[1,5] and [1,2] Acetyl Shifts in Diels–Alder Adducts of 2-Acetyl-6-methyl-1,4-benzoquinone

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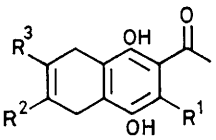
Summary Treatment of the Diels–Alder adduct 4a-acetyl-4a,5,8,8a-tetrahydro-3-methyl-1,4-naphthoquinone with pyridine–methanol or acetic anhydride leads to a [1,5] acetyl shift to the 3-position which can be followed by a [1,2] acetyl shift to the 2-position (adduct numbering).

FORMATION[1] of the acetyl–5,8-dihydro-1,4-dihydroxynaphthalenes (**1a**)—(**1d**) from the Diels–Alder adducts (**2a**)—(**2d**) *via* their $\Delta^{8a,1}$ enols requires that the 3-position be unsubstituted so that the immediate products (**3a**)—(**3d**) of the [1,5] acetyl migration can aromatise by enolisation.

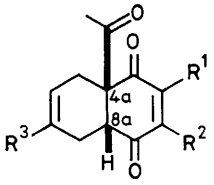
Treatment of the Diels–Alder adduct (**2e**), obtained from buta-1,3-diene and 2-acetyl-6-methyl-1,4-benzoquinone, with pyridine–methanol[1] (1 : 1, v/v) at 22 °C causes the expected [1,5] acetyl shift and gives a good yield of the triketone (**4a**) which, in the same medium at 65 °C, smoothly isomerises into the 5,8-dihydro-1,4-dihydroxynapthalene (**1c**), identical with that obtained by rearrangement[1] of the adduct (**2c**) in pyridine–methanol or acetic acid. Compound (**4a**) is readily dehydrogenated (air or 2,3-dichloro-5,6-dicyano-1,4-benzoquinone) into the 2,3-dihydro-1,4-naphthoquinone (**5**) which also isomerises, although less rapidly than (**4a**), in pyridine–methanol (1 : 1, v/v) to give the 1,4-dihydroxynaphthalene (**6**).

Similar treatment of the isoprene adduct (**2f**) gives, *via* the intermediate triketone (**4b**), the 5,8-dihydro-1,4-dihydroxynaphthalene (**1e**) which is *different* from (**1d**), obtained from the isomeric adduct (**2d**) *via* the now well established[1] [1,5] acetyl shift. This confirms that aromatisation of the triketone system involves a [1,2] acetyl shift, *not* a [1,2] methyl shift. Representative examples are given in the Table.



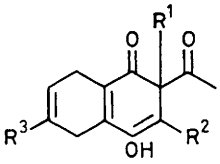
(1)

	R^1	R^2	R^3
a	H	H	H
b	H	Me	H
c	Me	H	H
d	Me	Me	H
e	Me	H	Me



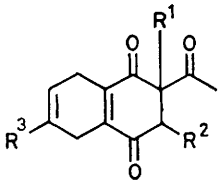
(2)

	R^1	R^2	R^3
a	H	H	H
b	H	H	Me
c	H	Me	H
d	H	Me	Me
e	Me	H	H
f	Me	H	Me



(3)

	R^1	R^2	R^3
a	H	H	H
b	H	H	Me
c	H	Me	H
d	H	Me	Me
e	Me	H	H
f	Me	H	Me



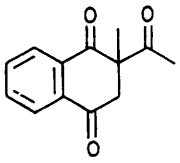
(4)

	R^1	R^2	R^3
a	Me	H	H
b	Me	H	Me

TABLE. Examples of [1,2] and [1,5] acetyl shifts.

