

Communications to the Editor

Ru₃(CO)₁₂-Catalyzed Decarbonylative Cleavage of a C–C Bond of Alkyl Phenyl Ketones

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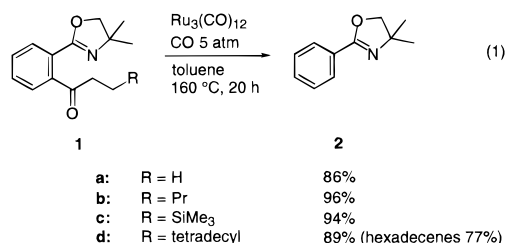
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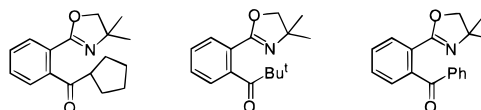
The cleavage of unreactive bonds, such as C–H, C–C, and C–F, by transition metals has received considerable attention over the past decades.¹ Although substantial progress has been made in this field, most studies have involved stoichiometric reactions. Recently, significant developments in catalytic reactions involving the cleavage of C–H bonds have been achieved via the use of Ru,^{2,3} Rh,⁴ and Co⁵ complexes as catalysts. In contrast, the cleavage of C–C bonds remains limited. In this context, the exploration of catalytic reactions which enable the cleavage of a C–C bond represents a challenging topic of considerable synthetic interest.⁶ While several catalytic reactions in which the cleavage of a C–C bond occurs have already been reported, most involve reactions of strained substrates and are based on the methodology which takes advantage of the release of ring strain and/or the presence of an activating functionality, such as a carbonyl group. Strained ketones, such as cyclopropanones,⁷ cyclobutanones,⁸ and cyclobutenones,⁹ are known to undergo C–C bond cleavage via catalysis by transition metal complexes. On the other hand, analogous catalytic reactions of unstrained ketones are rare. Kaneda reported the Rh-catalyzed decarbonylation of diketones to monoketones.¹⁰ Suggs and Jun found that rhodium complexes promote an exchange reaction of alkyl groups in the reaction of 8-quinolinyl alkyl ketones¹¹ or in situ generated *N*-pyridyl imines with olefins.¹² These results strongly suggest that chelation represents a promising approach to the cleavage of unstrained C–C bonds. In this paper, we report a new type of catalytic reaction, which involves the Ru₃(CO)₁₂-catalyzed decarbonylative cleavage of a C–C bond in aromatic ketones.

A substrate for the exploration of C–C bond-breaking reactions was designed, in which chelation can be utilized to bring a C–C bond into a coordination sphere, thus permitting cleavage of the C–C bond. We choose alkyl phenyl ketones bearing an oxazoline or pyridine on the phenyl group as model systems so as to directly observe unstrained C–C bond cleavage. The utility of these

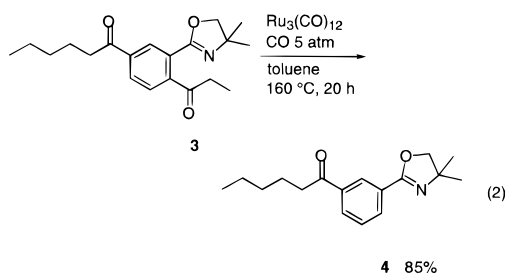
directing groups for the cleavage of C–H bonds has already been discussed.¹³ Treatment of 1-[2-(4,5-dihydro-4,4-dimethyl-2-oxazolyl)phenyl]-1-propanone (**1a**) with 5 mol % of Ru₃(CO)₁₂ under an atmosphere of nitrogen at 135 °C in toluene in a 50-mL screw-capped vial resulted in decarbonylation to give **2** in 62% yield, along with **1a** in 25% yield. The solution became black, indicating the decomposition of the catalyst. After optimizing the reaction conditions, we discovered that CO pressure maintains the catalyst in an active form, thus eliminating color formation. When the reaction of **1a** (0.5 mmol) under 5 atm of CO at 160 °C in toluene in the presence of Ru₃(CO)₁₂ (0.025 mmol) for 20 h in a 50-mL stainless autoclave gave **2** in 86% isolated yield, the final reaction solution was orange (eq 1).



The pentyl ketone **1b** and β -silylethyl ketone **1c** underwent decarbonylation to give **2** in high yields. The reaction of hexadecyl ketone **1d** afforded **2** in 89% yield, along with hexadecenes in 77% yield. The recovered olefins were comprised of at least five isomers of hexadecenes. The corresponding cyclopentyl ketone, *tert*-butyl ketone, and phenyl ketone failed to react. This may be



due to the steric bulkiness in the vicinity of the keto moiety. The use of a pyridine ring in place of an oxazoline ring as the directing group also gave good results. For example, the reaction of the corresponding pyridine isomer of **1a** gave 2-phenylpyridine in 81% yield under identical conditions (not shown). It is noteworthy that the presence of a directing group is critical for the decarbonylation reaction to proceed. Of additional importance is the fact that the directing group caused a site-selective reaction. Indeed, the reaction of diketone **3** involved site-selective decarbonylation at the ortho position to give decarbonylated product **4** in high yield (eq 2).



