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Preliminary communication

Palladium-catalyzed synthesis of coumarin

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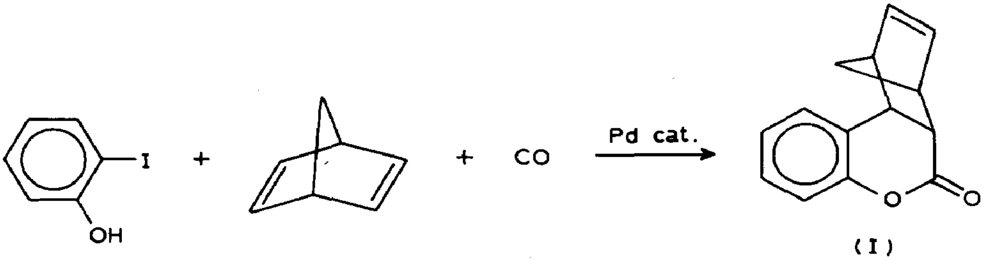
Abstract

A palladium-catalyzed synthesis of coumarin, involving ring formation from *o*-iodophenol, norbornadiene, and carbon monoxide, followed by elimination of cyclopentadiene, is described, and contrasted with a new synthesis of aurone, based on the reaction of iodophenol, carbon monoxide, and phenylacetylene.

Ring closure reactions to form aromatic compounds from simple substrates are an important objective of catalysis. Among the cyclic structures potentially accessible by transition metal catalysis, coumarin [1] is one of the most interesting. However, to our knowledge, no procedure for bringing about such reactions has been reported.

On the basis of our previous experience in palladium-catalyzed carbonylation of strained systems [2], we decided to try to synthesize a coumarin derivative (I), from *o*-bromophenol, norbornadiene, and carbon monoxide at 80 °C, but the reaction took a different course because protonation of the double bond occurred before C–Br bond cleavage, giving rise to the *o*-bromophenyl esters of *exo*-2-norbornene-5-carboxylic acid and of tricyclo[2.2.1.0^{2,6}]heptane-3-carboxylic acid in ca. 80% yield (5/1 molar ratio).

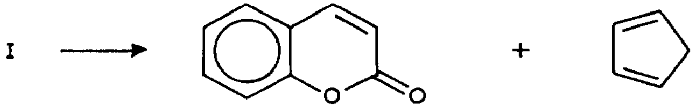
Protection of the hydroxyl group gave poor results, but we thought that a C–I bond, which enters into oxidative addition more readily than the C–Br bond, might have a chance to be cleaved before protonation took place and we found that under these conditions the reaction did indeed give the desired product I (m.p. 77–78 °C, eq. 1):



(I)

(1)

Unexpectedly, however, compound I underwent a retro-Diels–Alder reaction in part during the reaction, and completely at 150 °C, to give coumarin II (eq. 2):

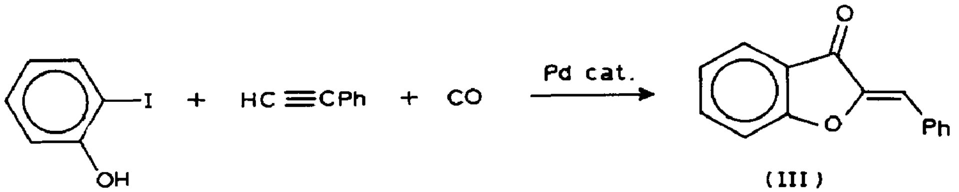


(II)

(2)

Thus a mixture of *o*-iodophenol (1.3 mmol), norbornadiene (2.6 mmol), potassium acetate (3.0 mmol), and $Pd(PPh_3)_4$ (0.02 mmol) in anisole (3.5 ml) was stirred at 80 °C for 4 h under carbon monoxide at atmospheric pressure. The mixture was then heated under reflux for 3 h, and anisole subsequently removed under reduced pressure. Water was added, and the coumarin distilled out (90% yield based on iodophenol taken). An excess of norbornadiene was used in order to avoid reaction of both double bonds. Norbornadiene-carbon monoxide copolymers were formed as by-products, but they did not interfere with the separation procedure.

The reaction is general for other substituted iodophenols, and is compatible with the presence of many other functional groups, including the formyl group. The overall procedure thus turns out to provide a one-pot synthesis, which actually employs only an iodophenol, acetylene and carbon monoxide, the acetylene being masked as norbornadiene. When used in place of norbornadiene, alkynes do not give coumarins under our conditions, probably because carbon monoxide insertion into the aryl–palladium bond occurs much more readily than aryl-acetylide coupling. This is clearly shown by the reaction with phenylacetylene in place of norbornadiene, which gives aurone III [3] in 82% yield (mainly *Z*, eq. 3):



(III)

(3)

Iodophenol can be prepared from phenol by a recently reported catalytic procedure, based on the use of iodine in the presence of copper acetate [4].

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