# A new catalytic transformation of diazo esters: hydride abstraction in dirhodium(II)-catalysed reactions

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Secondary benzylic and allylic diazoacetates undergo dirhodium(II)-catalysed diazo decomposition to form, competitively or exclusively, ketone and vinylidene products from intramolecular hydride abstraction in catalyst ligand-dependent molar ratios.

Transition metal-catalysed transformations of diazocarbonyl compounds are categorized as cyclopropanation, insertion and ylide generation.[1-6] Competing side reactions include, mainly, carbene dimer formation [eqn. (1)], which occurs by electro-

$$RCHN_2 \xrightarrow{ML_n} L_nM=CHR \xrightarrow{RCH=N_2} L_nM + N_2 + RCH=CHR \quad (1)$$
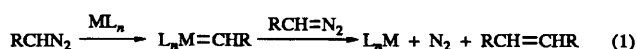
philic metal carbene addition to the reactant diazo compound,[7] and water-insertion [eqn.(2)], which produces either or both,

$$RCHN_2 + H_2O \xrightarrow{ML_n} RCH_2OH \xrightarrow{RCHN_2}{ML_n} (RCH_2)_2O \quad (2)$$
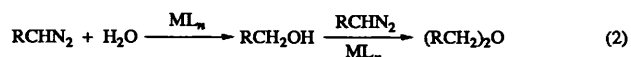
alcohol and ether, dependent on the amount of water present.[8-9] However, even when each of these competing side reactions is taken into account, the mass balance in many reactions of diazocarbonyl compounds is rarely complete. While investigating a potential dirhodium(II)-catalysed carbon–hydrogen insertion reaction of diazoacetate esters we came across a surprising transformation, not previously recorded in catalytic diazo chemistry, that appears that to be pervasive in transition metal-catalysed reactions of certain diazo esters.

Diazo decomposition of the diazoacetate ester of 1,2,3,4-tetrahydro-1-naphthol (α-tetralol) catalysed by the chiral dirhodium(II) tetrakis[methyl 2-oxopyrrolidine-5(S)-carboxylate], Rh₂(5S-MEPY)₄,[10] occurred efficiently in refluxing dichloromethane to produce, instead of the expected addition or insertion products, α-tetralone and α-methylenetetralin which were isolated in 69% yield (86:14 molar ratio) following distillation [eqn. (3), n = 2]. Carbene dimer formation and


1 (n = 1,2)   2   3
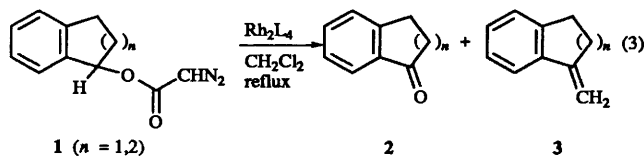
water insertion products were also observed, but their combined yield was less than 4%. The remaining materials were high molecular weight substances that were not further characterized.

With other chiral dirhodium(II) catalysts, including dirhodium(II) tetrakis[methyl 2-oxooxazolidine-4(S)-carboxylate], Rh₂(4S-MEOX)₄,[11] the same products were formed in approximately the same percentage yield (62%) after distillation, but with minor variations in the ratio of 2 to 3 (84:16), no carbene dimers and 6% of the water insertion product. Use of achiral dirhodium(II) tetracaprolactamate, Rh₂(cap)₄,[12] produced 2 and 3 in a 69:31 ratio but in low overall yield (26%) relative to that with chiral dirhodium(II) catalysts. With Rh₂(OAc)₄ these products were also observed but in limited

amounts (< 10% yield, 2:3 = 67:33). Carbene dimer formation [5% with Rh₂(cap)₄] and water insertion [1% with Rh₂(cap)₄] were the only other processes identified but, even so, the use of Rh₂(OAc)₄ or Rh₂(cap)₄ did not result in the formation of aromatic cycloaddition or C–H insertion products.

