Rearrangement of a 2-Aryloxycyclohex-2-enone. A New Enolate Claisen Rearrangement?

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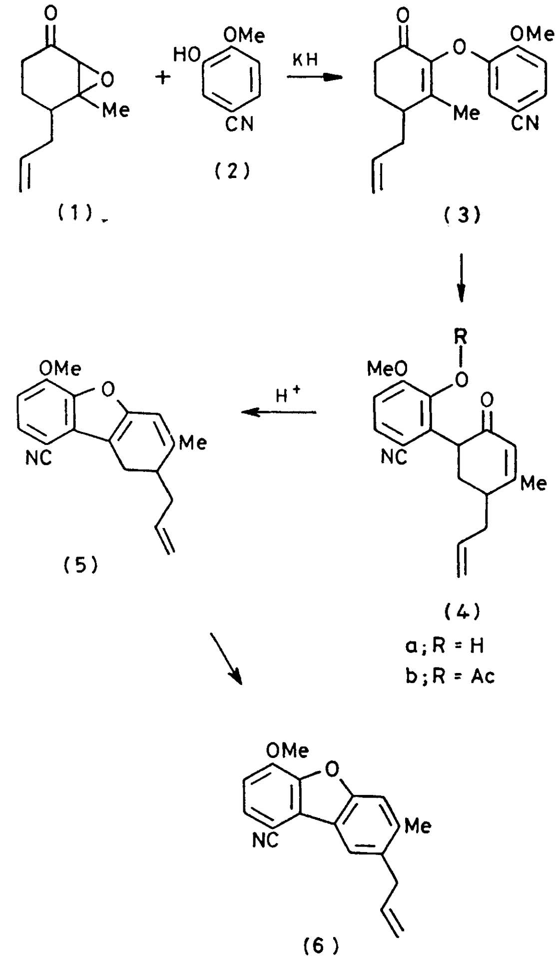
Summary The base-catalysed rearrangement of the 2-aryloxycyclohex-2-enone (**3**) to the enone (**4a**) is suggested to occur by an enolate-promoted 3,3-sigmatropic rearrangement of the enolate aryl ether (**7**).

THE base-catalysed reaction of phenols with epoxides derived from cyclohex-2-enones is a general method for the preparation of 2-aryloxycyclohex-2-enones.[1] An enone annelation method based on photocylization of aryloxy-enones to benzodihydrofurans has been developed[1] and applied to alkaloid total synthesis.[2] Herein we describe an unusual rearrangement encountered during the preparation of the aryloxy-enone (**3**) for photochemical study.[3] Our observation provides new information pertaining to enolate reactivity and helps to define the efficiency of aryloxy-enone preparation.

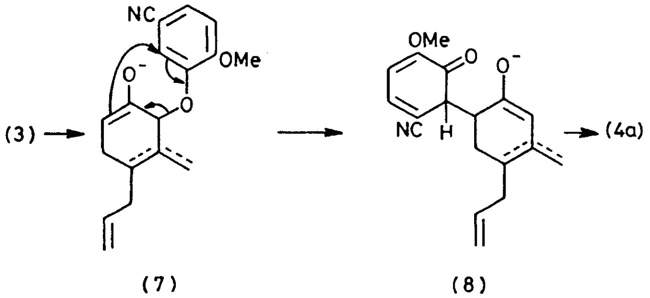


SCHEME 1

Reaction of the epoxide (**1**)† with 5-cyano-2-methoxyphenol (**2**) (1·3 equiv.)[4] and potassium hydride or potassium t-butoxide (0·1 equiv.) in refluxing 18-crown-6 (0·3 equiv.)–tetrahydrofuran (THF) solution is relatively slow (Scheme 1). After 20 h, only 40% of (**1**) is consumed and (**3**) (m.p. 116—117 °C) is isolated in 78% yield [based on (**1**) consumed]. If the reaction is continued for a total of 70 h, (**1**) (14%) is recovered, and (**3**) (15%) and the rearranged enone (**4a**) (57%) m.p. 169—170 °C are isolated.

The base-soluble enone (**4a**) displays key ^{1}H n.m.r. absorptions at δ 7·13, 6·77 (2H, AB q, J 9 Hz), 5·96 br. (1H, s), and 5·82 (1H, s, exchangeable with D$_2$O). Further structural confirmation was obtained by the conversion of (**4a**) into (**4b**) (m.p. 130—134 °C) with acetic anhydride–triethylamine, and of (**4a**) into (**5**) (86%, m.p. 57—59 °C) with toluene-*p*-sulphonic acid in refluxing methylene dichloride solution. On treatment with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in benzene at 25 °C, (**5**) is converted into the dibenzofuran (**6**) (73%, m.p. 143—144 °C).‡

Appropriate control experiments demonstrate that (**3**) is an intermediate in the formation of (**4a**).§ It is noteworthy that (**3**) is stable in refluxing THF in the absence of base. We suggest that a mechanism (Scheme 2) worthy of consideration involves conversion of (**3**) into the non-conjugated enolate (**7**), from which an enolate-promoted 3,3-sigmatropic rearrangement to (**8**) occurs.¶ Tautomerization of (**8**) to (**4a**) would effectively disrupt any equilibrium between (**7**) and (**8**).



SCHEME 2

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† See ref. 3 for details of the preparation of (**1**).

‡ Compounds (**3**), (**4a**), (**5**), and (**6**) gave satisfactory elemental analyses.

§ The conversion (**3**) → (**4a**) represents a potentially useful extension of the well studied Claisen rearrangement of allyl aryl ethers: D. S. Tarbell, *Org. React.*, 1944, **2**, 2; S. J. Rhoads and N. R. Raulins, *ibid.*, 1975, **22**, 1.

¶ For a related process, presumably involving an enolate Cope rearrangement, see A. de Groot and B. J. M. Jansen, *Recl. Trav. Chim. Pays-Bas*, 1976, **95**, 81; the analogous alkoxide-accelerated Cope rearrangement has been studied: D. A. Evans and A. M. Golob, *J. Am. Chem. Soc.*, 1975, **97**, 4765.

While we have not performed a detailed study of substituent effects, activation of the aromatic ring by an electron-withdrawing group *ortho* to the aromatic ring carbon atom undergoing C–C bond formation appears essential for rearrangement.[1] In this regard, Carpenter has noted the importance of substituents on the rates of sigmatropic rearrangements.[5]

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[4] J. H. Hunt, *Chem. Ind.* (*London*), 1961, 1873.

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