Pergamon

Tetrahedron Letters, Vol. 36, No. 9, pp. 1499-1502, 1995
Elsevier Science Ltd
Printed in Great Britain
0040-4039/95 \$9.50+0.00

0040-4039(95)00069-0

Rhodium(II)-Catalyzed Reaction of 1,3-Bis(diazo)indan-2-one with Alcohols: Formation of Unexpected 1,1-Dialkoxy Ketones

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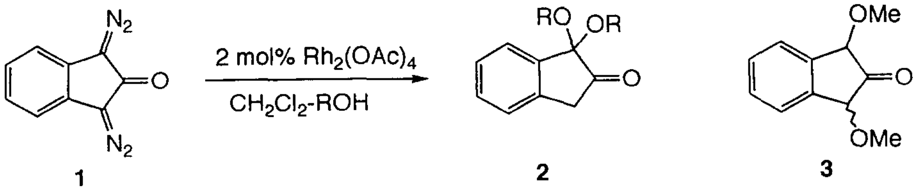
Abstract: The rhodium(II)-catalyzed decomposition of 1,3-bis(diazo)indan-2-one (**1**) in boiling dichloromethane containing primary alcohols gave 1,1-dialkoxyindan-2-ones (**2**) in good yields without any formation of 1,3-dialkoxy derivatives.

α,α'-Bis(diazo) ketones have been of interest not only as molecules for mechanistic studies of decomposition processes,[1] but as intermediates for the synthesis of highly strained compounds[2] and carbon oxides (C_nO_m).[3] Recently, we reported the detailed studies of photochemistry of 1,3-bis(diazo)indan-2-one (**1**), where it was concluded that the two diazo groups were cleaved independently in fluid solutions, as well as in matrices at cryogenic temperatures.[4] However, we now report that the interaction between the two reaction sites is first observed in rhodium(II) acetate [$Rh_2(OAc)_4$]-catalyzed decomposition of **1** in the presence of alcohols. Though the use of transition metal catalysts has recently been advanced for application of α-diazocarbonyl compounds to organic synthesis,[5] this is the first report dealing with the rhodium(II)-catalyzed decomposition of α,α'-bis(diazo) ketones.[6]

1,3-Bis(diazo)indan-2-one (**1**) was treated with 2 mol% $Rh_2(OAc)_4$ in refluxing dichloromethane containing 5% (v/v) methanol for 2 h. The starting material was completely consumed, and after chromatographical separation a single product was obtained in high yield. Based on the ^{1}H NMR data, we identified the product as 1,1-dimethoxyindan-2-one (**2a**).[7] The acetal structure of **2a** was confirmed by the hydrolysis with acidic wet silica gel[8] to indan-1,2-dione.[9] $Rh_2(OAc)_4$ was known to catalyze the insertion of carbenes into the OH bond of alcohols efficiently.[10] Thus, if the two diazo groups of **1** were decomposed



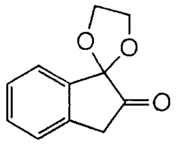
1 **2** **3**

a, R = Me; **b**, R = Et; **c**, R = *n*Bu
d, R = CH_2=$CHCH_2$-; **e**, R = $PhCH_2$-

Table 1. $Rh_2(OAc)_4$-Catalyzed Reaction of **1** with Alcohols[a]

alcohol	product	yield (%)[b]
MeOH	**2a**	68
EtOH	**2b**	60
*n*BuOH	**2c**	58
$CH_2{=}CHCH_2OH$	**2d**	20
$PhCH_2OH$	**2e**	16
$HOCH_2CH_2OH$	**4**	36

[a] Reaction conditions: **1** 20 mg, 0.11 mmol; $Rh_2(OAc)_4$ 1.0 mg, 0.002 mmol; CH_2Cl_2-alcohol (19 : 1, v/v) 4 mL. [b] Yield by isolation. All acetals were isolated as viscous oil.



