New Cyclisation of Butadiene with *p*-Quinones Co-ordinated to Palladium

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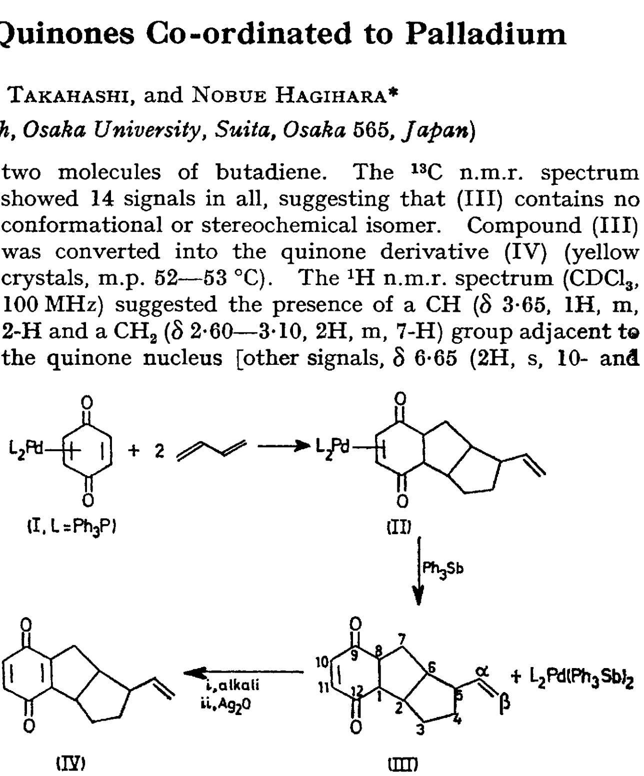
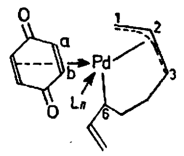
Summary Bis(triphenylphosphine)(*p*-benzoquinone)palladium(0) reacts with butadiene to afford complex (II) in which two molecules of butadiene are cyclised across one double bond of the *p*-benzoquinone ligand.

Organic molecules co-ordinated to transition metals frequently undergo quite different reactions from those in the free state, and such reactions provide useful methods for organic syntheses.[1] We now report that *p*-quinones, which are co-ordinated to zerovalent palladium, show distinctive behaviour towards butadiene.

In the Diels–Alder reaction, the presence of a transition metal and u.v. light is known[2] to alter the course of reaction or the product distribution. Dienophiles such as maleic anhydride and *p*-benzoquinone co-ordinated to a $Pd(PR_3)_2$ group strongly resist Diels–Alder reaction because of considerable electron drift from palladium to the dienophile.[3] *E.g.*, $(Bu^n_3P)_2Pd$ (*p*-benzoquinone)[3] did not react with a large excess of cyclopentadiene under the usual conditions and even heating at 60 °C for 10 days gave a poor yield (53%) of the normal Diels–Alder reaction product, $(Bu^n_3P)_2$-Pd(*endo-cis*-monocyclopentadienebenzoquinone) (m.p. 97—98 °C).

$(R_3P)_2Pd$(*p*-benzoquinone) also does not undergo the normal Diels–Alder reaction with butadiene, and a novel cyclisation takes place. When a benzene (or dichloromethane) solution of $(Ph_3P)_2Pd$(*p*-benzoquinone) (I) and butadiene was heated at 60 °C in a sealed glass tube, the mixture changed gradually from red to yellow and gave (II) [yellow crystals, m.p. 128—132 °C (dec.)] in 75% yield. Spectral data indicated that (II) was a π-olefin complex in which one double bond of the quinone had not reacted and remained co-ordinated to palladium. On treatment with Ph_3Sb,[4] (II) liberated the colourless organic molecule (III) [65%; m.p. 93—94 °C; δ ($CDCl_3$; 100 MHz) 6·64 (2H, s, 10- and 11-H), 5·78 (1H, m, α-H), 4·84—5·14 (2H, m, β-H), 2·80—3·40 (3H, m, 1-, 2-, and 8-H), and 1·20—2·46 (8H, m, 3-, 4-, 5-, 6- and 7-H)], $C_{14}H_{16}O_2$, which corresponds to an adduct derived from one molecule of *p*-benzoquinone and two molecules of butadiene. The ^{13}C n.m.r. spectrum showed 14 signals in all, suggesting that (III) contains no conformational or stereochemical isomer. Compound (III) was converted into the quinone derivative (IV) (yellow crystals, m.p. 52—53 °C). The ^1H n.m.r. spectrum ($CDCl_3$, 100 MHz) suggested the presence of a CH (δ 3·65, 1H, m, 2-H and a CH_2 (δ 2·60—3·10, 2H, m, 7-H) group adjacent to the quinone nucleus [other signals, δ 6·65 (2H, s, 10- and 11-H), 5·81 (1H, m, α-H), 4·90—5·18 (2H, m, β-H), 2·20—2·60 (2H, m, 5- and 6-H), and 1·34—2·20 (4H, m, 3- and 4-H)]. The u.v. spectrum, in which the formally forbidden π→π* transition is known[5] to be sensitive to strain in the ring adjacent to the quinone nucleus, showed an absorption band at 343 nm (ε 1015, in cyclohexane), implying that the ring adjacent to the quinone nucleus is five-membered or





(V)

more. The proposed structure for (IV) is consistent with the ^{13}C n.m.r. spectrum including off-resonance techniques and, therefore, (II) is unequivocally the novel cyclisation product, although we are unable at present to assign stereochemistry. The preliminary *X*-ray structure analysis of (II) supported the proposed structure.[7]

This novel reaction has been found to be generally applicable to other quinones (*e.g.* acetyl-*p*-benzoquinone, methoxycarbonyl-*p*-benzoquinone, and 1,4-naphthoquinone co-ordinated to a $Pd(Ph_3P)_2$ group to afford adducts analogous to (III). The mechanism of this cyclisation might involve an intermediate (V), similar to that proposed in the dimerisation of butadiene catalysed by a $(R_3P)_2Pd$-(dienophile) complex.[6] Bond formation apparently occurs between positions 1 and a, 3 and b, and 2 and 6.

(*Received, 7th February* 1975; *Com.* 137.)

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