*Organometallics* **1994,** *13,* 3758−3760

# Tail-to-Tail Dimerization Reaction of Acrolein

Yuji Ohgomori,* Shuji Ichikawa, and Naoko Sumitani

*Tsukuba Research Center, Mitsubishi Petrochemical Co. Ltd.,*
*8-3-1 Chuou, Ami, Ibaraki 300-03, Japan*

*Received May 16, 1994*[⊗]

*Summary: Ru(0) complexes such as Ru(cyclooctadiene)(arene) are shown to catalyze tail-to-tail dimerization of acrolein to form (E)-hex-2-ene-1,6-dial. The trimer (E)-6-hydroxy-5-formyl-oct-2,7-dienal is also formed, which easily polymerizes to acrolein oligomers. The coordinatively unsaturated Ru(COD)(acrolein)$_n$ species appears to play a key role in the catalytic activity.*

For many years, the transition-metal-catalyzed tail-to-tail dimerization reaction of functionalized alkenes has caused much attention in organic chemistry and in industry. It has been shown that acrylates,[1] acrylonitrile,[2] and methyl vinyl ketone[3] are dimerized by rhodium, palladium, or ruthenium catalysts to form linear bifunctional compounds, in which dihydromuconates and 1,4-dicyano-2-butenes are useful precursors to Nylon 66. Although acrolein (ACR) is classified in the same class as the above substituted electron-deficient alkenes, there have been no reports that it underogoes a tail-to-tail dimerization reaction to form hex-2-ene-1,6-dial, which is potentially important intermediate for both hexamethylenediamine and adipic acid. We report herein the first example of the title reaction catalyzed by zero valent ruthenium complexes.

Heating ACR with 0.5 mol % of ($\eta^4$-cyclooctadiene)($\eta^6$-cyclooctatriene)ruthenium (**1**)[4] at 70 °C under $N_2$ for 3 h afforded an orange-yellow homogeneous solution. The pure product, isolated by Kugelrohr distillation, was identified as (*E*)-hex-2-ene-1,6-dial ((*E*)-dimer) by spectroscopic evidence;[5] the spectra were identical with those for the authentic sample.[6] Gas chromatographic and GC/MS analyses indicated formation of very small amounts of (*Z*)-dimer (*E*/*Z* > 96/4) and propionaldehyde, along with considerable amounts of ACR trimer. Gel permeation chromatography suggested that large quantities of ACR were converted into unidentified oligomers having molecular weights less than 1200. Other substituted alkenes, such as acrolein diethyl acetal, methyl acrylate, methyl methacrylate, acrylonitrile, and methyl vinyl ketone, were not dimerized by our ruthenium catalysts under these conditions. Thus, the Ru(0) catalysts were found to be effective only for ACR dimerization. Catalytic activities of Ru(diene)(arene)-type complexes were then examined extensively, and the results are summarized in Table 1 together with results for **1**. Ru(COD)(arene) complexes[7] provide more active and selective catalysts toward (*E*)-dimer formation than **1**. When 5 mol % of **2** and 12.5 wt % of ACR in dioxane solvent were used, selectivity for (*E*)-dimer increased to 68% (run 3), and GPC analysis of the reaction solution showed that the oligomer formation was remarkably suppressed. The concentrations of both catalyst and ACR are suitable for suppression of the trimerization.

We have examined changes in product distribution with changes in reaction time. ACR was heated to 70 °C with 0.2 mol % of **2** for 30 min. The ACR conversion reached 13.1%, and products were mainly composed of (*E*)-dimer (26%), trimer (48%), and oligomers (26%). This product distribution changed to (*E*)-dimer (25%), trimer (5%), and oligomers (70%) after 3 h at an ACR conversion of 26.8%.[8] Selectivity for (*E*)-dimer was almost constant throughout the reaction period. However, the trimer, which was the major product after 30 min, oligomerized almost entirely into a complex mixture within an additional 2.5 h. This suggests that the trimer is a key intermediate to the oligomers in this reaction system. We have tried to isolate and characterize the trimer. A reaction of ACR was conducted with 0.05 mol % of **2** at 70 °C for 30 min; then the remaining ACR was distilled off by a half-volume under reduced pressure at −20 °C. A white cottonlike solid,[9] was precipitated by cooling the resultant solution to −78 °C; then the solid was removed by filtration. The filtrate was extracted with pentane several times to remove the remaining ACR. The product was assigned as (*E*)-6-hydroxy-5-formyl-oct-2,7-dienal by spectroscopic analyses.[10] This trimer is unstable and oligomerizes over several days even in the freezer. The highly labile complex **9** afforded the (*E*)-dimer at high rates. However, large quantities of trimer and oligomers were also formed (compare runs 3 and 14).[11] When the reaction using **3** was carried out under $H_2$, the rate and selectivity for (*E*)-dimer increased. Under just 1.0 atm of $H_2$ (compare runs 6 and 7), the selectivity for dimer