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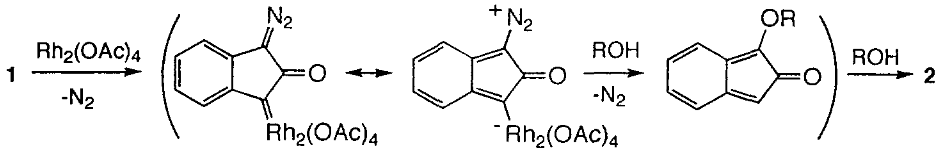
independently with $Rh_2(OAc)_4$ catalyst in the presence of methanol, the formation of 1,3-dimethoxyindan-2-one (**3**)[11] would be expected. However, no trace amounts of **3** could be detected in the mixture obtained from the $Rh_2(OAc)_4$-catalyzed reaction of **1** in dichloromethane containing methanol. The yields of 1,1-dialkoxyindan-2-ones isolated from the $Rh_2(OAc)_4$-catalyzed reaction of **1** with various alcohols are summarized in Table 1. It was reported that in the rhodium(II)-catalyzed reaction of α-diazocarbonyl compounds with unsaturated alcohols the cycloaddition to the double bond could compete with the insertion into the OH bond.[10] In the reaction of **1** with allyl alcohol, the corresponding 1,1-dialkoxyindan-2-one **2d** was obtained in 20% yield, together with large amounts of tar, where no products derived from cycloaddition to the double bond could be isolated. Furthermore, the $Rh_2(OAc)_4$-catalyzed reaction of **1** with *i*-propyl or *t*-butyl alcohol afforded a complex mixture, from which no corresponding 1,1-dialkoxyindan-2-one could be isolated. The failure to obtain **2** in the reaction with secondary or tertiary alcohols, as well as an extremely low yield of **2e**, can be attributed to the large steric repulsion between the geminal alkoxy groups.

Thus, the rhodium(II) catalyst has developed a unique reactivity of 1,3-bis(diazo)indan-2-one (**1**) toward alcohols, which is quite different from the reactivities observed in the photolytic[4c] and acid-catalyzed decomposition.[11] The 1,1-dialkoxy derivative **2** seems to be a primary product of **1**, since the analysis of the reaction by GC revealed that the formation of **2** was accompanied with the decrease of **1**, and no intermediate products were isolated or detected even at the early stage of the reaction.

Though the detailed process of decomposition of **1** with $Rh_2(OAc)_4$ has not been elucidated yet, we tentatively propose the following mechanism involving 1-alkoxyinden-2-one **5** as a reactive intermediate (Scheme 1). Electrophilic addition of $Rh_2(OAc)_4$ to one of the diazo groups resulted in the formation of a metal stabilized carbene **6**, where the other diazo group could be activated owing to an interaction between the two reaction sites

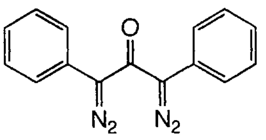


6 **6a** **5**

Scheme 1

as depicted in the structure **6a**. Thus, a succesive decomposition of the two diazo groups and the 1,4-addition of alcohol could be achieved to give the intermediate **5**,[12] which would immediately undergo the Markovnikov-type conjugate addition of alcohol to afford the final product **2**.[13]

To establish the general scheme of rhodium(II)-catalyzed decomposition of α,α'-bis(diazo) ketones, the reaction of several other bis(diazo) ketones was preliminarily examined. However, the rate of $Rh_2(OAc)_4$-catalyzed decomposition of 1,3-bis(diazo)-1,3-diphenylpropan-2-one (**7**),[1] 2,6-bis(diazo)-4-phenylcyclohexanone (**8**), or 2,4-bis(diazo)-1,3-dioxo-1,2,3,4-tetrahydronaphthalene (**9**)[14] in boiling dichloromethane was much slower than that of **1**. No corresponding 1,1-dialkoxy ketone was obtained in the $Rh_2(OAc)_4$-catalyzed decomposition of **7** or **8** in the presence of methanol, though the product derived from the Wolff-type ring contraction, *i.e.* methyl 4-phenyl-1-cyclopentenecarboxylate (**10**), was isolated in 32% yield in the $Rh_2(OAc)_4$-catalyzed reaction of **8** with methanol in benzene at 65 °C. On the other hand, the $Rh_2(OAc)_4$-catalyzed decomposition of **9** in refluxing dichloromethane containing 5% (v/v) methanol gave a mixture of 4,4-dimethoxy-1,3-dioxo-1,2,3,4-tetrahydronaphthalene (**11**)[15] and 2,4-dimethoxy-1,3-naphthalenediol (**12**)[16] in 10 and 13% yield, respectively, while in benzene-methanol at 65 °C the diol **12** was obtained exclusively (24%).



