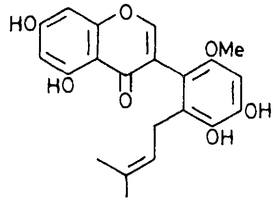
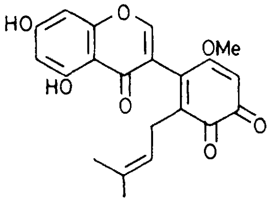
The Association of the Claisen Rearrangement with a Novel [1,5] Sigmatropic Rearrangement

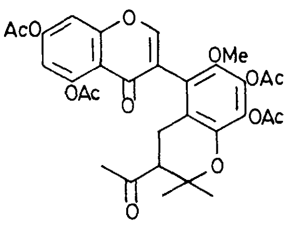
By Christopher P. Falshaw, Susan A. Lane, and W. David Ollis*
(*Department of Chemistry, The University, Sheffield* S3 7HF)

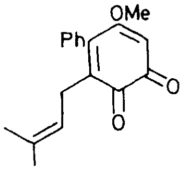
Summary Thermal rearrangement of the allyl aryl ether (**5**) gave, in addition to the expected Claisen rearrangement product (**6**), the isomer (**7**), and similarly thermal transformation of the allyl ether (**8**) gave the mixture (**9**) and (**10**); the formation of (**7**) and (**10**) is rationalised as involving a [1,5] acetyl shift.

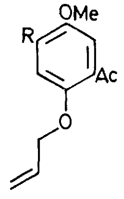
During the determination of the structure of the isoflavone, piscidone (**1**),[1] it was discovered that the derived piscidone-*o*-quinone (**2**) gave the cyclised product (**3**) under Thiele–Winter acetoxylation conditions.[2] To our knowledge the transformation (**2**) → (**3**) is without precedent during a Thiele–Winter reaction[2] and in order to investigate this unusual reaction further, we embarked upon the synthesis of the model *ortho*-quinone (**4**).

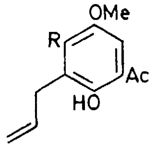

(1)

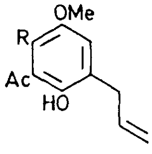

(2)

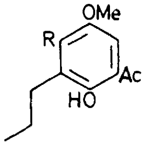

(3)

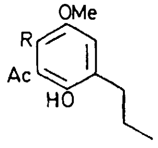

(4)

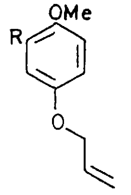

(5) R = Ph
(8) R = Me

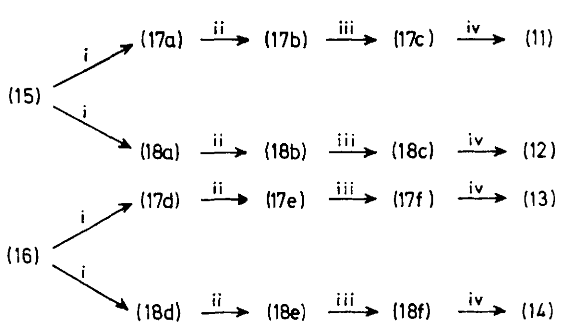

(6) R = Ph
(9) R = Me


(7) R = Ph
(10) R = Me

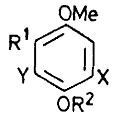

(11) R = Ph
(13) R = Me

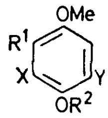

(12) R = Ph
(14) R = Me


(15) R = Ph
(16) R = Me

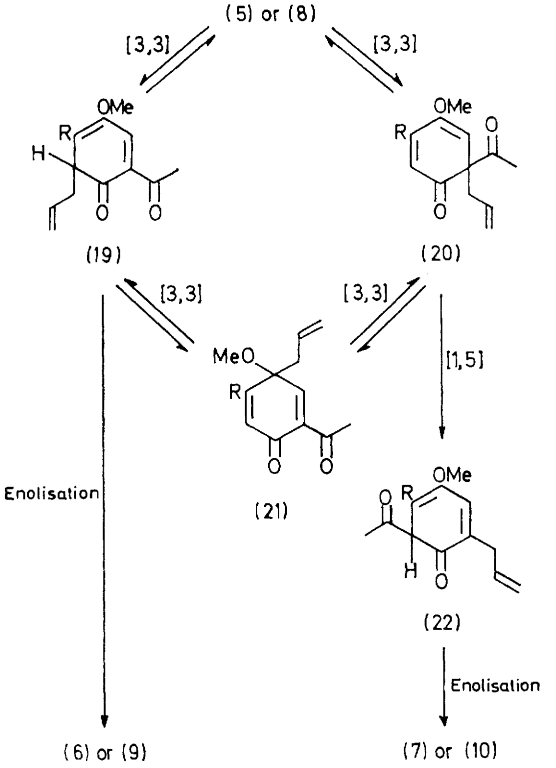


The allyl aryl ether (**5**) was selected as an initial synthetic objective since its transformation into the required *ortho*-quinone (**4**) *via* the phenol (**6**) should have been achievable using known synthetic routes for transforming $-CH_2-CH=CH_2$ into $-CH_2-CH=C(Me)_2$[3] and COMe into OCOMe. However, examination of Claisen thermal rearrangement (170°; *NN*-dimethylaniline) of the allyl aryl ether (**5**) gave, in addition to the expected phenol (**6**) (52%), an isomeric phenol (**7**) (33%). Catalytic hydrogenation of the thermal products (**6**) and (**7**) gave the corresponding dihydro-derivatives (**11**) and (**12**). Similarly attempted Claisen rearrangement of the ether (**8**) also gave two products (**9**) (42%) and (**10**) (22%) which were also reduced to their dihydro-derivatives (**13**) and (**14**). The constitutions of the thermal products, (**6**), (**7**), (**9**), and (**10**), were firmly established by the following syntheses of their dihydro-derivatives, (**11**), (**12**), (**13**), and (**14**).


