

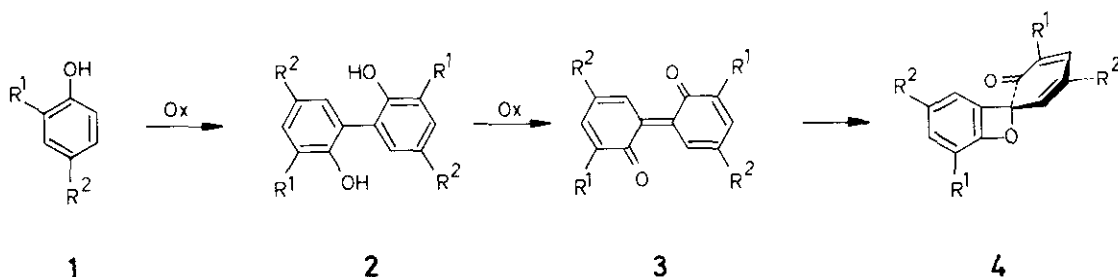
ON THE FORMATION OF SPIRO-SUBSTITUTED BENZOXETES BY PHENOL OXIDATION:
 PREPARATION AND VALENCE ISOMERIZATION OF
 3,3'-DI-TERT-BUTYL-5,5'-DITRITYL-2,2'-DIPHENOQUINONE

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The involvement of 3,3',5,5'-tetra-substituted o-diphenoquinones 3 in the oxidation of 2,4-di-substituted phenols 1 or 3,3',5,5'-tetra-substituted bi-phenols 2 to benzo-substituted oxetenes 4 has been inferred from the transient appearance of a characteristic blue or purple color observable under certain conditions.¹ However, it has never been established that o-diphenoquinones



actually are precursors of their valence isomeric benzoxetes. Indeed, within the class of quinonoid compounds, o-diphenoquinones remain a rare and elusive species, as no o-diphenoquinone of structure 3 has been isolated yet, and only few representatives such as 5a ($R^1=R^2=CH_3$, $R^3=OCH_3$),² 5b ($R^1=H$, $R^2=R^3=OCH_3$)³ and 5c ($R^1=H$, $R^2=tert-C_4H_9$, $R^3=OCH_3$),⁴ - neither of them undergoing valence isomerization - have been described in the literature. These examples, in conjunction



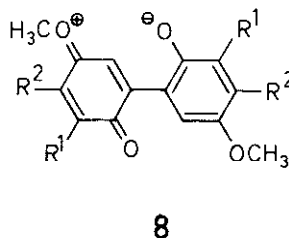
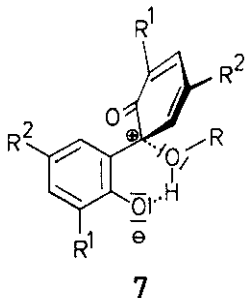
with the known stability of o-diacenoquinones 6⁵ have led to the conclusion ² that both substitution at C-4, C-4' and substitution by methoxy are essential prerequisites for the preparation of stable o-diphenoquinones.

We would like to report on the isolation of an o-diphenoquinone that is neither substituted by methoxy nor substituted at C-4, C-4', and which, in solution, significantly, isomerizes to a benzoxete. Thus, adding a solution of 3,3'-di-tert-butyl-5,5'-ditritylbiphenol 6 (2a; 1.26 g, 1.5 mmol) in benzene (150 ml) to a vigorously stirred solution of potassium ferricyanide (2 g) and potassium hydroxide (1.5 g) in water (100 ml) under nitrogen gives, within a few minutes, a dark purple organic layer which, after 10 min, was separated and washed with water (3 × 100 ml). Part of the solvent was vacuum evaporated and the dark purple precipitate thus obtained was washed with cold benzene and dried in vacuo (0.01 mm Hg) at 60° for 3 hr to give 800 mg (68%) of 3a (R¹=tert-C₄H₉, R²=CPh₃) as a dark purple crystalline powder, mp 193-194°. (Anal. Calcd for C₅₈H₅₂O₂ (781.05): C, 89.19; H, 6.71. Found: C, 88.95; H, 6.57).

