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Ruthenium(II) Porphyrin Catalyzed Formation of (*Z*)-4-Alkyloxycarbonyl-methylidene-1,3-dioxolanes from γ-Alkoxy-α-diazo-β-ketoesters

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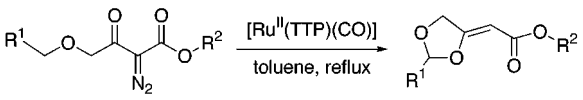
ABSTRACT



R^1 = aryl, allyl
R^2= methyl, 2,4-dimethyl-3-pentyl and (-)-menthyl

Ruthenum(II) porphyrins and dirhodium(II) acetate catalyze cyclization of γ-alkoxy-α-diazo-β-ketoesters to (*Z*)-4-(alkyloxycarbonylmethylidene)-1,3-dioxolanes selectively (ca. 68% yield) with no formation of 3(*2H*)-furanones. Reacting a diazo ketoester with [Ru^{II}(TTP)(CO)] [H_2TTP = *meso*-tetrakis(*p*-tolyl) porphyrin] in toluene afforded a ruthenium carbenoid complex, which has been isolated and spectroscopically characterized. A mechanism involving hydrogen atom migration from the C–H bond to the ruthenium carbenoid is proposed.

The transition metal carbenoid mediated C−H insertion reaction has proven to be a versatile and effective method for organic synthesis.[1] Notably "reactive rhodium carbenoid intermediates," derived from the reaction of dirhodium(II) carboxylates/carboximidates with diazo compounds, have been postulated to be active intermediates for highly stereo- and enantioselective intra- and intermolecular C−H bond insertions.[2] However, such species are too reactive for isolation and characterization.[3] Recent studies showed that diazo compounds[4] such as diphenyldiazomethane react with ruthenium(II) porphyrins[4f] to afford ruthenium carbene complexes, some of which have been structurally characterized.[4c−f] Of particular note is the fact that these carbenes can catalyze styrene cyclopropanation using ethyl diazoacetate with high product turnovers and *anti-syn* diastereoselectivity.[4f,5] Although oxo-[6] and imido-ruthenium[7] porphyrins can effect oxygen and nitrogen group insertion to saturated C−H bonds, there are few examples of C−H bond functionalization by ruthenium carbene complexes in the literature.

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(3) For isolation of a stable dirhodium tetracarboxylate carbenoid: Snyder, J. P.; Padwa, A.; Stengel, T.; Arduengo III, A. J.; Jockisch, A.; Kim, H.-J. *J. Am. Chem. Soc*. **2001**, *123*, 11318.

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Recently, we prepared a bis(diphenylcarbene)osmium porphyrin complex, [Os^{II}(TPFPP)(CO)] [H_2TPFPP = *meso*-tetrakis(pentafluorophenyl)porphyrin], which can undergo allylic C−H insertion reactions with cycloalkenes.[8] This has prompted us to investigate the reactivity of ruthenium carbene complexes toward C−H insertion. We were attracted to the finding by Adams and co-workers that dirhodium(II) acetate mediated stereoselective cyclization of γ-alkoxy-α-diazo ketones to 3(2*H*)-furanones via carbenoid insertion into the C−H bond adjacent to an ether oxygen.[9,10] Here we report that ruthenium porphyrins (Figure 1) and dirhodium acetate

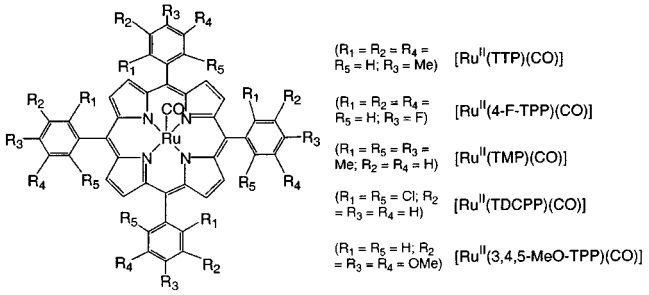
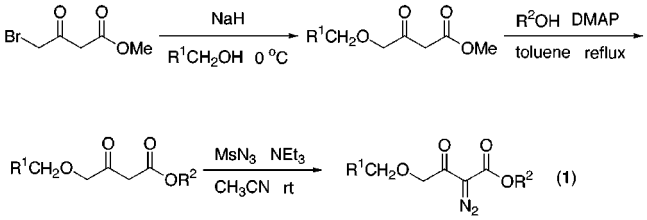


