Pergamon

Tetrahedron Letters 39 (1998) 6381–6382

TETRAHEDRON LETTERS

Site Selective C-H Insertion of Unactivated α-diazo-α-aroyl esters Catalysed by Rh(II) Carboxylates.

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Received 31 March 1998; accepted 23 June 1998

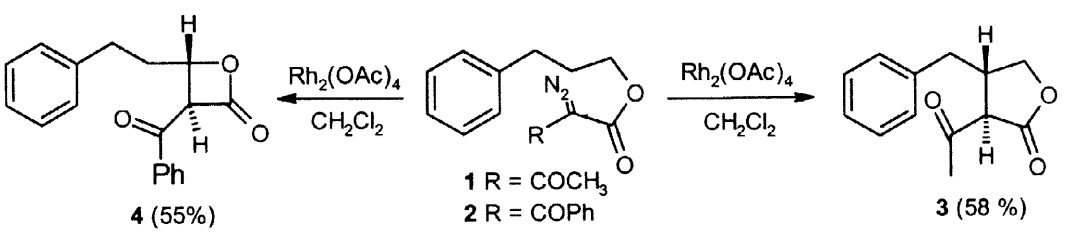
Abstract:

The results from the study of C-H insertion of unactivated α-diazo-α-aroyl esters catalysed by rhodium(II) carboxylates which give β-lactones indicate that steric effects may play a major role in product formation.

Key words: Carbenes and carbenoids; diazo compounds; insertion reactions; rhodium and compounds

Diazocarbonyl compounds have attracted considerable attention [1,2]. Rhodium(II) carboxylate mediated intramolecular C-H insertion involving bond formation to a previously unfunctionalised carbon atom is a powerful method for the construction of various cyclic compounds [3,4]. Although construction of γ-lactones using simple diazoacetates [4] or diazoacetoacetates [5] are well documented in literature, no report is available for Rh(II) catalysed C-H insertion of unactivated α-diazo-α-aroyl esters.

Intermediates like **1** and **2** as model compounds were required in continuation of our ongoing programme on the development of synthetic methods [6,7] for the construction of aryl lignans. Detailed studies have been carried out by Doyle *et.al.* [4] on the decomposition of diazoacetates with $Rh_2(MEPY)_4$ leading to γ-lactone formation with only 5 % of the corresponding β-lactone. We concurred that, if Rh-catalysed carbene insertion reactions of **1** and **2** proceed on the same lines, they would lead to the formation of the corresponding γ-lactones. Contrary to our expectations, the diazoester **2** yielded the corresponding β-lactone (**4**, **IR** 1822 cm^{-1}, $^3J_{trans}$=4.4Hz, [8]) as the only product whereas, γ-lactone **3** was the major product when **1** was subjected to diazo decomposition [¶]. The latter result is in accordance with Doyle's findings.



4 (55%)

1 R = $COCH_3$
2 R = COPh

3 (58 %)

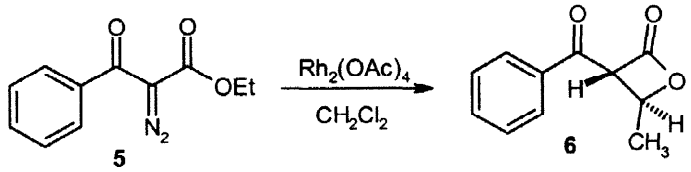
0040-4039/98/$ - see front matter
PII: S0040-4039(98)01314-8

In order to confirm our findings, several Rh(II) ligands [§] with different electronic properties were prepared and the reactions were carried out on **2** [¶]. In all the cases (**Table 1**), β-lactone **4** was the exclusive product and no γ-lactone product could be detected. Rh(II) trifluoroacetate did not yield any cyclic product. Both $Rh_2(MEPY)_4$ and $Rh_2(cap)_4$ also gave β-lactone **4** as the exclusive product in 69 and 63 % isolated yields respectively.

Table 1
C-H insertion of 2 with various catalysts

Entry	Rh (II) Ligand	Yield %
1	Acetate	55
2	Trimethylacetate	60
3	Octanoate	57
4	Methoxyacetate	58

Further support for our results was provided by the formation of only the β-lactone **6** in 58% yield from the simple aroyl diazoester **5**.



5 **6**

It is deduced that steric effects probably play a major role in product selectivity in these reactions. A mechanism similar to the one proposed by Lee *et.al.* [9] involving intrinsic conformational demands which place the metallocarbene closer to the oxygen of the ester functionality leading to preferential formation of β-lactone, may be operative here as well.

In summary, we have clearly demonstrated that Rh(II) catalysed C-H insertion of the unfunctionalised α-diazo-α-aroyl esters **2, 5** lead to the exclusive formation of the β-lactones **4, 6** respectively. According to a review on β-lactones J_{trans}=4-4.5 Hz and J_{cis}=6.5Hz [8]. Since we obtained a J value of 4.4Hz for the doublet at 4.75 δ (see footnotes), the stereochemisty of the β-lactones **4, 6** are unequivocally confirmed to be *trans*. Although diazomalonates are also reported to yield β-lactones [10], our first report of *exclusive* β-lactone formation from α-diazo-α-aroyl esters is unprecedented.

(B.S.B.) thanks CSIR, (INDIA) for a fellowship. Helpful discussions with Dr.H.R. Sonawane is acknowledged.

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¶ In a typical experiment the diazo compound (200 mg in 5 ml dry CH_2Cl_2) was added over a period of 10 hrs.(0.5 ml/hr) to a refluxing solution of the catalyst (2 mol %, 10 ml CH_2Cl_2). Removal of the solvent followed by purification (flash chromatography) yielded the products. Selected spectral data of compound **4** **IR** (neat) cm^{-1} 1822, 1710, 1600. **^{1}H NMR** (200 MHz, $CDCl_3$) 8.1-8.0 (m, 2H), 7.72-7.6 (m, 1H), 7.6-7.48 (m, 2H), 7.35-7.1 (m, 5H), 5.3-5.2 (m, 1H), 4.75 (d, J=4.4Hz, 1H), 3.0-2.85 (m, 1H), 2.85-2.7 (m, 1H), 2.5-2.15 (m, 2H).**^{13}C NMR** (75 MHz, $CDCl_3$) 188.11 (s), 167.65 (s), 142.05 (s), 139.77 (s), 134.33 (d), 129.19 (d), 128.84(d), 128.68 (d), 128.36 (d), 72.81 (d), 65.01 (d), 35.38 (t), 31.17 (t).

§ All the catalysts (except $Rh_2(OAc)_4$) were prepared by standard exchange procedure reported in literature.