In accordance with previous observations on quinonoid compounds, in the mass spectrum of 3a the most prominent peak in the molecular ion region appears at 782 (M+2), indicating easy reduction of 3a in the inlet system and ionization chamber.⁸ Likewise, reduction of o-diphenoquinone 3a in benzene solution with hydroquinone in ether occurs rapidly at room temperature to give biphenol 2a and quinhydrone. Significantly, benzoxete 4a (R¹=tert-C₄H₉, R²=CPh₃) was found to be stable towards treatment with hydroquinone, even in a refluxing benzene-ether mixture.

In the infrared spectrum of 3a (in KBr) a strong absorption at 1620 cm⁻¹ is attributed to the carbonyl stretching vibration.⁹ The NMR spectrum of 3a (in benzene-d₆) is in accord with a symmetrical structure as the two tert-butyl groups give rise to one signal at 1.09 δ ppm. The aromatic and quinonoid hydrogens appear as a multiplet between 7.4 and 7.0 δ ppm.

In isoctane solution, o-diphenoquinone 3a exhibits a broad longest wavelength absorption at 547 nm (ε, 7,800) (see Fig 1). The disappearance of 3a, subject to efficient catalysis by methanol and ethanol, was found to be due to a clean, thermal, conversion to benzoxete 4a in a first-order reaction. The catalytic effect of alcohols may be indicative of the involvement of a zwitterionic intermediate such as 7. Methoxy substitution at C-5, C-5', by contrast,



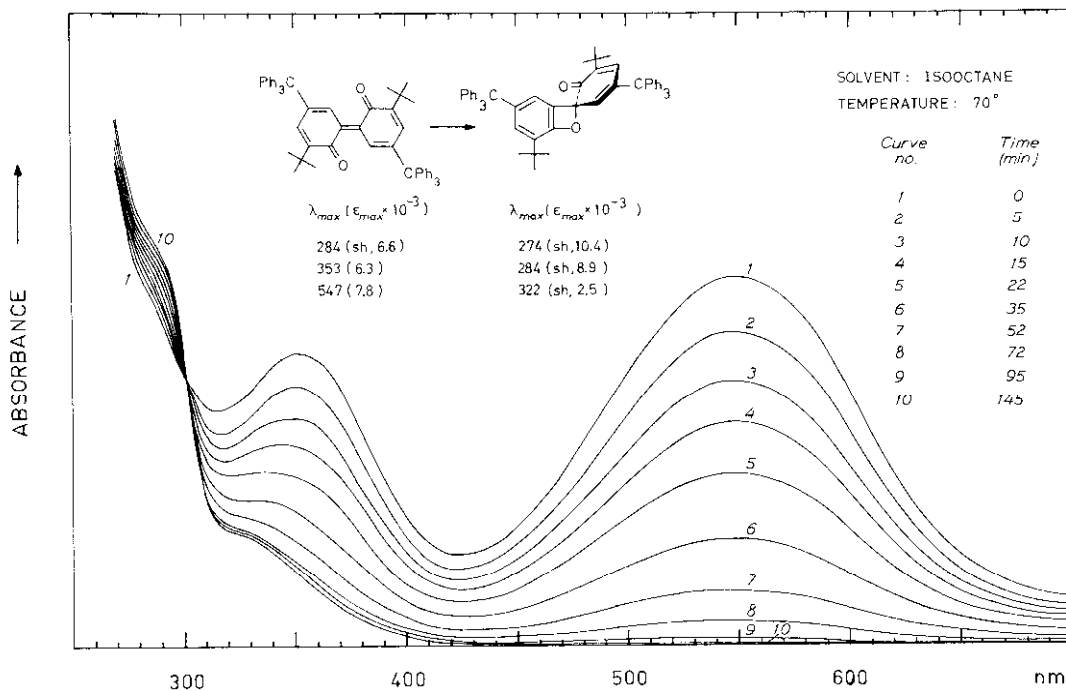


Figure 1. Thermal Isomerization of 3a to 4a.

contributes to the stabilization of the rather different zwitterionic species 8. Evidence for ionic resonance contributors to the o-diphenoquinone structure has been provided by spectroscopic means.⁴