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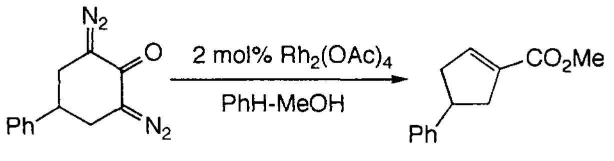
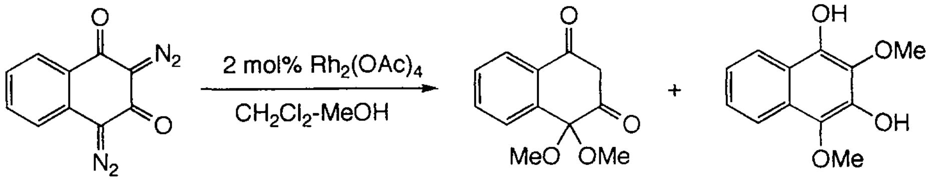


8 **10**



9 **11** **12**

Thus, the scheme of the rhodium(II)-catalyzed reaction of α,α'-bis(diazo) ketones with alcohols was found to be much dependent on the structure of the starting ketones, as well as reaction conditions. Further work is in progress to understand the detailed mechanism of the $Rh_2(OAc)_4$-catalyzed decomposition of α,α'-bis(diazo) ketones.

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7. **2a**: oil; ^1H NMR ($CDCl_3$) δ 3.48 (6H, s), 3.56 (2H, s), 7.34-7.42 (3H, m), 7.52 (1H, d, J = 7.6 Hz); GC-MS *m/z* (rel intensity) 192 (M^+, 4), 164 (M^+ - CO, 89), 163 (83), 161 (M^+ - OMe, 60), 119 (62), 105 (94), 91 (100).
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11. The diastereoisomers of **3** were formed in the CF_3CO_2H-catalyzed decomposition of **1** in methanol. One isomer, which was tentatively identified as *cis*-**3**, could be isolated by GPC separation of the reaction mixture: oil; ^1H NMR ($CDCl_3$) δ 3.61 (6H, s), 4.79 (2H, s), 7.44-7.54 (4H, m). The ^1H NMR signals of the other isomer *trans*-**3**, which could not be completely purified, appeared at δ 3.59 (3H, s), 4.86 (2H, s), and 7.44-7.57 (4H, m) in $CDCl_3$.
12. Attempts to capture **5** with a dienophile were not successful at the present stage.
13. It was reported that the conjugate addition of methanol to 1-methoxyisobenzofuran, which was formed from the Cu-catalyzed decomposition of [2-(methoxycarbonyl)phenyl]diazomethane, afforded 1,3-dihydro-1,1-dimethoxyisobenzofuran: Hamaguchi, M.; Ibata, T. *Chem. Lett.* **1976**, 287.
14. This new bis(diazo) ketone **9** was prepared in 49% yield by the KF-Al_2O_3-catalyzed diazo transfer from *p*-toluenesulfonyl azide to 1,3-naphthalenediol. The photochemistry of **9** has been preliminarily presented: Miyata, M.; Kongou, C.; Murata, S.; Tomioka, H. *Abstract of Papers*, 42nd Symposium on Organic Reactions of the Chemical Society of Japan, Osaka, November 1992; p 451.
15. **11**: oil; ^1H NMR ($CDCl_3$) δ 3.32 (6H, s), 3.84 (2H, s), 7.55-7.59 (1H, m), 7.65-7.69 (1H, m), 7.88 (1H, d, J = 7.6 Hz), 8.04 (1H, d, J = 7.8 Hz). The hydrolysis of **11** with acidic wet silica gel gave 2-hydroxy-1,4-naphthoquinone, the structure of which was confirmed by spectroscopic comparison with a commercially available authentic sample. The mechanism for the formation of **11** has not been elucidated yet, but we suppose that 1-methoxy-2,3-benzo-4,6-dioxobicyclo[3.1.0]hex-2-ene, which would be produced through a direct interaction between two reaction sites, is a short-lived intermediate.
16. The diol **12**, which showed ^1H NMR signals at δ 3.95 (3H, s), 4.03 (3H, s), 5.93 (1H, brs), 6.03 (1H, brs), 7.31-7.47 (2H, m), 7.87 (1H, d, J = 7.9 Hz), 8.11 (1H, d, J = 8.3 Hz) in $CDCl_3$, could only be identified in the reaction mixture, since **12** was easily oxidized to 2-hydroxy-3-methoxy-1,4-naphthoquinone (**13**) in the course of the chromatographical separation. **13**: yellow granules; mp 123-125 °C; ^1H NMR ($CDCl_3$) δ 4.20 (3H, s), 6.88 (1H, brs), 7.66-7.76 (2H, m), 8.06 (1H, d, J = 6.9 Hz), 8.10 (1H, d, J = 7.3 Hz).

(*Received in Japan* 7 *October* 1994; *accepted* 27 *December* 1994)