

[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).

FORMATION¹ 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–methanol¹ (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-dihydroxynaphthalene (**1c**), identical with that obtained by rearrangement¹ 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 established¹ [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.

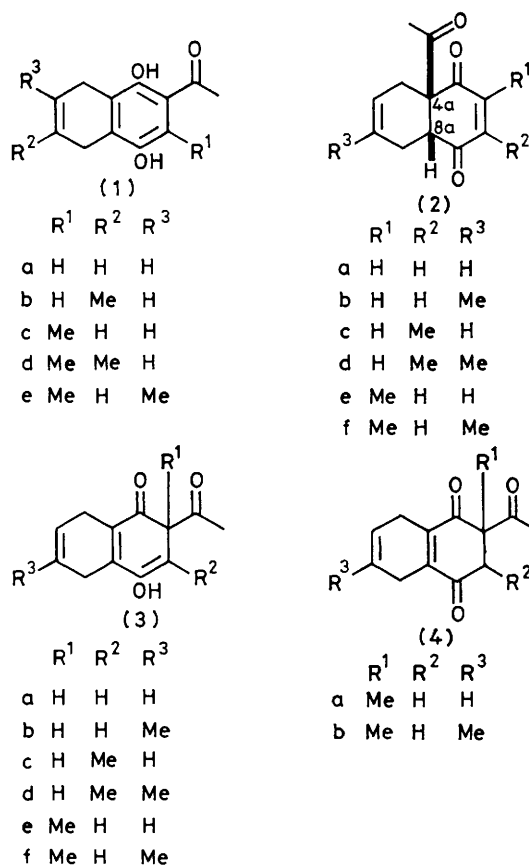
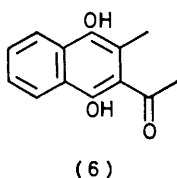
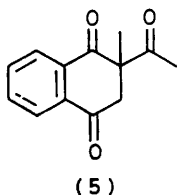


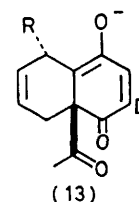
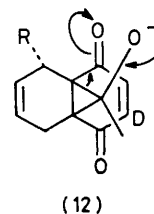
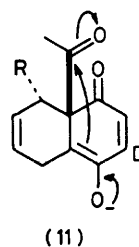
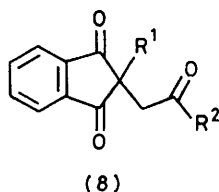
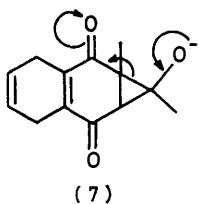
TABLE. Examples of [1,2] and [1,5] acetyl shifts.

Reactant	Method ^a	Product	isolated 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

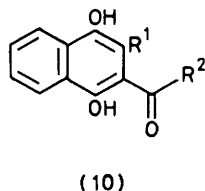
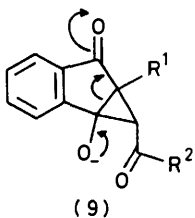
^a A, 8% in pyridine-methanol (1:1, v/v) degassed and sealed, then at 22 °C for 19 days; A', As A, but in air; B, As A, but at 65 °C for 24 h. ^b (4) and (5) in CDCl₃; (1) in (CD₃)₂CO; for (1) and (4), δ 5.5—5.8 (6-H, 7-H) and 2.9—3.3 (5-H, 8-H). ^c δ 3.11 and 2.52 (both d, *J* 17 Hz, CH₂). ^d Lit., 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, CH₂). ^g Ref. 1.



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.



a R = H
b R = Me



propaneoxide (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 comment² and many reactions can be accounted for in the terms of the above cyclopropane-oxide-retro-aldol sequence.³ Notably, the reductive ring-expansion⁴ of 3-bromo-analogues of the triketone (5) and the base-induced conversion⁵ 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

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 regio-specific 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.

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 cyclo-

Evidence for an analogous migration of benzoyl groups and the (late) Pahlavi Foundation (J.K. and K.S.) for Studentships. 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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¹ F. B. H. Ahmad, J. M. Bruce, J. Khalafy, V. Pejanović, K. Sabetian, and I. Watt, preceding Communication.

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³ Cf. F. Bohlmann and H. Kapteyn, *Tetrahedron Lett.*, 1972, 1895.

⁴ G. Read and V. M. Ruiz, *J. Chem. Soc., Perkin Trans. 1*, 1973, 1223.

⁵ E. Markova, J. Freimanis, and E. Ozola, *Latv. P.S.R. Zinat. Akad. Vestis, Kim. Ser.*, 1975, 613 (*Chem. Abs.*, 1976, **84**, 17008); B. Lukats and O. Clauder, *Acta Chim. (Budapest)*, 1972, **71**, 93 (*Chem. Abs.*, 1972, **76**, 59287); F. M. Beringer and S. A. Galton, *J. Org. Chem.*, 1963, **28**, 3250; C. F. Koelsch and S. Wawzonek, *J. Am. Chem. Soc.*, 1943, **65**, 755; C. F. Koelsch and D. J. Byers, *ibid.*, 1940, **62**, 560; G. Gheorgiu, *C.R. Acad. Sci.*, 1934, **198**, 755; D. Rădulescu and G. Gheorgiu, *Ber.*, 1927, **60**, 186.

⁶ L. P. Zalukaev and A. I. Shcherban, *Tr. Voronezh. Gos. Univ.*, 1972, **95**, 46 (*Chem. Abs.*, 1973, **78**, 43102); E. Ozola and G. Vanags, *Zh. Org. Khim.*, 1967, **3**, 2201 (*Chem. Abs.*, 1968, **68**, 78008).

⁷ Cf. S. C. Cooper and P. G. Sammes, *J. Chem. Soc., Chem. Commun.*, 1980, 633.

⁸ R. Al-Hamdany, J. M., Bruce, R. T. Pardasani, and I. Watt, following Communication.