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LETTERS

Isochromenes and their Quinones through Cyclisations with Bisacetonitriledichloropalladium(II)

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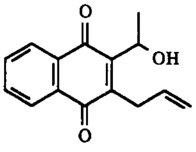
Abstract: Bisacetonitriledichloropalladium(II) is found to cyclise *ortho*-alkenylbenzyl alcohols rapidly to the corresponding isochromenes. The reaction also proceeds rapidly for a 2-allyl-3-hydroxyalkyl-1,4-naphthoquinone, when the product is a benzoisochromenequinone.

Recent reports of the natural occurrence of benzoisochromenequinones[1] have prompted us to seek a short, versatile route, which we now describe, to the isochromene and benzoisochromene ring systems, as well as to their quinones.

Catalytic quantities of bisacetonitriledichloropalladium(II) are known to isomerise an (*E*)/(*Z*) mixture of styrenes into the pure (*E*)-isomer.[2] We have now found that treatment of 2-allyl-3-(1'-hydroxyethyl)-1,4-naphthoquinone **1** with greater quantities of the same palladium complex afforded 1,3-dimethylbenzoisochromenequinone **2**. An optimised yield of 60% was achieved with the complex (0.15 molar equiv.) on reaction for five minutes at room temperature in dry dichloromethane, whereupon 28% of the starting material was also recovered unchanged.[4]



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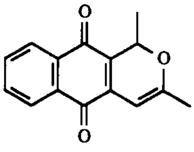

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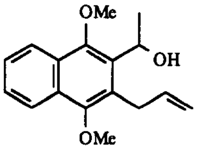

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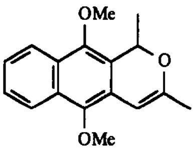

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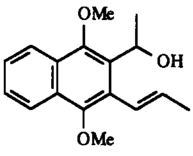

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Similar reaction of the related 2-allyl-3-(1'-hydroxyethyl)-1,4-dimethoxynaphthalene **3** with the palladium complex (0.3 molar equiv.) gave rise to the benzoisochromene **4** in a yield of 47%.[4] The conjugated (*E*)-isomer **5** (20%) of the starting material **3** was obtained as a by-product, and this was converted in a separate experiment into the product **4** (48%) on reaction with the palladium complex (1 molar equiv.). It is worth noting that non-cyclised material **5** recovered from the reaction of naphthalene **3** was conjugated,

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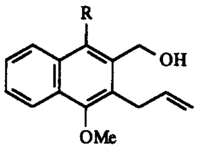
whereas this was not so for the quinone **1** under the conditions used.

Attempted oxidative demethylation of the benzoisochromene **4** to afford the 5,10-quinone **2** led instead to decomposition of starting material using either cerium(IV) ammonium nitrate or silver(II) oxide.

The generality of the reaction was confirmed with three further examples, in which the palladium complex (1 molar equiv.) was used in the cases of substrates **6** and **7**. For naphthalene **6**,[5] the benzoisochromene **8** was isolated in a yield of 50%, together with the by-product **10** (21%) observed only as the (*E*)-isomer. Similarly, the less crowded naphthalene **7**[5] was converted into the benzoisochromene **9** (60%) and the (*E*)- alkene **11** (13%).



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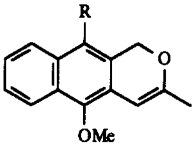
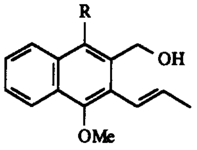
7 R = H

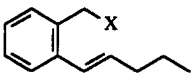


8 R = Et
9 R = H

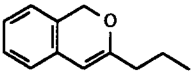


10 R = Et
11 R = H

The (*E*)-pent-1-enylbenzyl alcohol **12**[2] reacted with the palladium complex (1.1 molar equiv.) to afford the isochromene **14**. An optimised yield of 44% was obtained after 37 min. Also isolated in this instance was the benzyl chloride **13** (6%). An (*E*-)/(*Z*-) mixture corresponding to **12** behaved similarly.[6]



12 X = OH
13 X = Cl



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References

1. e.g.(a) Hari, L.; de Buyck, L. F.; de Pooter, H. L. *Phytochem.*, 1991, **30**, 1726. (b) Poch, G. K.; Gloer, J. B.; *Tetrahedron Lett.*, 1989, **30**, 3483; (c) Ali, A.; Read, R. W.; Sotheeswaran, S.; *Phytochem.*, 1994, **35**, 1029; (d) Potterat, O.; Zahner, H.; Volkmann, C.; Zeeck, A. *J. Antibiotic*, 1993, **46**, 346.
2. Giles, R. G. F.; Lee Son, V. R.; Sargent, M. V. *Aust. J. Chem.*, 1990, **43**, 777.
3. Quinone **1** was obtained in a yield of 86% through oxidation of the corresponding hydroquinone dimethyl ether **3**[7] with cerium(IV) ammonium nitrate.
4. Larger quantities of catalyst led to total consumption of starting material but lower yields of product.
5. The synthesis of this compound will be described in a full paper.
6. All reactions were performed on scales of 0.1 to 1 mmole substrate. Larger scales were not examined.
7. Giles, R. G. F.; Green, I. R.; Hugo, V. I.; Mitchell, P. R. K. *J. Chem. Soc., Perkin Trans. 1*, 1983, 2309.