Reactant	Method[a]	Product	solated yield/%	M.p./°C	δ[b] (Product) OH	OH	Ac	R^1	R^2	R^3
(2e)	A	(4a)	83	oil	—	—	2·10	1·50	[c]	[b]
(4a)	B	(1c)	63	154—155[d]	11·75	4·25	2·65	2·45	[b]	[b]
(2e)	A′	(5)	76	oil	—	—	2·10	[e]	—	—
(2f)	A	(4b)	70	oil	—	—	2·11	1·52	[f]	1·75
(2f)	B	(1e)	38	141—143	11·20	6·85	2·58	2·39	[b]	1·80
(2d)	B	(1d)	70	164—166[g]	10·98	6·88	2·58	2·39	1·80	[b]

[a] A, 8% in pyridine–methanol (1:1, v/v) degassed and sealed, then at 22 °C for 19 days; A′, As A, but in air; B, As A, but at 65 °C for 24 h. [b] (4) and (5) in $CDCl_3$; (1) in $(CD_3)_2CO$; for (1) and (4), δ 5·5—5·8 (6-H, 7-H) and 2·9—3·3 (5-H, 8-H). [c] δ 3·11 and 2·52 (both d, J 17 Hz, CH_2). [d] Lit., ref. 1, m.p. 153—153·5 °C. [e] δ 1·60 (2-Me). [f] δ 2·99 and 2·57 (both d, J 17 Hz, CH_2). [g] Ref. 1.



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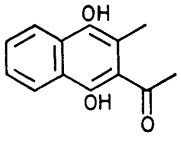
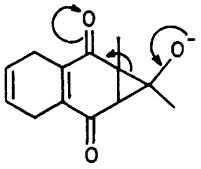


(6)

When aromatisation by enolisation after both the [1,5] and [1,2] shifts is prevented, as for the rearrangement of the buta-1,3-diene adducts of 2-acetyl-5,6-dimethyl-1,4-benzoquinone and 2-acetyl-1,4-naphthoquinone, treatment with pyridine–methanol causes de-acetylation and formation of the corresponding 5,8-dihydro-1,4-dihydroxynaphthalenes and 5,8-dihydro-9,10-dihydroxyanthracenes.



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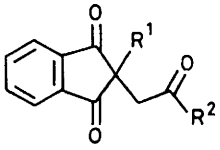

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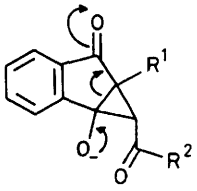

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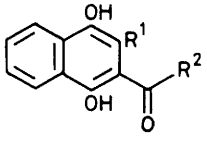
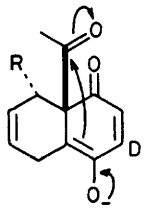


(10)

The [1,2] shift can be rationalised in terms of an internal nucleophilic attack of the enolates (**3e**) and (**3f**) (both with O^- instead of OH) on the acetyl group to give the cyclopropaneoxide (**7**) followed by a retro-aldol opening of the three-membered ring, as shown. The considerable ease of cyclopropane formation *via* intramolecular nucleophilic attack has received comment[2] and many reactions can be accounted for in the terms of the above cyclopropane–oxide–retro-aldol sequence.[3] Notably, the reductive ring-expansion[4] of 3-bromo-analogues of the triketone (**5**) and the base-induced conversion[5] of the indan-1,3-diones (**8**) *via* the intermediates (**9**) into the 2-acyl-1,4-dihydroxynaphthalenes (**10**) can occur under extremely mild conditions.[6]



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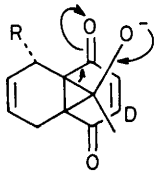

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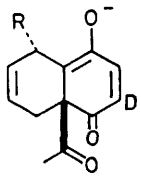

(13)

a R = H
b R = Me

A similar cyclisation of the enolates (**11a**) and (**11b**) gives the cyclopropaneoxides (**12a**) and (**12b**) which can either revert into (**11**) or, as shown, undergo ring-opening in the opposite sense to give the isomers (**13a**) and (**13b**). A [1,5] acetyl shift in the enol of (**13**) places the acetyl group on the deuterium-bearing carbon and the deuterium is then lost on aromatisation, thus accounting for the partial loss of label noted in the preceding Communication.[1] Little loss of deuterium occurs when the solvent is pyridine alone, but about 10% is lost when an equal volume of methanol is present, consistent with the higher concentration of the enolate expected in pyridine–methanol. Highly regiospecific migrations are therefore favoured by the use of pyridine either alone, or in a non-polar solvent,[7] and reactions in these media are likely to provide the most useful synthetical applications.

Evidence for an analogous migration of benzoyl groups from C-4a to C-8a in Diels–Alder adducts of benzoyl-1,4-benzoquinones is presented in the following Communication.[8]

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