Novel Dimerization, Alkoxylation, and Sulfidation of Olefins Catalyzed by $RuCl_3{\cdot}nH_2O$

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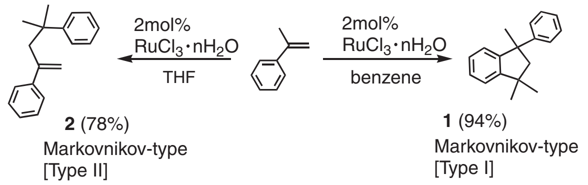
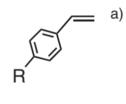
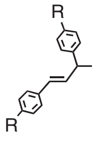
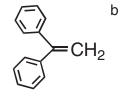
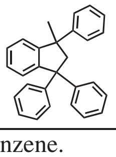
Novel ruthenium-catalyzed reactions that employ ruthenium trichloride *n*-hydrate ($RuCl_3{\cdot}nH_2O$) were investigated and dimerization, alkoxylation and sulfidation of olefins were noted. Adducts of Markovnikov type and anti-Markovnikov type were obtained in a stereospecific manner and in good yield, depending on the type of olefins used as the starting materials.

In recent years, various catalytic reactions of ruthenium compounds have been developed. Generally speaking, most of interest is focused on the unique carbon–carbon bond formation to contribute to organic synthesis. One of most common reactions is olefin metathesis. Since the discovery of Grubbs catalysts, those catalysts and their preparation have been the focus of many investigators.[1] First off, olefin metathesis was studied by using of simple olefins, and nowadays it expands to the use of dienes and enones.[2–5] More recently, it is reported that ruthenium catalyzes cyclization reactions of dienes, in which isomer selectivity is excellent.[3] Some other reactions are also investigated.[6–12] These reactions are interesting as atom-economy reaction to minimize waste production.[13] However, in many cases, the necessity and role of such metal ligands in reaction mechanisms are not clearly elucidated. Therefore, we have investigated novel ruthenium-catalyzed reactions employing $RuCl_3{\cdot}nH_2O$ as commercially available and more economical catalyst, instead of expensive or complex catalysts requiring some work-up for preparation, wherein we have gotten some interesting and significant information.

Our initial attempt at this investigation began with α-methylstyrene as a substrate. A mixture of α-methylstyrene (10 mmol) and 2 mol % $RuCl_3{\cdot}nH_2O$ in benzene (10 mL) was refluxed under N_2 for 24 h. The reaction mixture was monitored by TLC. After filtration and solvent-evaporation, the residue was purified by SiO_2 column chromatography to give α-methylstyrene dimer **1** in excellent yield. When the solvent was replaced with THF, dimer **2** was obtained in good yield (Scheme 1). Indan type dimers were named type I and all other dimers were named type II. Styrene derivatives were also allowed to react with $RuCl_3{\cdot}nH_2O$, and gave the corresponding dimers in THF. In benzene, however, it polymerized. Table 1 shows the results of dimerization of olefins. Type I and II dimers can be classified as Markovnikov-type adducts. The classification of Markovnikov-type and anti-Markovnikov-type is the same as that for addition of halogenated acid to olefins: The hydrogen of intermediate Ru–H bonds to carbon on which more hydrogens are present, and ruthenium bonds to carbon in which less hydrogens are present.

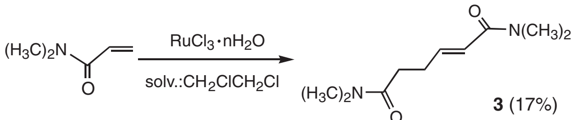
Table 1. Dimerization of olefins



Entry	Olefin	Dimer			Yield/%
1	 a)		type II	R=H CH_3 OCH_3 Cl	65 83 81 70
2	 b)		type I		64

solvent: a) THF b) benzene.

Ruthenium-catalyzed reactions of enones with olefins were studied and discussed on their selectivities.[5] We also examined the reaction of conjugate enones (Scheme 1). Although their reactivity was relatively low, compared with that of simple olefins, formation of anti-Markovnikov type dimer **3** was exclusively observed along with small amount of unidentified trimer.[14]



3 (17%)
anti-Markovnikov-type

Scheme 1. Dimerization of *N*,*N*-dimethylacrylamide.

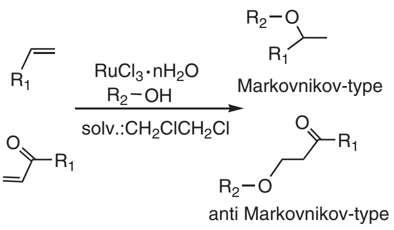
Alcohol is sometimes employed as a solvent for ruthenium-catalyzed reactions. Therefore we carried out the reactions in the presence of EtOH. The reactions gave alkoxylated adducts almost as sole product.