Determination of the rate constants for the valence isomerization at five different temperatures between 45 and 85° (in isooctane solution; see Table I)

Table I
Rate Constants for Thermal Isomerization of 3a to 4a

| Temperature (K): | 322 | 328 | 336 | 343 | 354 |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|------------------|
| $k \times 10^4$ (s^{-1}) | 0.94 ± 0.06 | 1.36 ± 0.06 | 2.81 ± 0.08 | 5.07 ± 0.10 | 14.56 ± 0.40 |

afforded $\Delta H^\ddagger = 79 \pm 5 \text{ kJ mol}^{-1}$ ($19 \pm 1 \text{ kcal mol}^{-1}$).¹⁰ Interestingly, the negative change in entropy ($\Delta S^\ddagger = -78 \pm 13 \text{ J mol}^{-1}\text{K}^{-1}$, or $-19 \pm 3 \text{ cal mol}^{-1}\text{K}^{-1}$) indicates that the conversion of o-diphenoquinone 3a to benzoxete 4a is associated with a limitation in the number of degrees of freedom.¹¹

In summary, our results, in conjunction with the available literature data¹⁻⁴ on the oxidation of other 2,2'-dihydroxybiphenyls, suggest that o-diphenoquinones 3 are the kinetically favored precursors of the thermodynamically more stable benzoxetes 4.

Referenses and Notes

1. a) J. Baltes and F. Volbert, *Fette, Seifen und Anstrichmittel*, **57**, 660 (1955); b) E. Müller, R. Mayer, B. Narr, A. Rieker and K. Scheffler, *Liebigs Ann.*, **645**, 25 (1961); c) E. C. Horswill and K. U. Ingold, *Can. J. Chem.*, **44**, 269 (1965); d) D. F. Bowman and F. R. Hewgill, *J. Chem. Soc.(C)*, 1777 (1971).
2. D. Schulte-Frohlinde and F. Erhardt, *Liebigs Ann.*, **671**, 92 (1964).
3. C. J. R. Adderley and F. R. Hewgill, *J. Chem. Soc.(C)*, 1434 (1968).
4. F. R. Hewgill and D. G. Hewitt, *J. Chem. Soc.(C)*, 723 (1967).
5. Cf. R. H. Thomson in "The Chemistry of Quinonoid Compounds", S. Patai, Ed., Wiley, New York, N.Y., 1974, pp 111-161.
6. The biphenol 2a was prepared by refluxing a solution of benzoxete 4a⁷ (4.33 g, 5 mmol) and sodium iodide (10 g) in a 3:1 mixture (200 ml) of acetic acid and chloroform for 45 min. The precipitate obtained after removal of chloroform and reduction of iodine with thiosulfate solution (0.1 M) was filtered off and recrystallized from acetic acid to give 3.30 g (78%) of biphenol 2a containing one molar equivalent of acetic acid, mp 138-143° (depending on the rate of heating); NMR (CDCl₃; δ ppm) 7.19 (s, 32H), 6.94 (d, $J=2.5$ Hz, 2H), 5.19 (br s, 2H), 2.03³ (s, 3H), 1.26 (s, 18H). Anal. Calcd for C₅₈H₅₄O₂·CH₃COOH (843.12): C, 85.48; H, 6.93. Found: C, 85.41; H, 6.96. (Attempts to obtain a solvent-free crystalline product were unsuccessful).
7. Prepared by oxidation of 2-tert-butyl-4-tritylphenol (CuCl₂-pyridine catalyst), H.-D. Becker and K. Gustafsson, to be published.
8. Cf. K.-P. Zeller in "The Chemistry of Quinonoid Compounds", S. Patai, Ed., Wiley, New York, N.Y., 1974, pp 231-256.
9. For the carbonyl stretching frequency of other o-diphenoquinones, cf. ref 2-4.
10. Rate constants and activation parameters were obtained from least-squares fits. The uncertainties are given as standard errors.
11. Rotation about the central carbon-carbon double bond in diphenoquinones (p,p' and o,p') has been studied by NMR spectroscopy¹².
12. A. Rieker and H. Kessler, *Chem. Ber.*, **102**, 2147 (1969).