We next used ketones which contain no hydrogen β to the ketone, to circumvent the formation of alkenes, in the expectation that it would lead to new reactions. These substrates, however,

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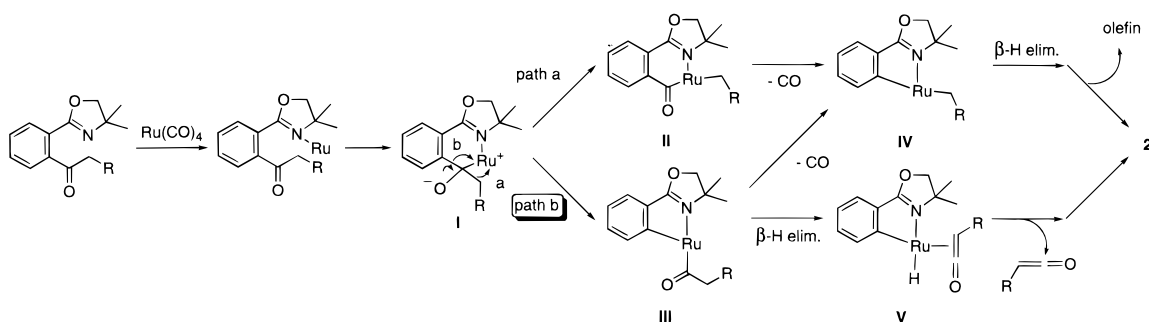
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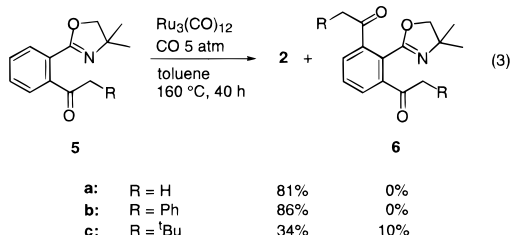
(6) For a recent review focused on catalytic reactions involving the cleavage of C–C bonds, see: Murakami, M.; Ito, Y. In *Activation of Unreactive Bonds and Organic Synthesis*; Murai, S., Ed.; Springer: Berlin, 1999; pp 97–129.

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Scheme 1



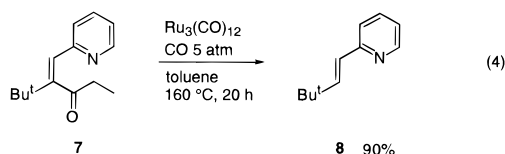
again gave **2** (eq 3). The reaction of methyl ketone **5a** gave **2** in 81% yield. No other products were detected by GC–MS and ^1H NMR of the crude reaction mixture. Benzyl ketone **5b** provided **2** in 86% yield. Interestingly, when the solvent was changed to CH_3OH , **2** (73%) and $\text{PhCH}_2\text{C}(\text{O})\text{OMe}$ (31%) were formed. The formation of $\text{PhCH}_2\text{C}(\text{O})\text{OMe}$ suggests the generation of phenylketene, which is captured by CH_3OH . The reaction of **5c** gave quite unexpected results, giving **2** and diketone **6** in 34% and 10% yields, respectively, and **5c** was recovered at 49%.



We propose a reaction mechanism, as shown in Scheme 1. Coordination of the nitrogen to ruthenium provides the metal with a more nucleophilic character, as well as bringing it close to the ketonic carbon. The coordinated ruthenium attacks the carbonyl group to generate **I**. The first C–C bond cleavage to form **II** or **III** (via path a or path b), followed by decarbonylation (second C–C bond cleavage), would generate Ru–alkyl intermediate **IV**. At the present time, it is not clear which C–C bond (aryl–carbonyl or alkyl–carbonyl) cleaves first. If an aryl group rearranges in **I**, then the five-membered metallacycle **III**, which might be more stable than a six-membered metallacycle **II**, is formed. With the support of this hypothesis, the formation of methyl phenylacetate and **6** in eq 3 suggests that path b is more likely. The Ru–alkyl intermediate **IV** undergoes β -hydrogen elimination, followed by reductive elimination, to give **2** and olefins. Based on the results in eq 3, another pathway involving β -hydrogen elimination from intermediate **III** to give **V** is also possible when β -hydrogen elimination is not possible for steric reason.¹⁴ Methyl phenylacetate, which is derived from the reaction

of **5b**, is probably formed by the capture of phenylketene with methanol.¹⁵ In addition, the formation of **6c** can be explained on the basis of reaction of **5c** with *tert*-butyl ketene.¹⁶

The present reaction is applicable not only to alkyl phenyl ketones but also to α,β -unsaturated ketones. The reaction of α,β -unsaturated ketone **7** gave 2-[(*E*)-3,3-dimethyl-1-butenyl]pyridine (**8**) in high yield (eq 4).



In summary, we report a new catalytic reaction involving decarbonylative C–C bond cleavage. Although the decarbonylation of aldehydes, acyl halides, acyl cyanide, acyl phosphonates, and acylsilanes are well known,¹⁷ analogous reaction of ketones appears to be limited to specific substrates.^{8a,8b,10} A key feature is the utilization of the chelation of nitrogen to Ru, which assists in the formation of a metallacycle during the cleavage of the C–C bond.¹⁸

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Supporting Information Available: Lists of special data and elemental analyses for the products (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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