Preparation of 3-Acetylbenzofuran-2(3*H*)-ones and 3-Acetylnaphthofuran-2(3*H*)-ones *via* Intramolecular Rhodium Carbenoid Insertion

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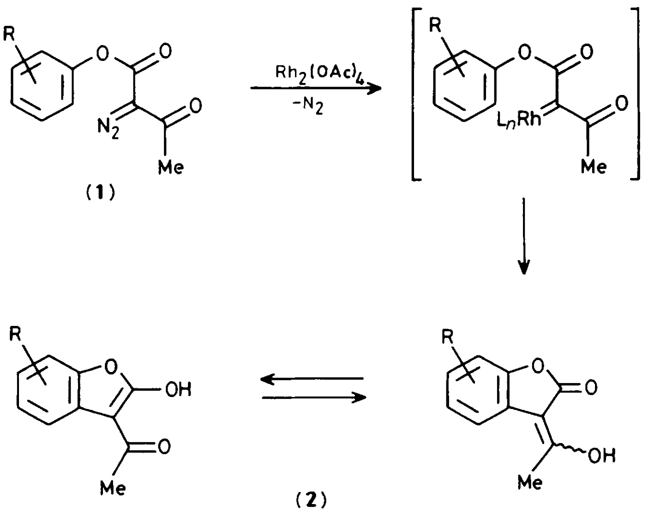
Rhodium(II) acetate catalysed decomposition of aryl 2-diazobutyrates and naphthyl 2-diazobutyrates results in the formation of 3-acetylbenzofuran-2(3*H*)-ones and 3-acetylnaphthofuran-2(3*H*)-ones respectively.

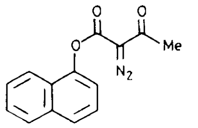
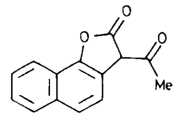
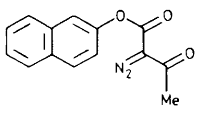
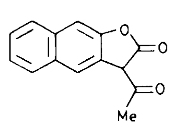
The insertion of rhodium carbenoids into carbon–hydrogen bonds has been the subject of many recent investigations. While many examples of rhodium carbenoid insertions into aliphatic C–H bonds exist,[1] there are relatively few cases in which products resulting from the formal insertion into an aromatic C–H bond are observed.[2] We have recently shown that α-diazo-β-phenylmethanesulphonyl esters give useful yields of 1-carboalkoxy-1,3-dihydrobenzo[*c*]thiophene-2,2-dioxides,[3] and Nakatani has reported the formation of indan-2-ones[4] from 1-diazo-3-arylpropan-2-ones with rhodium(II) acetate in dichloromethane. It had been previously shown that 4-aryl-2-hydroxy-1-naphthoates[5] can be prepared from 2-diazo-3-oxo-5,5-diarylpent-4-enoates, that α-diazoketones derived from 3-arylpropionic acids give 2-tetralones,[6] and that benzyl ketones[7] can be obtained from benzene and α-diazoketones by rhodium(II)trifluoroacetate catalysis. In the last two examples, cycloheptatrienes, the result of cyclopropanation[8] and ring expansion have been shown to be intermediates. The ring expanded products can be re-aromatized to the 2-tetralones and the benzyl ketones, the products of a formal carbenoid insertion into an aryl C–H bond, upon short exposure to trifluoroacetic acid.

We now report that the α-diazo-β-keto-esters (**1**), readily obtained by reaction of the appropriate phenol with diketene followed by diazo transfer, are transformed into 3-acetylbenzofuran-2(3*H*)-ones (**2**) simply by stirring with 5 mol% rhodium(II) acetate in dry dichloromethane for 1 h at room temperature. The products were obtained in greater than 90%



Scheme 1

Table 1. Intramolecular rhodium carbenoid insertions.

Diazo compound	Product	m.p./°C	Yield/%
(1) R = H	(2) R = H	133—134	98
(1) R = 2-Me	(2) R = 7-Me	112—113	98
(1) R = 2-Br	(2) R = 7-Br	164—166	92
(1) R = 3,4-OCH_2O–	(2) R = 5,6-OCH_2O–	211—212	91
		175—177	90
		214—216	94

yield after the catalyst was filtered off and the solvent evaporated.†

The parent compound in the series (**2**, R = H) was identical with an authentic sample prepared by reaction of *o*-hydroxyphenylacetic acid with acetic anhydride–pyridine, followed by acidification.[9] The 300 MHz ^{1}H n.m.r. spectrum of (**2**, R = H), obtained in CCl_4 solution, showed resonances at δ 2.23 (s, 3H), 7.04—7.24 (m, 4H) and 11.9 (br., 1H), confirming its existence as an enol.[10] The i.r. spectrum ($CHCl_3$) displayed peaks at 1725, 1710, and 1637 cm^{-1}.

A series of aryl-substituted α-diazo-β-ketoesters (**1**) were prepared in order to determine if any interference with the aromatic C–H insertion would be observed. The results are summarized in Table 1. In cases where an *ortho*-substituent was present, no competitive insertion into either the benzylic C–H, the aryl C–C or C–Br bond was observed and only the product arising from formal insertion into an aryl C–H bond was obtained. The 3,4-methylenedioxy substituted compound (**1**, R = 3,4-OCH_2O–) gave only the isomer shown, as evidenced by the presence of two, one-proton singlets at δ 6.49 and 7.38. The α-naphtho derivative gave only 3-acetylnaphtho[1,2-*b*]furan-2(3*H*)-one [^{1}H n.m.r. (300 MHz) δ 2.53 (s, 3H), 7.39—7.59 (m, 4H), 7.77 (d, 1H, *J* 8.3 Hz), 8.06 (d, 1H, *J* = 8.3 Hz)] by insertion into the β-position; no *peri* C–H bond insertion products were detected. The β-naphtho derivative gave as its sole product 3-acetylnaphtho[2,3-*b*]-furan-2(3*H*)-one [^{1}H n.m.r. (300 MHz) δ 2.73 (s, 3H), 7.39—7.91 (m, 4H), 7.47 (s, 1H), 8.21 (s, 1H)].

Reaction of (**1**, R = 2D) with rhodium(II) acetate in the usual manner afforded (**2**), bearing 72.5(±1.5)% of the original deuterium content, thus indicating a deuterium isotope effect of *ca.* 2.65. This suggests an insertion mechanism rather than an intramolecular electrophilic aromatic substitution mechanism, since typical H/D isotope effects for electrophilic aromatic substitutions are less than 1.3 unless the formation of the initial σ-complex is reversible.[11]

The intermediacy of a norcaradiene derivative in these reactions, while not disproven, is considered less likely than for the 2-tetralone formation owing to the highly strained structure of the tricyclic intermediate. No norcaradienes have been observed in insertion reactions leading to five-membered ring products such as indan-2-ones.[4,7] The observed isotope effect also mitigates against this mechanism, unless one assumes fast reversibility of the norcaradiene forming step.

α-Diazo-β-ketoamides analogous to (**1**) have been shown to give excellent yields of 2-hydroxy-3-acetylindoles.[12] Extensions of this methodology to the preparation of other benzofused heterocycles should be possible.

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† Crude products were recovered in near quantitative yield and were shown to be homogeneous by ^{1}H n.m.r. spectroscopy and t.l.c. Analytic samples were obtained by recrystallization from hexane–diethyl ether or methanol. All new compounds gave satisfactory exact masses, i.r., ^{1}H and ^{13}C n.m.r. spectra.