---

[⊗] Abstract published in *Advance ACS Abstracts,* September 1, 1994.

(1) Pd: Nugent, W. A.; Hobbs, F. W. *J. Org. Chem.* **1983**, *48*, 5364−5366. Ru: McKinney, R. J.; Colton, M. C. *Organometallics* **1986**, *5*, 1080−1085. Rh: Brookhart, M.; Sabo-Etienne, S. *J. Am. Chem. Soc.* **1991**, *113*, 2777−2779.

(2) Misono, A.; Uchida, Y.; Hidai, M.; Inomata, I. *J. Chem. Soc. D* **1968**, 704−705.

(3) Kovalev, I. P.; Strelenko, Y. A.; Ignatenko, A. V.; Vinogradov, M. G.; Nikishin, G. I. *J. Organomet. Chem.* **1991**, *420*, 125−133.

(4) Itoh, K.; Nagashima, H.; Ohshima, T.; Oshima, N.; Nishiyama, H. *J. Organomet. Chem.* **1984**, *272*, 179−188.

(5) MS (EI; *m/z* (relative intensity)): 94 ($M^+$), 83 (100), 68 (58), 55 (67), 39 (35), 29 (51). MS (CI; *m/z* (relative intensity): 113 ($MH^+$, 100), 95 (8), 85 (3). $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 9.82 (1H, s), 9.50 (1H, d, $J$ = 7.6 Hz), 6.89 (1H, dt, $J$ = 15.6, 6.4), 6.13 (1H, ddt, $J$ = 15.6, 8;1), 2.70 (2H, m) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 24.82, 41.46, 133.33, 156.01, 193.70, 200.15 ppm.

(6) Hudlicky, T.; Luna, H.; Barbieri, G.; Kwart, L. *J. Am. Chem. Soc.* **1988**, *110*, 4735−4731.

(7) Pertici, P.; Simonelli, G. P.; Vitulli, G. *J. Chem. Soc., Chem. Commun.* **1977**, 132−133.

(8) Conversion of ACR and composition of the products were determined by GC and GPC, respectively. Relative area percentages of the chromatogram are given in parentheses.

(9) Attempts to identify this compound failed because of a high lack of stability. The compound converted into a dark brown oil by warming to room temperature; $^1$H NMR spectra of this oil were similar to those for the trimer. We suppose this compound to orginate from catalysts.

(10) Diastereomer mixture (erythro:threo = 6:4). MS (EI; *m/z* (relative intensity)): 168 ($M^+$), 151 (7), 113 (3), 71 (100), 41 (65). MS (CI; *m/z* (relative intensity)): 169 ($MH^+$, 24), 113 (100), 71 (63). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 9.74 (1H, s), 9.44 (1H, s), 6.91 (1H, m), 6.10 (1H, dd, $J$ = 15. 7, 7.8 Hz), 5.94 (1H, m), 5.35 (1H, dd, $J$ = 17.1, 1.6), 5.22 (1H, dd, $J$ = 10.4, 1.5), 4.62 and 4.40 (1H, br s × 2), 4.28 and 4.24 (1H, br s × 2), 2.62 (3H, m) ppm. $^{13}$C NMR ($CDCl_3$, 75 MHz): erythro, $\delta$ 203.7, 194.8, 157.7, 140.2, 135.2, 116.9, 72.1, 56.9, 28.1 ppm; threo, $\delta$ 203.7, 195.7, 156.8, 140.7, 135.5, 116.9, 73.1, 56.8, 30.0 ppm.

