Ruthenium Complex-catalyzed Selective Syntheses of 3,5-Dienoic Acid Derivatives by Coupling of 1,3-Dienes or Allylic Carbonates with Acrylic Compounds

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Abstract: Ru(cod)(cot) catalyzes highly selective codimerization of 1,3-dienes with acrylic compounds and first linear coupling reaction of allylic carbonates with the acrylic amide to give 3,5-dienoic acid derivatives; cod = cycloocta-1,5-diene, cot = cycloocta-1,3,5-triene.

Ruthenium complex-catalyzed highly selective carbon-carbon bond forming reactions involving the codimerization of olefins and acetylenes have been developed.¹ Ru(cod)(cot) has turned out to be an excellent catalyst for these reactions.^{1,2} On the other hand, conjugated dienes are of considerable importance in organic chemistry in themselves,³ as well as for their utilization in the Diels-Alder reaction. We now report the highly selective syntheses of 3,5-dienoic acid derivatives (e.g. (A) in eq. (1)) by catalytic codimerization of 1,3-dienes with acrylic compounds. The first example of a linear coupling reaction of allylic compounds with these olefins⁴ (eq. 2) is also described. In both reactions, a π -allylruthenium complex would be a common intermediate.



Representative reaction procedures are as follows. To a two necked 20 ml flask with a reflux condenser and a rubber septum was added Ru(cod)(cot) (0.10 mmol, 0.031 g), 1,3-diene (10.0 mmol), N,N-dimethylacrylamide (5.0 mmol, 0.51 ml) and N-methylpiperidine (5.0 mmol, 0.61 ml) under an argon atmosphere. The mixture was stirred magnetically at 80 °C for 0.5~9.0 h. The products were separated from the reaction mixtures by Kugelrohr distillation.

Stereochemistry of the products was determined by means of NMR spectra (1 H, 13 C, H-H COSY, DEPT and DNOE). The reaction of 1,3-butadiene was performed in a heavy-walled glass tube. The reactions of allylic carbonates with *N*,*N*-dimethylacrylamide were carried out in a similar manner.



Table 1 Ru(cod)(cot)-catalyzed codimerization of dienes with acrylic compounds.^a

^a Diene 10 mmol, olefin 5 mmol, Ru(cod)(cot) 0.2 mmol and N-methylpiperidine 5 mmol were used under argon at 80°C. ^bYields by Kugelrohr distillation. ^cOnly conjugated dienes were detected, see text. ^d A mixture of cis- and trans-1,3-pentadiene (50:50) was used. ^e At 100°C.

1,3-Butadiene, isoprene, 1,3-pentadiene and 2,3-dimethylbutadiene reacted with acrylic compounds in the presence of a catalytic amount of Ru(cod)(cot) to give the corresponding linear codimers, 3,5-dienoic acid derivatives, in high yields. Representative results are summarized in Table 1. The reaction of 1,3-butadiene with N,N-dimethylacrylamide gave (3E,5Z)-N,N-dimethyl-3,5-heptadienamide (conjugated diene, A) as a major product (selectivity 90%) and (2E,5Z)-N,N-dimethyl-2,5-heptadienamide (skipped diene B) (Run 1). The reaction of isoprene with N,N-dimethylacrylamide gave two 3,5-dienamides, (3E)-N,N-dimethyl-6-methyl-3,5-heptadienamide and its regioisomer (3E,5Z)-N,N-dimethyl-5-methyl-3,5-heptadienamide (55:45) in 67% yield (Run 3). No skipped diene was detected. 2,3-Dimethylbutadiene reacted with N,N-dimethylacrylamide to give the corresponding codimers in 81% yield and the ratio of the conjugated and skipped dienamides was 90:10 (Run 7). In the absence of the Ru catalyst, Diels-Alder adducts of 1,3-dienes and N,N-dimethylacrylamide were obtained.

It has been reported that the linear codimerization or co-oligomerization of methyl acrylate with butadiene is catalyzed by Fe(acac)3-Sb(C6H5)3-Al(C2H5)3,5 cobalt,6,7 and nickel complexes,⁸ but yields and/or selectivity for 3,5-dienoic acid derivatives were low.⁵⁻⁸

Since the stereochemistry of (5Z)in the products in Run 1 strongly suggested that the reaction proceeds via a π -allylruthenium complex, reactions of allylic compounds with N, N-dimethylacrylamide were performed. Results are shown in Table 2. The reactions of crotyl methyl carbonate and 1-methyl-2-propenyl methyl carbonate gave the corresponding (5Z)-3,5-dienamides in 42~35% yield (GLC yields were ca. 60%). 3-Methyl-2-butenyl methyl carbonate reacted with N,N- dimethylTable 2 Ru(cod)(cot)-catalyzed coupling reactions of allylic carbonates with *N*,*N*-dimethylacrylamide.^a



^a Carbonate 2.5 mmol, N,N-Dimethylacrylamide 5 mmol, Ru(cod)(cot) 4 mol%, N-Methylpiperidine 2.5 mmol,80°C, 5 hr under Ar. ^bYield by Kugelrohr distillation (Figures in the parentheses are GLC yield). ^cN-Methylpiperidine was not added.

acrylamide to afford two isomers of 3,5-dienamide, **a** and **b** (Table 2, Run 12, a/b = 55/45), which are the same products in the reaction of isoprene with N,N-dimethyl-acrylamide (Table 1, Run 3). Although the yields of these products are not high, to our knowledge, this reaction is the first example of the catalytic linear coupling of allylic compounds with olefins.⁴ Ru(cod)(cot) is the best catalyst in these reactions. Ru3(CO)12 and RuCl3•nH2O gave the products in low yields and Pd(PPh3)4, RhCl(PPh3)3 and Mo(CO)6 showed no catalytic activity.

A possible mechanism of the present reactions is shown in Scheme 1. In the reaction of 1,3-butadiene, η^4 -coordination of 1,3-butadiene to a hydridoruthenium species such as (5) would give (1) (path A) and the addition of the metal hydride would afford an *anti*-methyl(π -allyl)ruthenium complex (2). Insertion of acrylic acid derivative into the less hindered carbon-ruthenium bond gives (3). β -Hydride elimination and isomerization of the olefinic group gives the 3,5-dienoic acid derivatives. The stereochemistry of (5Z) in the product is determined by the step from (1) to (2).

In the reaction of allylic carbonates, e.g., crotyl methyl carbonate oxidatively adds to a Ru[0] complex to give a σ -allyl-[Ru] complex (6) with evolution of CO₂ (path B). Then an *anti*-methyl(π -allyl)ruthenium complex (2) would be formed via a η^4 -butadiene ruthenium complex (1) by the same mechanism in the reaction of 1,3-butadiene. The facts that (5*E*) isomer was not detected and the reaction of cinnamyl methyl carbonate was slow (Run 13) show that there is an unclarified reason that interferes the direct insertion of olefin into the σ -allyl-[Ru] bond in the complex (6). Further efforts are being devoted to clarify the mechanism and the scope of these reactions.

In conclusion, a method of selective preparation of 3,5-dienoic acid derivatives was established.



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