Figure 1. Ruthenium(II) porphyrins.

can catalyze intramolecular cyclization of γ-alkoxy-α-diazo-β-ketoesters to afford (*Z*)-4-(alkyloxycarbonylmethylidene)-1,3-dioxolanes exclusively and that the formation of C−H insertion products [i.e., 3(2*H*)-furanones] was not detected. Our preliminary results suggest that the reactions proceed by H-atom migration to ruthenium carbene complexes.

γ-Alkoxy-α-diazo-β-ketoesters **1** were prepared according to Scheme 1. Methyl γ-bromoacetoacetate was converted to its γ-alkoxy derivatives by reaction with appropriate alcohols;[11] subsequent transesterification with other alcohol derivatives gave γ-alkoxy-β-ketoesters.[12] Diazo transfer with

Scheme 1. Synthetic Route for γ-Alkoxy-α-diazo-β-ketoesters



mesyl azide furnished the γ-alkoxy-α-diazo-β-ketoesters **1** in overall yields of about 40%.[13]

When diazo ketoester **1a** (0.5 mmol) was treated with a catalytic quantity of [Ru^{II}(TTP)(CO)] [H_2TTP = *meso*-tetrakis(*p*-tolyl)porphyrin; 3 mol %] in refluxing dry toluene under an inert atmosphere, the dioxolane product **2a** was produced in 68% isolated yield (Table 1, entry 1). Diazo esters **1b**−**e** bearing bulky ester groups such as 2,4-dimethyl-3-pentyl and (−)-menthyl groups also underwent facile conversion to their corresponding dioxolanes **2b**−**e** in 55−67% yields (entries 2−6). When the diastereoselectivity of cyclization of **1c** to dioxolane **2c** was analyzed by chiral HPLC (chiral OJ column; 1% propan-2-ol, 99% hexane), less than 7% de was observed. However, after recrystallization of **2c** by diffusing hexane into the dichloromethane solution, we obtained a diastereomerically pure (>99% de) crystalline solid according to chiral HPLC analysis. The molecular structure of **2c** was confirmed by X-ray crystallography (see Supporting Information).

Previously, McKervey and co-workers[10a] described that [$Rh_2(CH_3CO_2)_4$] and derivatives catalyzed cyclization of γ-alkoxy-α-diazo-β-ketoesters via C−H insertion to form 3(2*H*)-furanones selectively. Recently Clark and co-workers[10e,f] reported a similar Rh-catalyzed reaction of α-diazo ketones in which 3(2*H*)-furanones were formed as major product; a minor formation of dioxolanes (ca. 10−40% yield) was also observed. In this work, we found that [$Rh_2(CH_3CO_2)_4$] (3 mol %) also catalyzed cyclization of the diazo ketoester **1a** in dichloromethane at room temperature to afford dioxolane **2a** selectively (Table 1, entry 1); no C−H insertion product [i.e., 3(2*H*)-furanone] was detected. Likewise, other sterically encumbered diazo ketoesters **1b**−**e** were found to give the corresponding dioxolanes in 51−67% yields.

Using benzyl α,α-d_2-alcohol (98% D) as starting material, we prepared a deuterium-labeled diazo ketoester **1c′**. Under the reaction conditions denoted in Table 1, both [Ru^{II}(TTP)(CO)] and [$Rh_2(CH_3CO_2)_4$] were found to effect cyclization of **1c′** to dioxolane **2c′** (ca. 68% yield) (Table 1, entry 4). On the basis of ^{1}H NMR and mass spectroscopic analyses, the deuterium content was conserved upon cyclization to dioxolane. The NMR spectrum of **2c′** unequivocally reveals that the deuterium atom at the exocyclic C=C bond

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(10) See also: (a) Ye, T.; McKervey, M. A.; Brandes, B. D.; Doyle, M. P. *Tetrahedron Lett.* **1994**, *35*, 7269. (b) Taber, D. F.; Song, Y. *J. Org. Chem.* **1996**, *61*, 6706. (c) Lee, E.; Choi, I.; Song, S. Y. *J. Chem. Soc., Chem. Commun.* **1995**, 321. (d) Mander, L. N.; Owen, D. J. *Tetrahedron Lett.* **1996**, *37*, 723. (e) Clark, J. S.; Dossetter, A. G. *J. Org. Chem.* **1997**, *62*, 4910. (f) Clark, J. S.; Wong, Y.-S.; Townsend, R. J. *Tetrahedron Lett.* **2001**, *42*, 6187.

