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A Pauson–Khand-Type Reaction between Alkynes and Olefinic Aldehydes Catalyzed by Rhodium/Cobalt Heterobimetallic Nanoparticles: An Olefinic Aldehyde as an Olefin and CO Source

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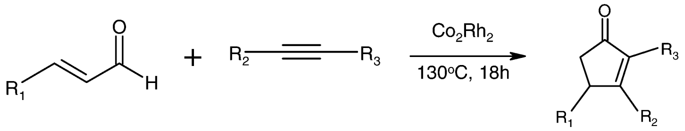
ABSTRACT



Co/Rh (Co:Rh = 2:2) heterobimetallic nanoparticles derived from $Co_2Rh_2(CO)_{12}$ react with alkynes and α,β-unsaturated aldehydes such as acrolein, crotonaldehyde, and cinnamic aldehyde and release products resulting from [2 + 2 + 1]cycloaddition of alkyne, carbon monoxide, and alkene. α,β-Unsaturated aldehydes act as a CO and alkene source. These reactions produce 2-substituted cyclopentenones.

The development of new processes that are simultaneously economically sustainable and environmentally responsible is a challenge for the twenty-first century.[1] In this respect, catalysis plays a central role in the development of environmentally safe and clean chemical processes. Thus, the design and development of new catalysts providing cleaner alternative synthetic pathways has attracted a lot of attention. The achievements of developing transition metal catalysts for multicomponent cycloaddition reactions have been especially remarkable.

The Pauson−Khand reaction (PKR) is a carbonylative cycloaddition reaction involving selective incorporation of three different molecules, i.e., an alkyne, an alkene, and carbon monoxide. The PKR has become one of the most convergent and versatile methods in the construction of five-membered rings.[2] However, increasing environmental awareness has made the use of carbon monoxide undesirable and created pressures to find an alternative process without using carbon monoxide or with a substitute for carbon monoxide. Recently, the use of decarbonylated CO from formates or aldehydes has been utilized in the PKR[3] and other transition metal-catalyzed reactions.[4] Substitution of one of the reaction components, carbon monoxide, by an aldehyde or a formate completely changes the reaction process. By extrapolation, if a substance could be used instead of both carbon monoxide and an alkene, a much simpler and cleaner process could be

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developed. Moreover, the application of cleaner heterogeneous catalysts with readily available starting materials would allow the minimization of inorganic as well as organic waste production.

Our own research interests have recently focused on the use of transition metal nanoparticles as heterogeneous catalysts in the PKR and related reactions.[1] They provide a clean and reusable catalytic system for the intra- and intermolecular PKR. Our recent study of the use of Co/Rh heterobimetallic nanoparticles as catalysts in the PKR in the presence of an aldehyde instead of carbon monoxide[6] gave us the novel idea to use unsaturated aldehydes as a source of CO and alkene. It has been well documented[7] that the reaction of aldehydes on metal surfaces releases hydrocarbons and carbon monoxide by decarbonylation. Thus, we studied the use of α,*β*-unsaturated aldehydes as a source of CO and alkene. In this paper, we report our preliminary results. We expect that this study will provide an environmentally clean, safe, and sustainable process.

Our recent study showed[6] that cobalt/rhodium (Co_2Rh_2) heterobimetallic nanoparticles derived from $Co_2Rh_2(CO)_{12}$ were an excellent catalyst in the Pauson−Khand-type reaction. During the present study, we also confirmed this previous work. Thus, Co_2Rh_2 was our catalyst of choice.

In the beginning, we screened organic substrates that could be easily decarbonylated by transition metals. α,*β*-Unsaturated aldehydes were screened using Co_2Rh_2 as a catalyst (Scheme 1 and Table 1).[8] As expected, a PKR product was obtained in reasonable to high yields with the concomitant formation of a coupling product in the case of acrolein. It is well-known[9] that the PKR alkenes attached to electron-withdrawing groups (all *π*-conjugating) react anomalously, giving 1,3-dienes, although some electron-deficient alkenes can be appropriate substances in the Pauson−Khand reaction under certain circumstances such as in the presence of a promoter.[10]