0276-7333/94/2313-3758$04.50/0

**Table 1. Catalytic Dimerization of Acrolein (ACR) by Ruthenium Complexes[a]**

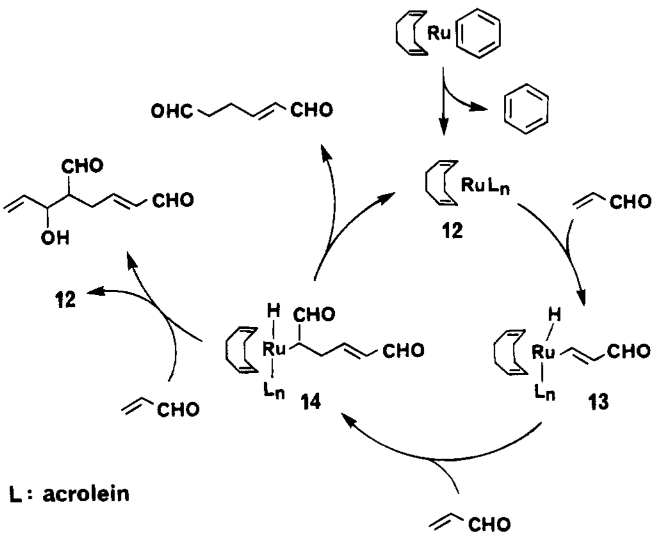
| run no. | Ru complex[b] | compd no. | amt of ACR/Ru/equiv | time/h | conversn/%[c] | selectn/%[c,d] | TON[c] |
|---|---|---|---|---|---|---|---|
| 1 | Ru(COD)(COT) | **1** | 197 | 3 | 75.6 | 24.2 | 18 |
| 2 | Ru(COD)($C_6H_6$) | **2** | 196 | 3 | 81.7 | 30.7 | 25 |
| 3[e] | | **2** | 20 | 7 | 88.0[f] | 68.0[f] | 6[f] |
| 4 | | **2** | 531 | 3 | 44.2 | 32.2 | 44 |
| | | | | 10 | 47.5 | 31.6 | 43 |
| 5[g] | | **2** | 550 | 12 | 67.1 | 35.8 | 66 |
| | | | | 27 | 78.7 | 34.3 | 74 |
| 6 | Ru(COD)($C_6H_5$-Me) | **3** | 196 | 3 | 74.0 | 27.6 | 20 |
| 7[h] | | **3** | 228 | 1 | 70.6 | 37.4 | 30 |
| 8[i] | | **3** | 209 | 1 | 92.8 | 38.3 | 37 |
| 9 | Ru(COD)($C_6H_4$-1,4-$Me_2$) | **4** | 219 | 3 | 70.6 | 29.9 | 23 |
| 10 | Ru(COD)($C_6H_4$-1-Me-4-*i*-Pr) | **5** | 193 | 3 | 64.5 | 28.0 | 17 |
| 11 | Ru(COD)($C_6H_5$-OMe) | **6** | 186 | 3 | 92.0 | 29.6 | 25 |
| 12 | Ru(COD)($C_6H_5$-COMe) | **7** | 197 | 3 | 93.8 | 31.1 | 29 |
| 13 | Ru(COD)($C_6H_5$-Cl) | **8** | 522 | 3 | 40.3 | 18.0 | 19 |
| 14 | Ru(COD)($C_6H_4$-1,3-$F_2$)[j] | **9** | 20 | 0.25 | 73.6[f] | 48.3[f] | 4[f] |
| 15 | Ru(CHD)($C_6H_6$) | **10** | 188 | 3 | 9.1 | 6.4 | 1 |
| 16 | Ru(NBD)($C_6H_4$-1-Me-4-*i*-Pr) | **11** | 479 | 8 | 12.5 | 6.3 | 2 |

[a] Reaction conditions: *T*, 70 °C; ACR used contains 0.1% hydroquinone as stabilizer. [b] Abbreviations: COD, cycloocta-1,5-diene; CHD, cycloocta-1,3-diene; NBD, norborna-2,5-diene. [c] Determined by GC. [d] 2(mol of dimer)(mol of ACR, converted)$^{-1}$ × 100. [e] 12.5 wt % ACR in dioxane-$d_8$ was used. [f] Determined by $^1$H NMR. [g] 50 wt % ACR in COD was used. [h] Under 1 atm of $H_2$. [i] Under 5 atm of $H_2$. [j] 17.8 wt % ACR in dioxane-$d_8$ was used. Trimer was obtained in a TON of 1.8.

