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Rapid Ruthenium-Catalyzed Synthesis of Pyranopyrandiones by Reconstructive Carbonylation of Cyclopropenones Involving C−C Bond Cleavage

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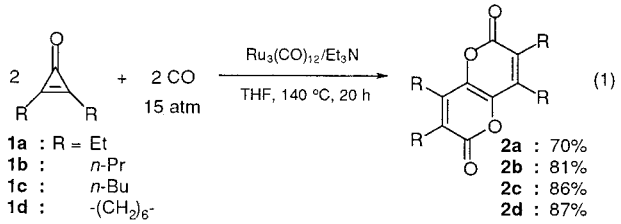
The catalytic cleavage of C−C bonds has been one of the most difficult challenges in the fields of organic and organometallic chemistry. This chemistry has recently received much scientific and technological interest and has opened the door to a new field of synthetic organic chemistry.[1] The next challenging subject is the reconstruction of new carbon skeletons after C−C bond cleavage, leading to the rapid and selective synthesis of novel organic molecules which cannot be obtained by the simple combination of traditional synthetic methods.[2] In our recent report on the unusual ruthenium-catalyzed coupling of cyclobutenediones with alkenes, we demonstrated the explicit cleavage of C−C bonds leading to the reconstruction of new carbon skeletons.[2i] In that reaction, a ruthenacyclobutenone is postulated to be a key intermediate, and we have continued our efforts to find a more efficient and direct method to generate an active ruthenacyclic intermediate. Among the various possibilities, we focused our attention on the reactivity of cyclopropenones.[3] Several stoichiometric reactions of cyclopropenones with transition-metal complexes to give metallacyclobutenones,[4] maleoylmetal complexes,[5] and dinuclear complexes[6] via C−C bond cleavage have been reported; however, few transition-metal complex-*catalyzed* reactions using cyclopropenones directed toward organic synthesis have been reported.[7] Therefore, we started our initial research to develop a novel ruthenium-catalyzed codimerization of cyclopropenones with unsaturated compounds via C−C bond cleavage. After many trials, we developed an unprecedented ruthenium-catalyzed carbonylative dimerization of cyclopropenones involving C−C bond cleavage, which gave a novel organic functional monomer, pyranopyrandione, in high yield.[8] Furthermore, cross-carbonylation of cyclopropenones with internal alkynes was also found to give unsymmetrically substituted pyranopyrandiones.

Treatment of cyclopropenone (**1**) with 3.3 mol % of $Ru_3(CO)_{12}$ and 10 mol % of NEt_3 in THF under 15 atm of carbon monoxide at 140 °C for 20 h gave a novel carbonylative dimerization product, tetrasubstituted pyranopyrandione (**2**), in high isolated yield with high selectivity (eq 1). In all cases, the starting cyclopropenones were completely consumed, and the only products detected by GLC were the corresponding pyranopyrandiones.

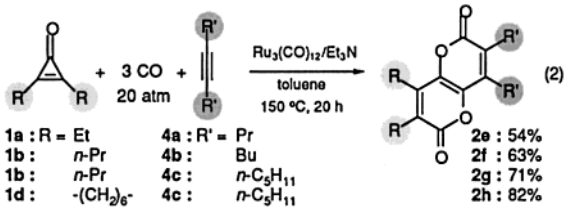
First, the effects of the catalysts and ligands were examined in the synthesis of **2b** from **1b**. An appropriate catalyst combined with a ligand was critical for the success of the reaction. For example, the catalytic activity of $Ru_3(CO)_{12}$ *itself* was quite low, and **3a**, 4-oxa-1,2,6,7-tetrapropylspiro[2.4]hepta-1,6-dien-5-one, a dimer of **1a**, was produced thermally without the catalyst in 89% yield.[3a,9] The concomitant use of a NEt_3 ligand completely suppressed the formation of **3a** and dramatically increased the catalytic activity of $Ru_3(CO)_{12}$ to give **2b** in the best yield of 81%. Other ruthenium catalysts, such as Ru(η^4-cod)(η^6-cot) [cod = 1,5-cyclooctadiene, cot = 1, 3, 5-cyclooctatriene] (**2b**, 73%), $[RuCl_2(CO)_3]_2$ (**2b**, 53%), Ru(η^6-cot)(η^2-dmfm)$_2$ [dmfm = dimethyl fumarate] (**2b**, 49%), and Cp*RuCl(cod) [Cp* = pentamethylcyclopentadienyl] (**2b**, 46%), in the presence of a NEt_3 ligand, also showed moderate to good catalytic activity, while $RuCl_2(PPh_3)_3$, $RuH_2(CO)(PPh_3)_3$, and $RuCl_3 \cdot 3H_2O$ were almost ineffective even in the presence of NEt_3. No pyranopyrandione **2b** was obtained with several other transition-metal complexes, such as $Fe_3(CO)_{12}$, $Co_2(CO)_8$, $Rh_4(CO)_{12}$, and/or $RhCl(PPh_3)_3$[5a] and $Pt(PPh_3)_4$,[4a] which are known to react with cyclopropenones to give several metallacycles.