Scheme 1

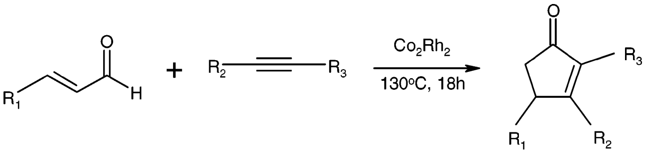

Table 1. Pauson−Khand-Type Reaction Catalyzed by Immobilized Co_2Rh_2 on Charcoal Using α,*β*-Unsaturated Aldehydes[a]

	substrate			
entry	R_1	R_2	R_3	yield (%)
1	H	H	Ph	48[b]
2	H	H	Ph	49[b]
3	H	H	Ph	60
4	H	H	Bu	51
5	H	H	C_5H_{11}	54
6	H	H	TMS	43
7	H	Ph	Ph	74
8	H	Me	Ph	57
9	CH_3	H	Ph	77
10	CH_3	H	Bu	70
11	CH_3	H	TMS	56
12	CH_3	Ph	Ph	71
13	Ph	H	Ph	75
14	Ph	H	Bu	71
15	Ph	H	TMS	69
16	Ph	Ph	Ph	70
17[c]	Ph	H	Ph	72
18[d]	Ph	H	Ph	73
19[d]	Ph	H	Ph	73
20[d]	Ph	H	Ph	70

[a] Isolated yields. Reaction conditions: aldehyde (15.8 mmol), alkyne (9.1 mmol), catalyst (0.029 mmol), and THF (5 mL). [b] THF solution (0.32 M). [c] Catalyst: recovered from entry 13. [d] Catalyst: recovered from the preceding entry.

Thus, it is very interesting that electron-deficient alkenes such as α,*β*-unsaturated aldehydes known as poor substrates for the PKR can be used as a source of CO and alkene. α,*β*-Unsaturated aldehydes such as acrolein are adsorbed in an η^4-(C,C,C,O) configuration and decarbonylate at lower temperatures than the aliphatic analogue, propanal.[7] Thus, α,*β*-unsaturated aldehydes have a dual function, slowly and continuously producing both olefin and CO in situ.

When acrolein (entries 1−8) was used as a CO and olefin source, the reaction yields (based on the enyne used) were moderate to high (43−74%), presumably due to the complex decomposition of acrolein on the surface of the nanoparticles. It is known[21] that the main thermal decomposition path of acrolein is via its decarbonylation to carbon monoxide and ethene and that small amounts of propene and ketene are also formed. However, a product derived from propene was not observed. In addition to the PKR product, a coupling product **B**, alkynyl aldehyde, was obtained in 7−13% yield, presumably due to an incomplete decarbonylation of acrolein.[8] The yield of the coupling product varied depending upon subtle changes in the reaction conditions. The yield of

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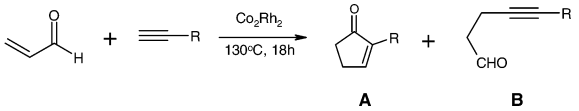
(8) See Supporting Information.



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the PKR product (entries 1−3) is moderately dependent upon the reaction conditions. When a 0.32 M solution of acrolein in THF was used, the yield was 48−49%. The use of a highly concentrated solution of acrolein in THF boosted the yield to 60%. However, when neat acrolein was used, the reaction was too complex to characterize. Treatment of butylacetylene (entry 4) afforded the expected product at a 51% yield. TMS-substituted acetylene (entry 5) gave 43% of the product, and the cyclohexyl-substituted alkyne (entry 6) gave 54% of the product. When diphenylacetylene (entry 7) was used, the yield of the product was 74%. Treatment of the unsymmetric internal alkyne (entry 8) afforded one isomer as the sole product.

In contrast to acrolein, crotonaldehyde thermally decomposes to carbon monoxide and propene.[12] The use of crotonaldehyde (entries 9−12) gives the expected cyclopentenones in high yields (56−77%). In most cases, the yields were improved compared to those obtained through the use of acrolein with acetylenes. Moreover, the reaction was quite regioselective with respect to alkenes and alkynes. As with the traditional PKR, terminal alkynes yielded predominantly 2-substituted ketones. It has been well-known[13] that neither terminal nor internal alkenes usually demonstrate meaningful regioselectivity in reaction with alkynes. Thus, the high regiocontrol is highly noteworthy.