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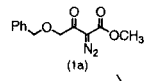
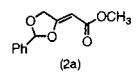
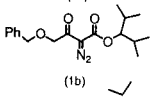
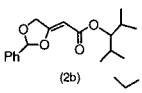
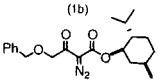
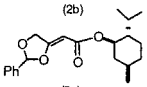
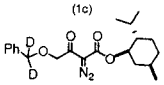
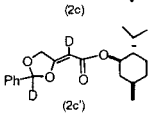
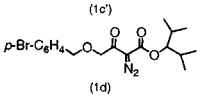
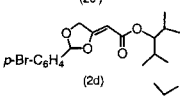
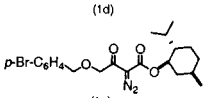
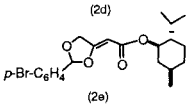
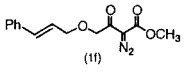
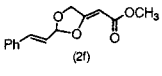
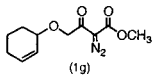
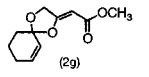
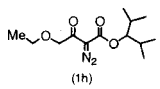
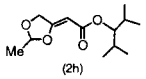
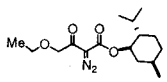
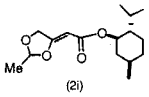
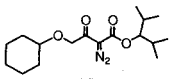
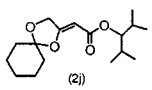
Table 1. Metal-Catalyzed Cyclization of γ-Alkoxy-α-diazo-β-ketoesters to Dioxolanes[d]

entry	substrate	product	[Ru^{II}(TTP)(CO)] yield %[a]	[Rh$_2$(CH$_3$CO$_2$)$_4$] yield %[a]
1	 (1a)	 (2a)	68	66
2	 (1b)	 (2b)	64	51
3	 (1c)	 (2c)	62	67 (92)[b]
4	 (1c')	 (2c')	68	67
5	 (1d)	 (2d)	55	65
6	 (1e)	 (2e)	67	63
7	 (1f)	 (2f)	57	52
8	 (1g)	 (2g)	55	65
9	 (1h)	 (2h)	- [c]	73
10	 (1i)	 (2i)	- [c]	76 (94)[b]
11	 (1j)	 (2j)	- [c]	76 (90)[b]

[a] Isolated yield. [b] Yield determined by ^{1}H NMR analysis of the crude reaction mixture. [c] No formation of dioxolanes was detected by ^{1}H NMR. [d] Reaction conditions: A mixture of diazo ketoesters **1** (0.5 mmol) and metal catalyst (3 mol %) was stirred in refluxing toluene (25 mL) (for Ru) or dichloromethane at room temperature (for Rh). The reaction was monitored by TLC for complete disappearance of starting materials. The solvent was then removed by vacuum evaporation and, the residue was purified by flash chromatography.

originates from the benzylic C−D bond. This result suggests that the Ru-/Rh-catalyzed intramolecular cyclization reaction involves cleavage of the benzylic C−H bond as the principal step.

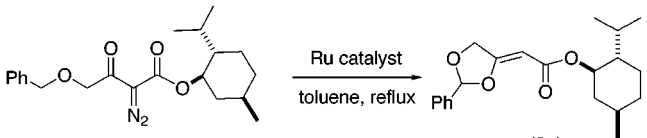
Apart from activation of benzylic C−H bonds, both [Ru^{II}(TTP)(CO)] and [Rh$_2$(CH$_3$CO$_2$)$_4$] can catalyze cyclization of diazo esters such as **1f** and **1g** containing allylic C−H bonds to produce dioxolanes in ca. 55% yields (entries 7 and 8). In all cases, the diazo esters were completely consumed after the reactions. ^{1}H NMR analysis of the crude reaction mixtures revealed the dioxolane compounds as the only identifiable products; no cyclopropanation products were found.

