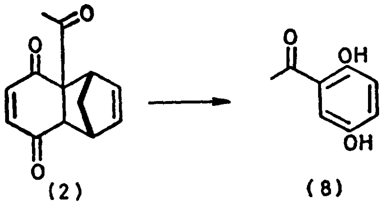
(1,5)-Acetyl Shifts in Cycloadducts derived from 2-Acetyl-1,4-benzoquinones

By SIMON C. COOPER and PETER G. SAMMES*
(*Department of Organic Chemistry, The University of Leeds, Leeds* LS2 9JT)

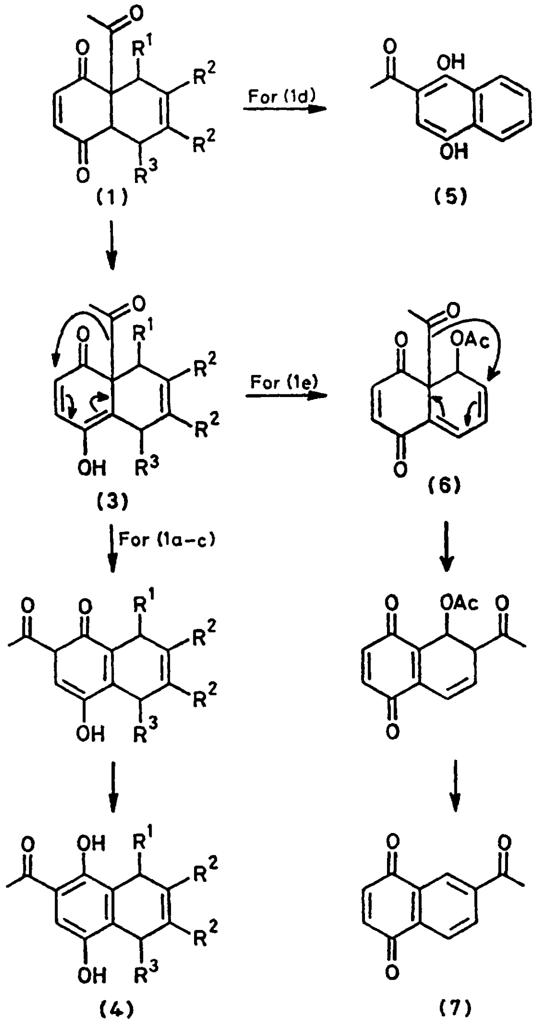
Summary (1,5)-Acetyl shifts have been investigated in a number of cycloadducts prepared from 2-acetyl-1,4-benzoquinone and dienes, and it has been shown that the direction of migration depends on the nature of the diene substituents.

CYCLOADDITIONS of 2-acetyl-1,4-benzoquinones with dienes are known to favour addition across the 2,3-π-bond to form, initially, the *cis*-fused 1,4,4a,5,8,8a-hexahydronaphthalenes (**1**), with the acetyl group occupying one of the angular positions.[1] A range of such adducts has been prepared (Table) and shown to be thermally stable at temperatures of up to 140 °C, except for the cyclopentadiene adduct (**2**), which underwent a retro-Alder reaction at 120 °C, to give (**8**).



(**2**) (**8**)

Since enolisation of the 1-oxo-group leads to the corresponding cyclohexadiene structures (**3**) (see Scheme), it was of interest to examine the possibility of (1,5)-acetyl shifts by heating the cycloadducts (**1**) in the presence of a trace of base. On heating the adduct (**1a**)[2] at 140 °C in xylene containing a few drops of pyridine, a smooth rearrangement occurred within 3 h to produce 2-acetyl-1,4-dihydroxy-5,8-dihydronaphthalene (**4a**). Similar results were obtained when using the quinone adducts (**1b**) and (**1c**), which produced the rearranged products (**4b**) and (**4c**), respectively. The rearrangement product of the 1-acetoxybutadiene adduct (**1d**) lost acetic acid under the reaction conditions to produce the napthaquinol (**5**). In contrast, the 1,4-diacetoxybutadiene adduct (**1e**) appeared to extrude one molecule of acetic acid before acetyl migration to produce the alternative cyclohexadiene unit (**6**) (see Scheme) allowing the transposition of the acetyl group to position 6; final loss of second molecule of acetic acid produced the naphthaquinone (**7**).



SCHEME. For reaction conditions see the Table.
a; $R^1 = R^2 = R^3 = H$
b; $R^1 = R^3 = H, R^2 = Me$
c; $R^1 = Me, R^2 = R^3 = H$
d; $R^1 = OAc, R^2 = R^3 = H$
e; $R^1 = R^3 = OAc, R^2 = H$

TABLE. All new compounds gave satisfactory n.m.r. and microanalytical data.

Adduct	M.p /°C	Product	M.p /°C	Conditions °C, h	Yield /%
(1a)	85—87[a]	**(4a)**	173 (subl.)	140, 3	85
(1b)	79—81[b]	**(4b)**	175 (subl.)	140, 2	60
(1c)	100—101	**(4c)**	153	140, 3	50
(1d)	87—92	**(5)**	206[c]	110, 2	52
(1e)	168—169	**(7)**	110—112	120, 2	47
(2)	70—71	**(8)**	202—203[d]	120, 3	29

[a] Ref. 1 gives 85—87 °C. [b] Ref. 1 gives 79—81 °C. [c] Ref. 2 gives 206 °C. [d] C. G. Amin and N. M. Shah, *Org. Synth.*, Coll. Vol. III, 1955, p. 280.

(1,5)-Acetyl shifts have been observed previously and are known to compete with Claisen-type allyl migrations.[3] A study of the comparative rates of migration of several different acyl groups in 1-substituted cyclohexa-2,4-dienes has shown the sequence formyl ≫ acetyl > methoxycarbonyl, and more recently that formyl migrations in cyclopentadienyl systems occur rapidly at room temperature.[5] Since, in our systems, acetyl migrations occur smoothly at temperatures of up to 140 °C, similar shifts of other acyl substituents might be anticipated and these are currently under investigation.

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