Tetrahedron Vol. 34, pp. 1595–1596
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0040-4020/78/0801-1595/$02.00/0

OXIDATION OF ALKOXYPHENOLS—XXIV[1]

A DIPHENO-2,2'-QUINONE FROM SESAMOL

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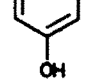
(*Received in the UK* 15 *November* 1977; *Accepted for publication* 1 *December* 1977)

Abstract—Oxidation of sesamol with ferric chloride or potassium ferricyanide gives 4,5,4',5'-bismethylenedioxy-dipheno-2,2'-quinone. Oxidation of sesamyl benzyl ether with vanadium oxytrifluoride leads exclusively to C_6 coupling, and provides a better route to the diphenoquinone.

Sesamol 1 is of significance as the natural anti-oxidant present in sesame oil.[2] In this capacity its action is to donate hydrogen to alkylperoxy radicals. The resulting sesamyl aryloxy radical may then react with another alkylperoxy radical or dimerise. As a result of the latter reaction the oxidative coupling products of sesamol may be ingested, and it is therefore of interest to identify these.

In 1907 Malagnini and Armanni reported that sesamol gave a violet brown colour with ferric chloride.[3] On repeating this reaction a low yield of indigo-coloured material was isolated, and oxidation of alkaline solutions of sesamol with potassium ferricyanide gave the same compound in higher yeild (66%). No other products could be isolated. This material was practically insoluble in most solvents, but could be recrystallised from nitromethane. Addition of water to a hot dimethylformamide solution resulted in immediate loss of colour. Although its limited solubility precluded examination by NMR, the similarity of other spectroscopic properties of the indigo material to those of the dipheno-2,2'-quinone produced on oxidation of 3,4-dimethoxyphenol[4,5] indicated that it was the diphenoquinone 2. The *trans* configuration is assumed on steric grounds.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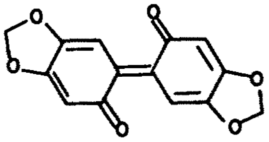
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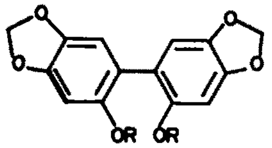
To establish structure 2 with certainty it was necessary to prepare the dihydroxybiphenyl 3. Numerous attempts to couple either 6-iodosesamyl benzoate, 6-iodosesamyl benzyl ether or 4,5 - methylenedioxy - 2 - nitrobromobenzene by the Ullmann reaction were unsuccessful, and resulted in reduction, accompanied by an almost explosive liberation of blue vapour in the former two cases. In view of the successful Ullmann coupling of 4-iodoveratrole[6] this is surprising. Vanadium oxytrifluoride has recently been shown to couple phenol ethers oxidatively in high yield.[7] Using this reagent sesamyl benzyl ether was easily converted into the dibenzyloxybiphenyl 4. Hydrogenolysis then gave the phenol 3, which was oxidised quantitatively by potassium ferricyanide to the quinone 2.


3: R = H
4: R = OCH_2Ph

The occurrence of these dipheno-2,2'-quinones is quite rare. Previous examples have been listed by Erdtman[4] and Becker.[5]

EXPERIMENTAL

M.ps were taken with a Kofler hot-stage. Microanalyses were by the Australian Microanalytical Service. NMR spectra were measured with a Varian A-60 spectrometer, mass spectra with a Varian MAT-CH7, UV spectra with a Beckman Acta MIV and IR spectra with a Perkin–Elmer 283 spectrometer. Extracts were dried with magnesium sulphate.

Oxidation of sesamol

(a) An excess of aqueous ferric chloride was added to a stirred solution of sesamol (0.70 g) in ethanol. The indigo precipitate was filtered off and washed with water, ethanol and chloroform. Recrystallisation of this (90 mg) from nitromethane gave 4,5,4',5' - bismethylenedioxydipheno - 2,2'-quinone 2 (30 g) as dark violet needles, m.p. 215–216°. $\lambda_{max}^{CHCl_3}$ 242 nm log ε 4.07, 254 (4.05), 375 (3.92), 550 (3.92), changing on standing during 5 h to 247 (3.96), 258 *sh* (3.94), 304 (3.90). $\nu_{max}^{CHCl_3}$ 1610 cm^{-1}. *m/e* M + 2^+ 274, M^+ 272. Found: C, 61.8; H, 3.2. Calc. for $C_{14}H_8O_6$: C, 61.8; H, 3.0%.