Similar results were obtained with indan-1-yl diazoacetate 1 (n = 1). Both indan-1-one 2 (n = 1) and 1-methylideneindane 3 (n = 1) were the primary products from reactions [eqn. (3)] catalysed by chiral dirhodium(II) catalysts: with Rh₂(5S-MEPY)₄, 78% yield (2:3 = 83 : 17); with Rh₂(4S-MEOX)₄, 82% yield (2:3 = 78:22). These same products were observed with the use of Rh₂(OAc)₄ (< 5% yield, 2:3 = 89:11) and Rh₂(cap)₄ (24% yield, 2:3 = 66:34) but, in contrast with chiral dirhodium(II) catalysts, carbene dimer formation and water insertion constituted the primary pathways for diazo decomposition [30%/12% with Rh₂(cap)₄, 25%/7% with Rh₂(OAc)₄]. In no case, however, were products from C–H insertion or aromatic cycloaddition observed. In contrast, indan-2-yl diazoacetate undergoes C–H insertion to form the γ-lactone product in moderate yields with the same catalysts without evidence for indan-2-one production.

Extension of these investigations to fluoren-9-yl diazoacetate 4, benzhydryl diazoacetate 5 and cyclohex-2-enyl diazoacetate

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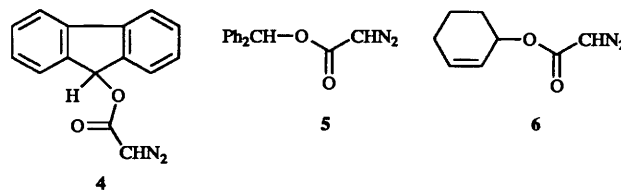
6 Rh₂(5S-MEPY)₄ and Rh₂(4S-MEOX)₄ catalysts gave ketone and vinylidene products in higher overall yield than did Rh₂(cap)₄ or Rh₂(OAc)₄, and the R₂C=O/R₂C=CH₂ ratio varied widely with the catalyst ligand (Table 1). Fluoren-9-yl diazoacetate formed ketone and vinylidene products, in addition to water-insertion products and those from carbene dimer formation, but the product(s) from aromatic cyclo-addition was not observed. In contrast, the major product from diazo decomposition of benzhydryl diazoacetate was generally that from intramolecular aromatic cycloaddition 7,

7   8
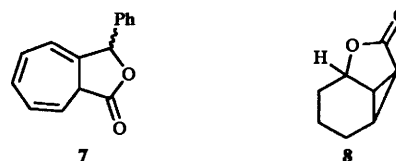
in amounts dependent on the catalyst employed, but benzo-phenone was also formed in all catalytic reactions. Cyclo-
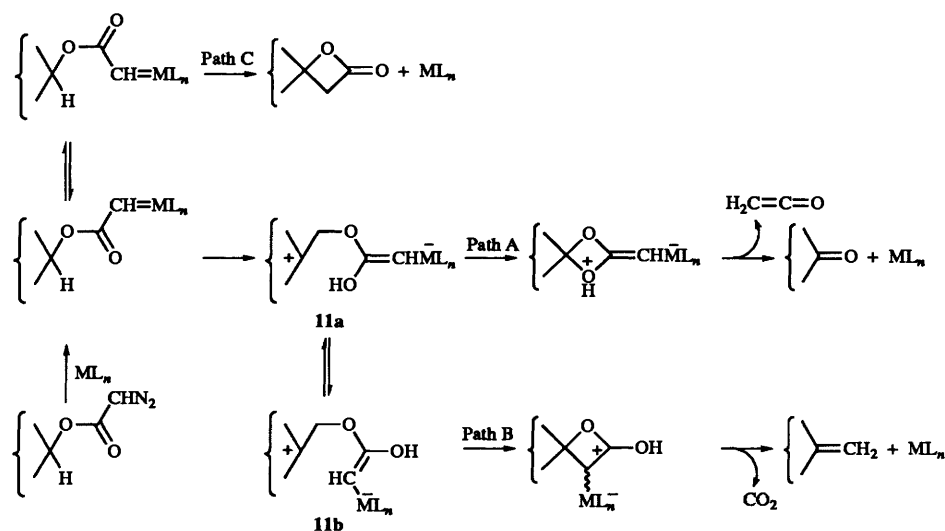
Scheme 1

Table 1 Products from diazo decomposition of representative benzylic and allylic diazoacetates

