Generation and Dimerisation of 1,2-Napthoquinone-1-methide

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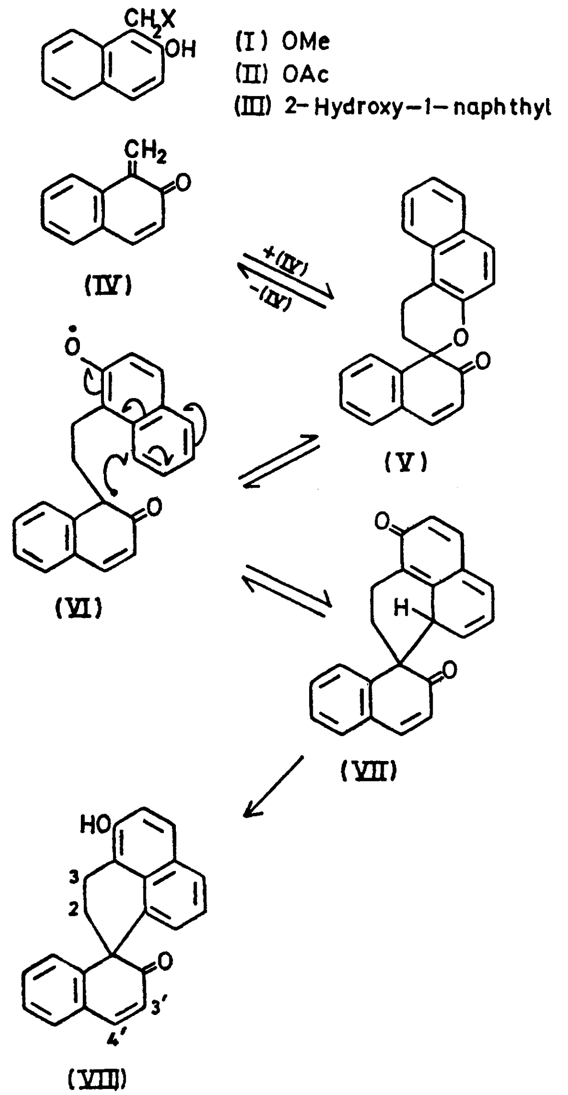
Summary The Diels–Alder reaction between two molecules of 1,2-naphthoquinone-1-methide (IV) yields 1′,2′-dihydrobenzo[*f*]chroman-2-spiro-1′-naphthalen-2′-one (V) (kinetically favoured) which rearranges irreversibly to 1′,2,2′,3-tetrahydro-4-hydroxyphenalene-1-spiro-1′-naphthalen-2′-one (VIII) (thermodynamically favoured); the ease of generation of 1,2-naphthoquinone-1-methide (IV) from the dimer (V) and its potential use in synthesis is described.

RECENT interest[1] in the synthetic use of the quinone methide (IV) generated from its dimer (V), prompts this



report of findings on the dimerisation of this quinone methide and the potential use of the dimers in synthesis.

1-Methoxymethyl-2-naphthol (I), in glacial acetic acid at 35°, slowly affords (IV) which is rapidly consumed by the solvent to produce the unstable 1-acetoxymethyl-2-naphthol (II) which was trapped as its 2,4-dichlorobenzoyl derivative,† m.p. 98—99°. Over long reaction times the commonly isolated dimer (V) of the quinone methide (IV) is produced, but this process is only kinetically favoured because above 80° rearrangement of (V) occurs at a measurable rate to yield the hitherto unobserved thermodynamically favoured dimer 1′,2,2′,3-tetrahydro-4-hydroxyphenalene-1-spiro-1′-naphthalen-2′-one (VIII); m.p. 239—241°; *m/e* 312 (100%); i.r. ν (KBr) 3400 (OH) 1635 cm^{-1} (conjugated ketone); ^{1}H n.m.r. δ [(CD$_3$)$_2$SO, Me$_4$Si] 2·13 (2H, t, *J* 6 Hz, 2-CH$_2$), 2·93 (2H, t, 3-CH$_2$), 6·20 (1H, d, *J* 10 Hz, 3′-H), 6·63—8·00 (10H, complex, 4′-H + Ar-H), 7·82 (4′-H from field sweep decoupling), 9·66 (1H, b, OH). The dimer (VIII) forms a methyl ether, m.p. 146—147°, whose structure is analogous to that of the methyl ether of the dimer of 10-methyleneanthrone.[2]

On heating (I) under reflux in mesitylene (30 min for 100% conversion), decalin (15 min for 97%), or n-dodecane (10 min for 100%) the dimer (V) is quickly formed. Experiments, using 2-naphthol to trap the quinone methide (IV) as the methylene dinaphthol (III), show the rate of formation of (IV) from its dimer (V) increases with the boiling point of the solvent: n-dodecane (100% trapped in 4 min) > decalin (100% in 10 min) > mesitylene (93% in 50 min) > acetic acid [29% in 360 min together with stable dimer (VIII) 63%]. At the boiling point of the solvent the dimer (V) is more stable in mesitylene [(VIII) 14% produced in 24 h] than acetic acid [(VIII) 76% in 6 h], decalin or n-dodecane [complete transformation within 12 and 6 h, respectively, to (VIII) and other unidentified products]. Thus, for high yields, Diels–Alder reactions using (IV) generated from (V) should be carried out in boiling mesitylene. Under similar experimental conditions the dimer (VIII) is unaffected, and hence it cannot be used in preparations as a source of (IV). These results suggest the isomerization of the dimer (V) to its stable form (VIII) proceeds through the intermediates (VI) and (VII).

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† All new stable compounds gave satisfactory analytical figures for C and H.

[1] M. S. Chauhan, F. M. Dean, D. Matkin, and M. L. Robinson, *J.C.S. Perkin I*, 1973, 120 and refs. therein.

[2] W. H. Starnes, *J. Org. Chem.*, 1970, **35**, 1974.