

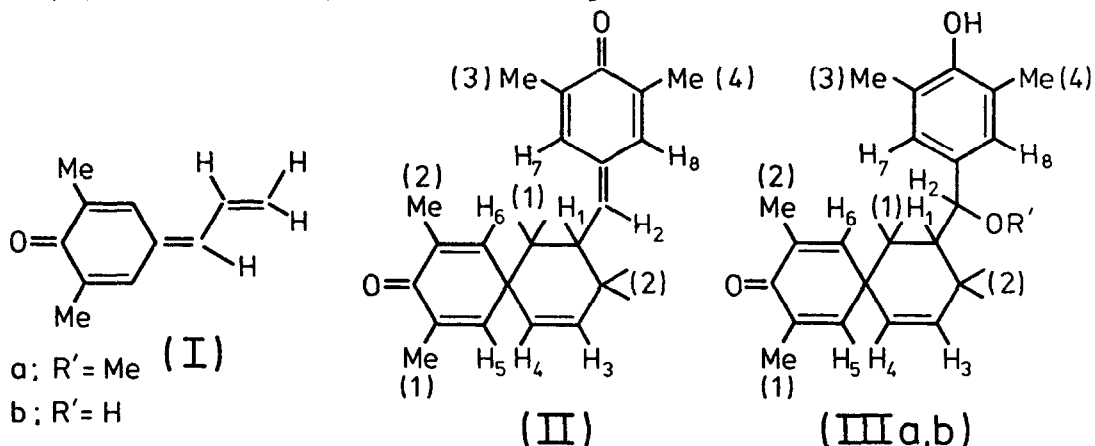
A NOVEL QUINONE METHIDE FROM DIMERIZATION OF THE QUINONE
METHIDE 4-ALLYLIDENE-2,6-DIMETHYL-CYCLOHEXA-2,5-DIENONE

Jacqueline A. Hemmingson

Chemistry Division, D.S.I.R., Private Bag, Petone, New Zealand.

(Received in UK 14 June 1977; accepted for publication 29 June 1977)

The dimerization of quinone methides without a substituent in conjugation with the methylene carbon, e.g. 2,6-di-*t*-butyl-4-methylenecyclohexa-2,5-dienone, is reported to involve tail to tail coupling and to give stilbene quinones, 4,4'-dihydroxy-1,2-diphenylethanes and 4,4'-dihydroxystilbenes.^{1,2,3} We now report that, in contrast, the quinone methide 4-allylidene-2,6-dimethylcyclohexa-2,5-dienone (I),⁴ which has a vinyl substituent in conjugation with the methylene carbon, in concentrated solution in aprotic solvents and in the solid state, forms a dimer (II) which is also a quinone methide.



Dimer (II) had λ_{\max} 304 nm, ϵ 22,000 (Et₂O); λ_{\max} 312 (MeOH), 322 (H₂O). It reacted with methanol and water to give the addition products (IIIa,b). Compounds (II) and (IIIa,b) were unstable solids isolated and purified by p.l.c. Acetylated (IIIa) was sufficiently stable for microchemical analysis. Found C 75.73, H 7.96. C₂₅H₃₀O₄ requires C 76.11, H 7.67. U.v. λ_{\max} values, at shorter wavelengths for (II) than for (I),⁴ and rates of reaction with methanol and water, faster for (II) than for (I),^{2,4} indicated the presence of a quinone methide moiety with the structure shown. ((II) $k_1^{25^\circ\text{C}}$ $3.8 \times 10^{-4} \text{ s}^{-1}$ (MeOH), $5.6 \times 10^{-3} \text{ s}^{-1}$ (H₂O); (I) $k_1^{25^\circ\text{C}}$ $6.8 \times 10^{-5} \text{ s}^{-1}$ (MeOH), $3.8 \times 10^{-4} \text{ s}^{-1}$ (H₂O)).

The mass spectrum of dimer (II) showed fragments corresponding to regeneration and fragmentation of (I). m/e M⁺ found 320.177230, calcd for C₂₂H₂₄O₂ 320.177614, Δ 1.2ppm. The mass spectra of (IIIa), m/e M⁺ 352 and (IIIb), m/e

M^+ 338 showed a fragment (m/e 320), attributed to regeneration of (II), and a major fragment (m/e 165 (IIIa), 151 (IIIb)) corresponding to 4-hydroxy-3,5-dimethyl-1-methoxymethyl-benzene or 4-hydroxy-3,5-dimethyl-benzenemethanol.

Strong i.r. absorption at 1629 cm^{-1} and u.v. absorption at 246 nm (ϵ 9,900, Et_2O) was shown by (IIIa) and indicated the presence of a cyclohexadienone moiety.⁵ In (IIIa,b), the strong absorption by the cyclohexadienone moiety at 246-250 nm would mask that of the aromatic moiety. In basic methanol or water solution a shoulder at 283 nm was observed.

The major evidence for the spiro[5,5]undecatrienone structure came from the n.m.r. spectra of (II), (IIIa) and acetylated (IIIa). (δ CCl_4 , TMS) (II) 1.80^A, 1.92^{B1}, 2.00^C, 1.92^{B2}, d, J 1.1Hz, $\text{CH}_3(1)-(4)$; 1.80-2.36^D, m, $\text{CH}_2(1)$, (2); 2.83-3.23^E, m, H_1 ; 5.83^E, d, J 10.4Hz, H_2 ; 5.80-6.10^{D,F}, m, H_3 ; 5.16^F, d, J 9.9Hz, H_4 ; 6.37^A, 6.63^{B1}, 7.12^C, 6.70^{B2}, br.s, H_{5-8} . (Protons with the same superscript are coupled). In the spectrum of (IIIa), $\text{CH}_3(3)$ and $\text{CH}_3(4)$ are singlets, H_2 is a broad singlet at 3.50 ppm coupled to H_1 , which is centred at 1.90 ppm, H_7 and H_8 are singlets at 6.55 ppm, and CH and CH_3O are at 4.74 and 2.96 ppm respectively. Overlap of the methylene and methyl absorptions unfortunately prevented discrimination between the structure presented here and that for the alternative more hindered product of dimerization, i.e. that having the quinone methide moiety on the carbon atom adjacent to the spiro carbon atom. However, the corresponding 2,6-di-*t*-butyl dimer showed multiplets centred at 1.90 ppm for $\text{CH}_2(1)$ and 2.30 ppm for $\text{CH}_2(2)$ and irradiation at 1.80-2.00 ppm did not collapse the H_1 multiplet at 2.67-3.17 ppm to a doublet, which suggested that this dimer has the structure shown for (II) and not the alternative structure. This compound also showed the H_5 H_6 and H_7 H_8 couplings (J 3Hz), which were masked by allylic coupling in (II).

The dimerization of vinyl-substituted quinone methides like (I) appears to be a Diels-Alder addition, with the quinone methide acting as both diene and dienophile.

ACKNOWLEDGEMENTS

The author thanks Professor A.D. Campbell and associates of Otago University for the microchemical analysis and Dr L.K. Pannell of Chemistry Division, D.S.I.R., Christchurch for the mass measurement.

REFERENCES

1. R.H. Bauer and G.M. Coppinger, Tetrahedron **19** 1201 (1963).
2. L.J. Filar and S. Winstein, Tetrahedron Letters **9** (1960).
3. A.B. Turner, Quart. Rev., **18** 359 (1964).
4. J.A. Hemmingson, J. Chem. Soc. Perkin II, 616 (1977).
5. J.D. McClure, J. Org. Chem., **27** 2365 (1962).