(b) An aqueous soln of potassium ferricyanide (1.32 g) and sodium carbonate (0.6 g) was shaken with a soln of sesamol (275 mg) in chloroform. The almost solid violet mixture was filtered with difficulty, and the residue was washed with water, then ethanol, leaving 180 mg. Recrystallisation of a portion from nitrobenzene gave the diphenoquinone 2, m.p. and m.m.p. 215–216°.

Oxidation of sesamyl benzyl ether

Sesamyl benzyl ether was prepared as described by Beroza[9] and had n_D^{28} 1.5855 (lit.[9] n_D^{25} 1.5850). Crystallisation from light petroleum gave prisms, m.p. 45–46°. The ether (6.1 g) was dissolved in dichloro-methane (50 ml) containing acetic acid (10 ml) and cooled to 0°. To this a solution of vanadium oxytrifluoride (3.6 g) in acetic acid (30 ml) was added dropwise with stirring over 20 min. The mixture was poured into water and extracted with CH_2Cl_2. The extract was washed with sodium bicarbonate, then water, dried and concentrated to a brown gum. Chromatography on alumina and elution with hexane–chloroform (9:1) gave 2,2' - dibenzyloxy - 4,5,4',5' - bismethylenedioxybiphenyl 4 (5.2 g) as elongated plates, m.p. 107–108°, from ethanol. NMR ($CDCl_3$) δ 4.88 (4 $ArCH_2$), 5.90 (4 OCH_2O), 6.59 (2 ArH), 6.73 (2 ArH), 7.20 (10 ArH). Found: C, 74.2; H, 4.9. Calc. for $C_{28}H_{22}O_6$: C, 74.0; H, 4.9%.

4,5,4',5'-Bismethylenedioxybiphenyl 2,2'-diol 3

The ether 4 (0.6 g) was hydrogenated in acetic acid over Pd/C, taking up 2 mole equivalents of hydrogen. After filtering, the acetic acid was removed under reduced pressure and the residue was taken up in ether and washed with sodium bicarbonate, then water, dried and concentrated. Recrystallisation of the residue from benzene gave the diol 3 (225 mg) m.p. 207–207.5°. NMR (Me_2CO) δ 5.92 (4 OCH_2O), 6.52 (2 ArH), 6.70 (2 ArH). Found: C, 61.4; H, 3.7 Calc. for $C_{14}H_{10}O_6$: C, 61.3; H, 3.7%. The dibenzoate crystallised as prisms from benzene, m.p. 169–170° with partial melting and resolidification at 120°. Found: C, 73.1; H, 4.3. Calc. for $C_{28}H_{18}O_8 \cdot C_6H_6$: C, 72.9; H, 4.3%.

Oxidation of the diol 3 in dilute potassium hydroxide with excess of potassium ferricyanide gave a quantitative yield of the quinone 2, m.p. and m.m.p. 215–216°.

Iodination of sesamol derivatives

Sesamyl benzyl ether (1.9 g) and silver trifluoroacetate (1.82 g) were stirred in chloroform while a solution of iodine (2.1 g) in chloroform was added dropwise. Filtration and concentration gave a crystalline residue of 6-iodosesamyl benzyl ether which was obtained as prisms, m.p. 87–88° (2.4 g) from ethanol. NMR (CCl_4) δ 4.99 (2 $ArCH_2$), 5.87 (2 OCH_2O), 6.43 (ArH), 7.13 (ArH), 7.33) (m, 5, ArH). Found: C, 47.6; H, 3.2; I, 35.8. Calc. for $C_{14}H_{11}O_3I$: C, 47.2; H, 3.2; I, 36.0%.

Sesamyl benzoate (m.p. 56–57°, lit.[9] 56–56.5°) (1.0 g), silver trifluoroacetate (0.91 g) and iodine (1.05 g) were reacted as above. Recrystallisation of the product from ethanol gave 6-iodosesamyl benzoate (1.25 g) m.p. 133–134°. NMR ($CDCl_3$) δ 6.02 (2 OCH_2O), 6.78 (ArH), 7.22 (ArH), 7.5–8.4 (m, 5 ArH). Found: C, 45.8; H, 2.7; I, 34.5. Calc. for $C_{14}H_9O_4I$: C, 45.4; H, 2.5; I, 34.7%.

Reaction of these iodo compounds with various forms of copper either without solvent or in dry dimethylformamide gave the desiodo compounds as the only identifiable products.

Acknowledgement—We thank the Australian Reaearch Grants Committee for financial assistance.

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