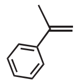
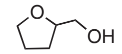
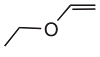
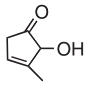
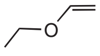
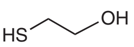
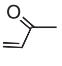
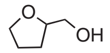
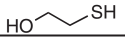
Table 2 shows the results of alkoxylation. Olefins reacted with primary alcohols and diols to give alkoxylated products in moderate to good yields. However, they did not react with tertiary alcohols or phenol. The products obtained in these reactions were Markovnikov-type, whereas products in the addition of alcohols to conjugate enones were anti-Markovnikov-type, which showing the coincidence with the result in olefin dimerization above mentioned.

Furthermore, a reaction of methyl vinyl ether with mercaptoethanol was conducted. As expected, sulfidated product was obtained in excellent yield. In case of Table 2, Entries 3 and 5, we obtained the products which olefins or enones reacted with both hydroxy group (–OH) and mercapto group (–SH). It is understandable that the reactivity of mercapto group (–SH) should be much greater than that of hydroxy group (–OH). When ethanditiol was used, not one but two mercapto groups reacted with olefins and enones.

We do not have any confirmed information on the initial ac-

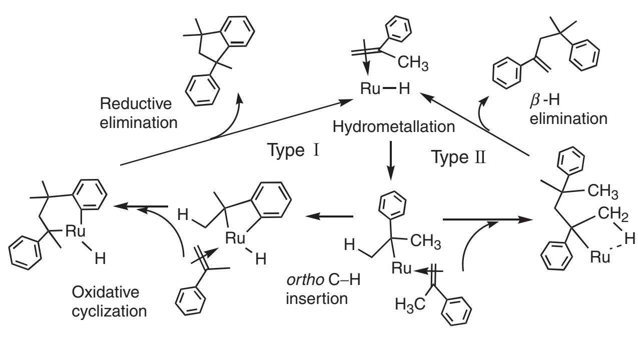
Table 2. Alkoxylation of olefins and enones



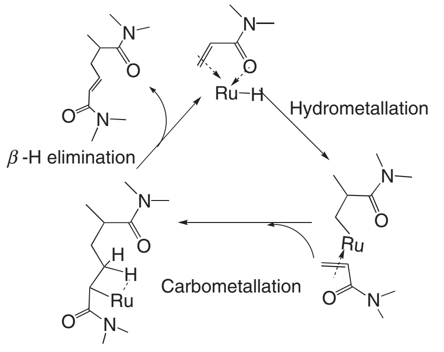
Entry	Olefin or enone	Alcohol	Yield/%
1			68
2			90 a)
3			99
4			65
5			90

a) solv.: THF

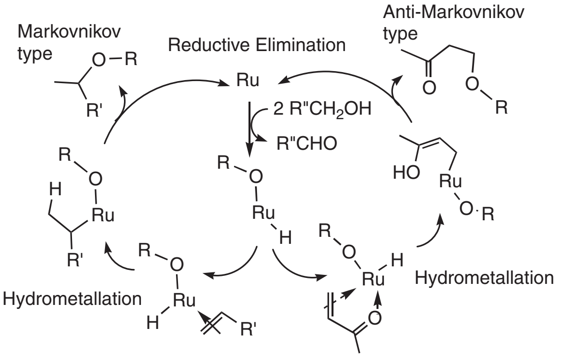
tive species of ruthenium catalyst in the present reactions. However, the formation of initial ruthenium hydride (Ru–H)[15] might be suggested from the structure of isolated products and from lots of precedence of similar reactions. The proposed reaction mechanism is outlined in Scheme 2–4. After the initial coordination of olefin onto ruthenium hydride species followed by 1,2-hydrometallation of Markovnikov-type, carbometallation of second olefin takes place, followed either by α-elimination of ruthenium (formation of type II products) or by oxidative cyclization into aromatic C–H bond (formation of type I product), as shown in Scheme 3. In the case of conjugate enones, anti-Markovnikov-type products are formed, because oxygen of the carbonyl group may affect the coordination of enones to Ru–H (Scheme 4). Scheme 4 shows a proposed mechanism of alkoxylation. Ruthenium hydride could be formed from alkoxylated ruthenium,[16,17] and subsequent hydrometallation and reductive elimination take place in the same manner as of dimerization. It is possible that sulfidation occurs in the same manner.



Scheme 2. Proposed catalytic cycle for styrene dimer.



Scheme 3. Proposed catalytic cycle for *N*,*N*-dimethyacrylamide dimer.



Scheme 4. Proposed catalytic cycle for alkoxylation.

In summary, we discovered novel catalytic reactions in which two kinds of olefin dimers, Markovnikov type and anti-Markovnikov type, were obtained regioselectively and in good yield. Alcohols and thiols also reacted with olefins and gave two types of adducts. The type of adduct obtained depended on the starting material. We are interested in reactions of olefins with optically active substances, which are currently in progress.

References and Notes

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14 Because of the low yield, the structure is not identified yet.
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