(1)

Catalyst systems combined with other amine ligands (NBu_3, *N*-methylpiperidine, pyridine, and *N*,*N*-diethylaniline) and phosphorus ligands (PCy_3 and PBu_3) showed moderate catalytic activity, while good reproducibility was observed for the amine ligand, and the best result was obtained with the NEt_3 ligand.

Furthermore, unsymmetrically substituted pyranopyrandiones (**2e**−**h**) were generally obtained in good to high yields by novel ruthenium-catalyzed cross-carbonylation of cyclopropenones (**1**) with internal alkynes (**4**) (eq 2).



(2)

Use of ^{13}CO gave the corresponding ^{13}C-labeled pyranopyrandiones, **2b**-^{13}C and **2e**-^{13}C, respectively (eqs 3 and 4). The result shown in eq 3 suggests that the carbonyl group of one molecule of the cyclopropenone is exchanged for the external carbon monoxide in the carbonylative reaction of two molecules of cyclopropenone (**1b**). Further, the result shown in eq 4 clearly indicates that 3 equiv of the external carbon monoxide are incorporated into the product **2e**.

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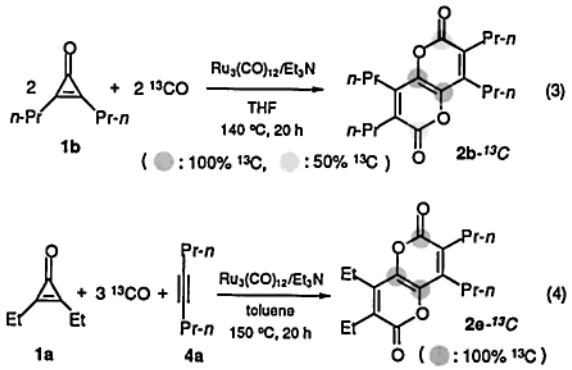
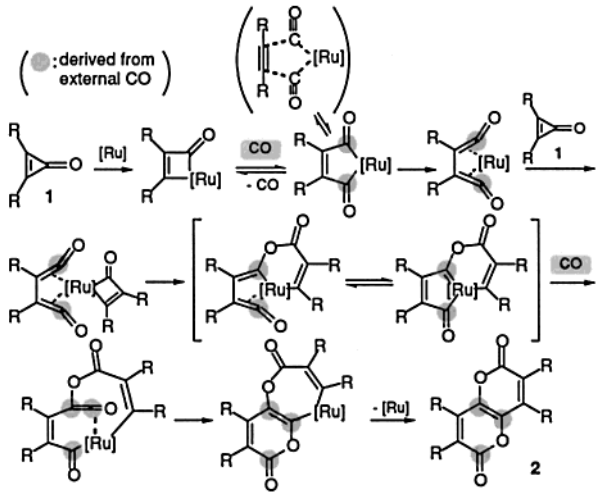


While the reaction mechanism is not yet clear, the most plausible mechanism to explain the results obtained in ^{13}C-labeling experiments is illustrated in Scheme 1. We now believe that the initial

Scheme 1



step in the present reaction might consist of oxidative addition of the C−C bond between a carbonyl and the α-carbon in cyclopropenone **1** to an active ruthenium center to give a ruthenacyclobutenone intermediate. Carbonylation of ruthenacyclobutenone (or carbonylative cyclization of alkynes on the ruthenium[10]) would initially give a maleoylruthenium intermediate. Subsequent isomerization of a maleoylruthenium intermediate produces an active (η^4-bisketene)ruthenium intermediate,[11] which reacts with another molecule of cyclopropenone by oxidative addition and insertion reactions to give a (ketene)ruthenium intermediate. Rapid tautomerization would give a ruthenium carbene intermediate, and insertion of carbon monoxide into a carbene−ruthenium bond would give a new ketene intermediate.[12] Finally, insertion of a carbonyl group of a ketene moiety into an acyl−ruthenium bond and reductive elimination give the desired pyranopyrandione **2**.

In conclusion, we have developed a novel and rapid ruthenium-catalyzed synthesis of pyranopyrandiones by the reconstructive carbonylation of cyclopropenones. All pyranopyrandiones prepared in this study are new compounds, which are quite attractive as novel functional monomers due to their characteristic physical and chemical properties. The isolation of possible intermediates to elucidate the mechanism and the use of pyranopyrandiones to synthesize a functional polymer are the subjects of current investigation.

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Supporting Information Available: Complete experimental procedures, lists of spectral data and elemental analyses for all of the new compounds (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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