(17)


(18)

	R^1	R^2	X	Y
a	Ph	H	H	$-CH_2CH=CH_2$
b	Ph	H	H	$-CH_2CH_2Me$
c	Ph	Ac	H	$-CH_2CH_2Me$
d	Me	H	H	$-CH_2CH=CH_2$
e	Me	H	H	$-CH_2CH_2Me$
f	Me	Ac	H	$-CH_2CH_2Me$



SCHEME

The sequences used in these syntheses were (i) Claisen rearrangement [constitutions of the pairs of products (**17a** and **18a**) and (**17d** and **18d**) were established by n.m.r. spectroscopy], (ii) catalytic hydrogenation, (iii) acetylation, and (iv) Fries rearrangement [thermal[4] (with $AlCl_3$) or photochemical[5] (in EtOH)].

These results clearly establish in the thermal rearrangements (**5**) → (**6** and **7**) and (**8**) → (**9** and **10**) that the formation of (**7**) and (**10**) involves a [1,5] shift of the aromatic acetyl substituent. This type of reaction is without precedent as an accompaniment of the Claisen rearrangement.[6] It is proposed (Scheme) that the Claisen rearrangement takes its usual course[6] and an equilibrium is established involving a sequence of [3,3] sigmatropic rearrangements, yielding the cyclohexa-2,4-dienones (**19**) and (**20**) and the cyclohexa-2,5-dienone (**21**) as intermediates. Leakage from these equilibrating intermediates by enolisation gives the normal Claisen rearrangement products, (**6**) and (**9**). Alternatively, a [1,5] sigmatropic migration of the acetyl group occurs (**20**) → (**22**) which, after enolisation, yields the unexpected products, (**7**) and (**10**). These [1,5] sigmatropic rearrangements resulting in the shift of an 'aromatic' acetyl group are novel, although other related [1,5] sigmatropic rearrangements have been recently proposed.[7]

(*Received*, 25*th April* 1973; *Com.* 580.)

---

[1] C. P. Falshaw, W. D. Ollis, J. A. Moore, and K. Magnus, *Tetrahedron*, 1966, *Supplement* No. 7, 333; E. R. Crossley, C. P. Falshaw, and W. D. Ollis, *J.C.S. Perkin I*, 1973, in the press.

[2] J. M. Blatchly and J. F. W. McOmie, *Org. Reactions*, 1972, **19**, 199; J. M. Blatchly and J. F. W. McOmie, *J. Chem. Soc.*, 1963, 5311; J. M. Blatchly, J. F. W. McOmie, and J. B. Searle, *J. Chem. Soc.* (*C*), 1969, 1350; J. M. Blatchly, R. J. S. Green, J. F. W. McOmie, and J. B. Searle, *ibid.*, 1969, 1353; *J.C.S. Perkin I*, 1972, 2286.

[3] H. D. Locksley, A. J. Quillinan, and F. Scheinmann, *Chem. Comm.*, 1969, 1505.

[4] A. Gerecs in 'Friedel-Crafts and Related Reactions', ed. G. A. Olah, Wiley-Interscience, New York, 1964, Vol. 3, pp. 499—533.

[5] V. I. Stenberg, *Org. Photochem.*, 1967, **1**, 127; D. Belluš, *Adv. Photochem.*, 1971, **8**, 109.

[6] A. Jefferson and F. Scheinmann, *Quart. Rev.*, 1968, **22**, 391; H.-J. Hansen and H. Schmid, *Chem. in Britain*, 1969, **5**, 111; S. J. Rhoads in 'Molecular Rearrangements', ed. P. de Mayo, Interscience, New York 1963, pp. 655—706; B. Miller in 'Mechanisms of Molecular Migrations,' ed. B. S. Thyagarajan, Interscience, New York, 1968, Vol. 1, pp. 247—313.

[7] B. Miller and K.-H. Lai, *Tetrahedron Letters*, 1972, 517; P. Schiess and P. Fünfschilling, *ibid.*, 1972, 5191, 5195; J. A. Berson and R. G. Salomon, *J. Amer. Chem. Soc.*, 1971, **93**, 4620; R. A. Baylouny, *ibid.*, 1971, **93**, 4621; M. Mahendran and A. W. Johnson, *Chem. Comm.*, 1970, 10; D. W. Jones and G. Kneen, *ibid.*, 1971, 1356; L. L. Miller and R. F. Boyer, *J. Amer. Chem. Soc.*, 1971, **93**, 650; D. Beck and K. Schenker, *Helv. Chim. Acta.*, 1971, **54**, 734; V. Boekelheide and E. Sturm., *J. Amer. Chem. Soc.*, 1969, **91**, 902.