Cyclization of the diazo ketoesters containing aliphatic alkoxy substituents (Table 1, entries 9−11) was also attempted. Subjecting these diazo esters to the ruthenium-catalyzed conditions (i.e. substrate = 0.5 mmol, Ru = 3 mol % in refluxing toluene) afforded no detectable dioxolanes, and complete substrate decomposition was observed according to NMR analysis. In contrast, [Rh$_2$(CH$_3$CO$_2$)$_4$] was found to be an effective catalyst for the cyclization of **1h**−**j** under ambient conditions, and **2h**−**j** were isolated in 73−76% yields (Table 1 entries 9−11). The molecular structure of **2i** has been determined by X-ray crystal analysis (see Supporting Information). Analogous to **2c**, while low diastereoselectivity (<5% de) was obtained for the intramolecular cyclization, analysis of the recrystallized sample of **2i** by chiral HPLC registered a diastereomeric purity of >99% de.

In the absence of the ruthenium or rhodium catalyst, heating **1a** in refluxing toluene resulted in complete substrate decomposition, and no dioxolane **2a** was detected by ^{1}H NMR analysis of the reaction mixture. Toluene was found to be the solvent of choice for the ruthenium-catalyzed reactions; other solvents such as benzene and acetonitrile gave considerably lower product yields of 45 and 26%, respectively. When the ruthenium-catalyzed reaction was performed in chloroform, tetrahydrofuran and dichloromethane, no dioxolane formation was observed and the starting material was recovered (ca. 85%).

Employing **1c** as the substrate, we have examined the effect of different ruthenium catalysts on the cyclization of γ-alkoxy-α-diazo-β-diketoesters (Table 2). Other ruthenium-

Table 2. Effect of Ruthenium Porphyrin Catalysts on Cyclization of (−)-Menthyl-γ-benzyloxy-α-diazo-β-ketoester[d]



(**1c**) (**2c**)

entry	Ru catalyst[a]	%yield of 2c[b]
1	[Ru^{II}(OEP)(CO)]	62
2	[Ru^{II}(4-F-TPP)(CO)]	67
3	[Ru^{II}(3,4,5-MeO-TPP)(CO)]	56
4	[Ru^{II}(TDCPP)(CO)]	< 5[c]
5	[Ru^{II}(TMP)(CO)]	< 5[c]

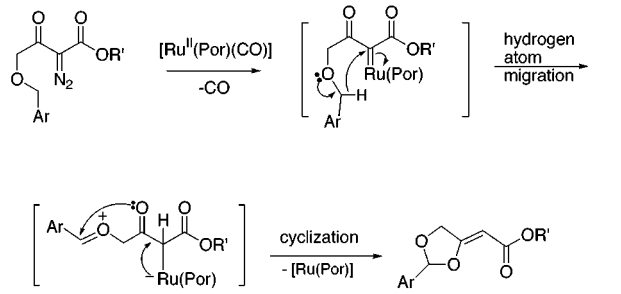
[a] See text for notations. [b] Isolated yield. [c] Based on ^{1}H NMR analysis of crude reaction mixture. [d] Reaction conditions: A mixture of **1c** (0.5 mmol) and Ru catalyst (3 mol %) was heated in refluxing toluene under an inert atmosphere for 2 h.

(II) porphyrin complexes [Ru^{II}(Por)(CO)] (H_2Por: H_2OEP = octaethylporphyrin; H_2-*p*-F-TPP = *meso*-tetrakis(*p*-fluorophenyl)porphyrin; H_2-3,4,5-MeO-TPP = *meso*-tetrakis(3,4,5-trimethoxyphenyl)porphyrin) were found to exhibit comparable catalytic activities to [Ru^{II}(TTP)(CO)], and similar yields (ca. 60%) of dioxolane **2c** were obtained (Table 2, entries 1−3). However, when [Ru^{II}(TDCPP)(CO)] [H_2-TDCPP = *meso*-tetrakis(2,6-dichlorophenyl)porphyrin] or [Ru^{II}(TMP)(CO)] [H_2TMP = *meso*-tetramesitylporphyrin] was employed as catalyst, **2c** was formed in <5% yield (entries 4 and 5). It should be noted that the reaction of **1c** with [Ru^{II}(TDCPP)(CO)] or [Ru^{II}(TMP)(CO)] in toluene did not give any ruthenium carbene complexes (see later sections). It is likely that steric hindrance of the bulky *ortho*-substituents at the porphyrin ligand would disfavor the carbene formation.

