

### Preparation of 2-Substituted-4-Monoketals of Benzoquinone

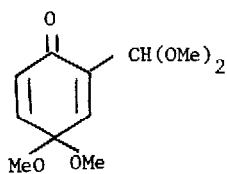
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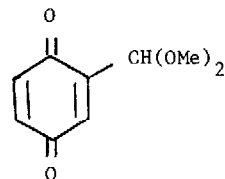
**Summary.** Oxidation of 2-formyl-4-methoxyphenol with thallium trinitrate in methanol and trimethylorthoformate gives 2-dimethoxymethyl-4,4-dimethoxycyclohexa-2,5-dienone whereas oxidation of 2-methoxycarbonyl-4-methoxyphenol gives 2-methoxycarbonyl-3,4,4-trimethoxycyclohexa-2-5-dienone

Monoketals of p-quinones are valuable as key intermediates in several syntheses and are prepared by selective hydrolysis of the corresponding bisketals or by oxidation of a p-alkoxyphenol with thallium trinitrate trihydrate (TTN).<sup>1,2,3</sup> We report the influence of electron withdrawing groups such as 2-formyl and 2-methoxycarbonyl on the oxidation of 4-methoxyphenols with TTN in dry methanol and trimethylorthoformate

With 2-formyl-4-methoxyphenol the TTN reagent at  $-20^{\circ}$  gives 2-dimethoxymethyl-4,4-dimethoxycyclohexa-2,5-dienone (1)  $\tau$  ( $\text{CDCl}_3$ ) 2.9 (1H, d, J 3Hz), 3.2 (1H, dd, J 10 and 3Hz), 3.7 (1H, d, J 10 Hz), 4.7 (1H, s), 6.6 (2H, s),  $\nu$ , 1680 and 1660  $\text{cm}^{-1}$ . 2-Formyl-4,4-dimethoxycyclohexa-2,5-dienone was not obtained and selective ketal exchange with acetone in the presence of a trace of p-toluenesulphonic acid gives 2-dimethoxymethylbenzoquinone (2), m.p. 80-81 $^{\circ}$ ,  $\tau$  ( $\text{CDCl}_3$ ) 3.2 (1H), 3.3 (2H), 4.7 (1H) 6.6 (6H),  $\nu_{\text{max}}$  1660, 1610  $\text{cm}^{-1}$ . The unusually rapid acetalisation of a formyl group also occurs during the TTN oxidation of the vanillins under similar conditions.<sup>4</sup>

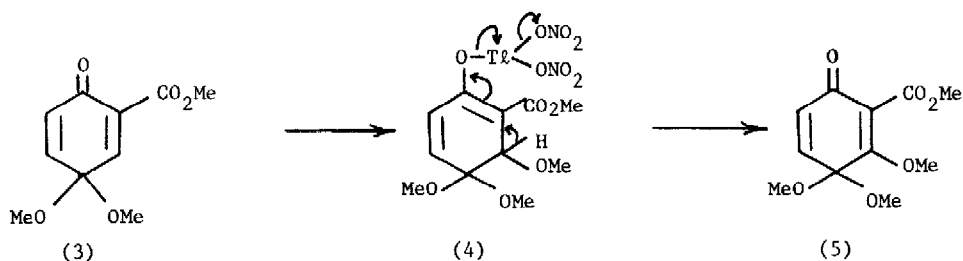


(1)



(2)

From the oxidation of methyl 2-hydroxy-5-methoxybenzoate with TTN in dry methanol and trimethylorthorformate at  $-20^{\circ}$  we were not able to isolate 2-methoxycarbonyl-4,4-dimethoxy-cyclohexa-2,5-dienone (3) but instead 2-methoxycarbonyl-3,4,4-trimethoxycyclohexa-2,5-dienone (5)  $\tau$  ( $\text{CDCl}_3$ ) 3.5 (1H, d, J 8Hz), 3.7 (1H, d, J 8Hz) 5.9 (3H, s), 6.7 (6H, s);  $\nu$  1740, 1680, 1630  $\text{cm}^{-1}$ ,  $M^+$  242 was obtained as a viscous liquid (90%) in high yield when two equivalents of reagent were used. It is likely that the expected product (3) undergoes rapid conjugate addition of methanol followed by further oxidation of (4) with TTN



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#### References

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