oxide $(Cr,Mo)O_2$ of rutile type has been prepared by heating mixtures of chromium(III)-oxide, molybdenum(IV)oxide and molybdenum (VI)oxide ($Cr_2O_3 + aMoO_2 + MoO_3$) in sealed, evacuated silica tubes and keeping the temperature at about 1 000°C for several days. For values of a of 3 – 7.5 the X-ray powder patterns showed that the products only contained the rutile type phase. The width of the homogeneity range was not determined. No indications were observed of the metal atoms being ordered. The following unit cell dimensions were obtained:

	a	c	V
$Cr_{0.33}Mo_{0.67}O_2$	4.696 Å	2.886 Å	63.64 Å^3
$Cr_{0.22}Mo_{0.78}O_2$	4.749	2.858	64.44
$Cr_{0.19}Mo_{0.81}O_2$	4.760	2.848	64.53

The increase of the unit cell volume with the molybdenum content is in accordance