Some non-porphyrin-type ruthenium catalysts such as [$(Me_3tacn)Ru^{III}(CF_3CO_2)_3 \cdot H_2O$] ($Me_3tacn$ = 1,4,7-trimethyl-1,4,7-triazacyclononane)[14] and [Ru^{II}(6,6′-Cl_2-bpy)$_2$(H_2O)$_2$](CF_3SO_3)$_2$ (6,6′-Cl_2-bpy = 6,6′-dichloro-2,2′-bipyridine)[15] were found to exhibit negligible catalytic activity under the standard experimental conditions [i.e., **1c** (0.5 mmol) and Ru catalysts (3%mol) in refluxing toluene]. No dioxolane product **2c** was obtained, and the diazo substrate was completely decomposed. When $Ru^{II}(PPh_3)_3Cl_2$ was used as catalyst,[16] heating diazo compound **1c** in refluxing toluene gave **2c** in 18% yield. Yet when the same reaction was carried out at room temperature, no dioxolane was produced and the substrate was completely recovered.

It has been reported that diazo compounds react with [Ru^{II}(Por)(CO)] (H_2Por = tetraphenylporphyrin,[4c] 5,10,15,20-tetrakis{(1*S*,4*R*,5*R*,8*S*)-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracene-9-yl}porphyrin)[4f] to give ruthenium carbene complexes. In this work, when [Ru^{II}(TTP)(CO)] reacted with 2,4-dimethyl-3-pentyl 2-diazo-3-oxo-heptanoate (2 equiv) in refluxing toluene for 3 h under an argon atmosphere, a color change from red to dark brown was observed. After purification with flash chromatography [hexane/ethyl acetate = 95:5 (v/v)], a dark red solid was isolated. The UV−visible spectrum of the ruthenium product in $CHCl_3$ shows an intense Soret band and a Q-band at λ_{max} = 407 and 534 nm, respectively. The ^{1}H NMR spectrum is characterized by two upfield doublet signals at δ_H 0.01 and −0.23 ppm that could be assigned to the methyl protons of the 2,4-dimethyl-3-pentyl moiety. The α-methylene protons were also found to exhibit significant upfield shifts relative to that in the unbound diazo ketoester. The ^{13}C NMR spectrum showed a downfield absorption at δ_C 287.5 ppm, which is characteristic of a Ru=C moiety.[4] FAB-MS analysis of the sample showed a molecular ion peak [$M^+ + 1$] at *m*/*z* = 1011; this is consistent with the [(TTP)Ru=CR^1R^2] [R^1 = C(O)C_4H_9; R^2 = C(O)OC_7H_{13}] formulation based on the excellent agreement between the experimental and calculated isotopic distributions.

Scheme 2. Proposed Mechanism



To account for the dioxolane formation in the ruthenium catalyzed cyclization of diazo esters, we propose that H-atom migration to the electrophilic carbenoid carbon atom would afford a reactive oxonium ion intermediate; intramolecular attack by the carbonyl oxygen would furnish the dioxolane compound. A similar mechanism was proposed by Clark and co-workers to explain the minor formation of dioxolanes in the rhodium-catalyzed intramolecular C−H insertion reactions.

In conclusion, we have discovered that ruthenium porphyrins catalyze effective cyclization of γ-alkoxy-α-diazo-β-ketoesters to form dioxolanes exclusively. With the isolation of ruthenium carbene intermediates, the parallel reactivity pattern for the reactions catalyzed by ruthenium(II) porphyrins and dirhodium(II) acetate supports postulation of reactive rhodium carbenoid species for the latter reactions.[3]

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Supporting Information Available: Experimental details and characterization data for the products and crystallographic data for dioxolanes **2c** and **2i**. This material is available free of charge via the Internet at http://pubs.acs.org.

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