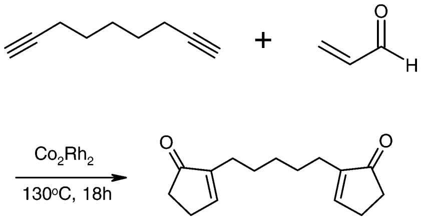
We next investigated the use of cinnamic aldehyde as a source of CO and styrene (entries 13−16). Styrene is known as a poor substrate in the Pauson−Khand reaction.[14] Thus, the use of styrene as an olefin substrate has been rare. To improve the yield of the PKR, DMSO has been added as a promoter.[15] However, under our reaction conditions, the expected PKR products were obtained in high yields (69−75%). Particularly, the yield for TMS-substituted acetylene was improved to 69%. Moreover, under our reaction conditions, no polymers derived from free styrenes were found. Therefore, use of these protocols might lead to slow generation of styrene.

When the reusability of the catalytic system was tested for the reaction between cinnamic aldehyde and phenylacetylene (entries 17−20), the catalytic activity of Co_2Rh_2 nanoparticles was retained for at least five runs; the maximum reusability has not been tested. Elemental analysis (by ICP-AES) of the reaction mixture after completion of the reaction showed that less than 0.1 ppm of cobalt and rhodium species were present.

When methacrolein was used, no reaction was observed, presumably due to the steric hindrance of the methyl group.

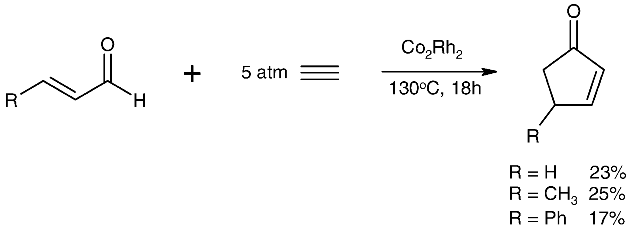
When 1,6-nonadiyne was reacted with acrolein, a double carbonylative cycloaddition product was obtained in a 70% yield (Scheme 2).[8]

Scheme 2



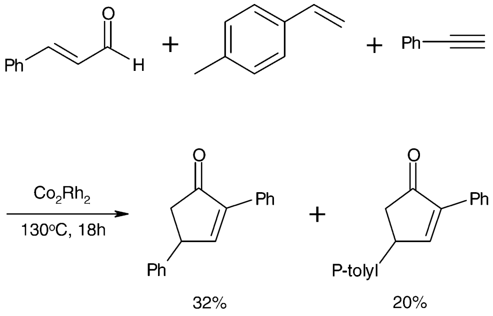
Treatment of acetylene with acrolein, crotonaldehyde, and cinnamic aldehyde afforded the corresponding cyclopentenones in 23, 25, and 17% yields, respectively (Scheme 3).[8]

Scheme 3



Recently, a rhodium-catalyzed synthesis of cyclopentenones via the intramolecular trans hydroacylation of alkynals was reported.[16] Thus, there could be other reaction pathways for our reaction. To confirm the reaction pathway, both cinnamaldehyde and substituted styrene were used as alkenes (Scheme 4). After workup, two Pauson−Khand products were isolated in 32 and 20% yields, respectively. Thus, the reaction follows the Pauson−Khand-type reaction.

Scheme 4



We attempted to develop an intramolecular version of the reaction (Scheme 5). However, after workup, the reactant was recovered. Unfortunately, the catalytic system was not effective for an intramolecular reaction. Further study will hopefully disclose a catalytic system that will be effective for an intramolecular reaction.

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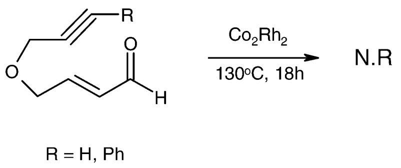
Scheme 5



Tremendous progress for the catalytic intramolecular PKR has been reported. However, the development of an efficient and general procedure for a catalytic intermolecular PKR lags far behind. We believe that our study provides conceptually a new model for a catalytic intermolecular PKR.

In conclusion, a new catalytic protocol has been developed for the formal [2 + 2 + 1]cycloaddition reaction of alkynes and α,*β*-unsaturated aldehydes to 2-substituted cyclopentenones. The procedure is characterized to be environmentally friendly because the transformation occurs in the absence of additives except for the catalyst, and the catalyst can be reused semipermanently without losing catalytic activity. Further studies are currently underway to extend the scope of this reaction and our associated asymmetric catalysis.

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Supporting Information Available: Detailed experimental procedures and compound characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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