Diazo compound	Catalyst	Isolated yields (%)		
		$R_2C=O$	$R_2C=CH_2$	Other
4	$Rh_2(5S-MEPY)_4$	32	18	20[a]
	$Rh_2(cap)_4$	18	1	32[b]
5	$Rh_2(5S-MEPY)_4$	37	< 1	25[c]
	$Rh_2(4S-MEOX)_4$	24	< 1	52[c]
	$Rh_2(cap)_4$	7	< 1	39[c]
	$Rh_2(OAc)_4$	5	< 1	5[c]
6	$Rh_2(cap)_4$	7	< 1	77[d]

[a] Product from O–H insertion. [b] Product from O–H insertion (15%); carbene dimer (17%). [c] Aromatic cycloaddition product **7**. [d] Intramolecular cyclopropanation product **8**.

hex-2-enone was formed in diazo decomposition reactions of cyclohex-2-enyl diazoacetate when, with $Rh_2(cap)_4$ catalysis, the principal product-forming pathway was intramolecular cyclopropanation **8**.

That the combination of ketone and olefin products is not due to the decomposition of an intermediate β-lactone is suggested by (1) the variation of **2**:**3** as a function of dirhodium(II) ligand and (2) the isolation of a stable β-lactone from diazo decomposition of tetrahydro-4*H*-pyran-4-yl diazoacetate **9**. In contrast with results from C–H insertion reactions of cycloalkyl diazoacetates, where γ-lactone formation is virtually the exclusive pathway for C$_r$H insertion,[13] β-lactone formation from **9** accounts for more than 50% of insertion
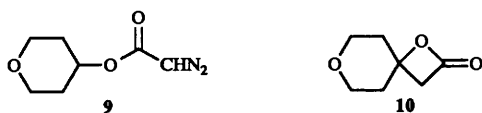
products in reactions catalysed by $Rh_2(4S-MEOX)_4$, $Rh_2(5S-MEPY)_4$ and $Rh_2(cap)_4$ (β-/γ-lactone = 54:56, 58:42 and 67:33, respectively). This β-lactone is stable towards distillation at ≤95 °C and is readily detected from its characteristic ^1H NMR signals and IR (C=O) absorptions; analogous β-lactone products from the diazo decomposition of compounds **1** and **4**–**6**, even for reactions performed at room temperature, were not observed (< 3%) by these analyses.[14]

The catalyst-dependent formation of ketone and vinylidene products is consistent with a hydride-abstraction mechanism

(Scheme 1) in which the ester carbonyl group serves as the hydride acceptor. Intramolecular trapping of the intermediate oxygen-stabilized carbocation **11** by the enol either at oxygen (Path A) or carbon (Path B) leads to the observed products. Ketene, which is expected from Path A, was trapped by 2,5-dimethylaniline from the $Rh_2(OAc)_4$-catalysed diazo decomposition of **1** (*n* = 2). The influence of solvent on selectivity, previously established by Davies to be an important consideration for selected metal carbene transformations,[15] was expected to be of minor importance in the selection between Paths A and B; indeed, using the pentane-soluble octadecyl ester analogue of $Rh_2(5S-MEPY)_4$, $Rh_2(5S-ODPY)_4$ **1** (*n* = 2) gave **2** and **3** in a 76:24 ratio in pentane (60% yield) which is very close to the ratio obtained by use of $Rh_2(5S-MEPY)_4$ in dichloromethane. Benzylic and allylic C–H bonds forgo direct C–H insertion (Path C). Similar processes to those reported here are observed with benzylic and allylic diazoacetoacetates; future reports will communicate the generality of these processes.

Experimental

Diazodecomposition of diazoacetates

To the dirhodium(II) catalyst (0.010 mmol, 1.0 mol%) in refluxing anhydrous dichloromethane (20 cm³) was added, under nitrogen by syringe pump, a solution of the diazo compound (1.00 mmol) in CH_2Cl_2 (5 cm³) at a rate of 0.5 cm³ h^{-1}. After addition was complete, the solvent was evaporated and the residue was analysed by spectroscopic methods; its purification by bulb-to-bulb distillation afforded the reported products. Ketene-trapping experiments were performed by placing 2,5-dimethylaniline on glass wool in a drying tube attached to the condenser on the reaction flask. Reactant diazo esters and all new products gave satisfactory elemental analyses. All products were analysed by chromatographic and spectroscopic methods.

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