increased by ca. 37%. Increasing the $H_2$ pressure to 5 atm led to only a minor change in the selectivity over that at 1 atm (run 8). In this case, very slow $H_2$ consumption was observed, and only propionaldehyde was obtained as an assignable hydrogenated product in ca. 2% selectivity. The role of $H_2$ is not yet clear. On the other hand, $H_2$ consumption was observed under 40 atm, and the rate of (*E*)-dimer formation decreased (turnover number (TON) = 7), while (*E*)-3-hydroxy-2-methylpent-4-enal was mainly found in the volatile products and was purified by Kugelrohr distillation.[12]

The catalyst deactivation was observed at an early stage of TON = 44 using a low catalyst concentration (run 4). A $^1$H NMR analysis of the reaction solution showed that COD and benzene ligands were gradually liberated from ruthenium during the reaction, and the above ligands were completely dissociated from the deactivated catalyst.[13] Attempts to isolate metal complexes from the deactivated catalyst failed. We also could not detect the deactivated species by NMR spectroscopy even at low temperatures (room temperature to −50 °C) and under a variety of reaction conditions. Complexes **10** and **11**, in which the diene ligand is not COD, afforded low reaction rates. The cycloocta-1,5-diene ligand appears to play an important role in the catalytic activity. It is noted that the ACR consumption and TON increased in COD as the solvent (compare runs 4 and 5), and the TON reached 74 at 78.7% conversion after 27 h (run 5). The ACR consumption in COD was correlated with the second-order reaction with respect to ACR concentration: $-d[ACR]/dt = k_{obs}[ACR]^2$; $k_{obs} = 0.218$ L·mol$^{-1}$·h$^{-1}$.[14] This rate is almost twice as large as that in the absence of COD (where the initial rate constant is 0.119). In this context, we have measured $^1$H NMR spectra of the reaction solutions composed of **2**/ACR/COD/dioxane-$d_8$ at 70 °C, and the spectra were compared with those obtained in the absence of COD.[15] The initial rate of ACR consumption using COD is almost 5 times as high as the rate in the absence of COD. Dissociation of the benzene ligand was observed during the reaction time in all cases. The COD ligand does not dissociate from ruthenium after 15 h in the presence of COD solvent, while 25% of the COD ligand dissociates during the same time period in the absence of COD solvent. The solvent effect of COD may be explained by suppression of the ligand dissociation process to stabilize the Ru(COD)$L_n$ species, which apparently plays an important role in the catalytic activity.

**Scheme 1**



A possible reaction pathway is shown in Scheme 1. Oxidative addition of a 3-H—C bond of ACR to the coordinatively unsaturated ruthenium species **12** takes

---

(11) $^1$H NMR analysis of the reaction solution at 70 °C showed rapid dissociation of the $C_6H_4$-1,3-$F_2$ ligand of **9** along with formation of the dimer and trimer.

(12) Diastereomer mixture. MS (EI; *m/z* (relative intensity)): 96 ($M^+ - H_2O$, 1), 68 (10), 57 (100), 41 (14), 29 (36). $^1$H NMR ($CDCl_3$, 300 MHz): δ 9.48 (1H, s), 5.95–5.65 (1H, m), 5.35–5.10 (2H, m), 4.25–4.15 (1H, m), 1.95 (1H, m), 0.78 and 0.77 (3H, d × 2, *J* = 7 Hz) ppm. Chemical shifts are similar to those for (*E*)-3-hydroxy-2-methylpent-4-enoic acid: Heathcock, C. H.; Jarvi, E. *Tetrahedron Lett.* **1982**, *23*, 2825–2828. $^{13}$C NMR ($CDCl_3$, 75 MHz): erythro, δ 203.9, 138.9, 115.4, 72.0, 51.7, 8.0 ppm; threo, δ 203.9, 139.9, 116.6, 74.3, 52.1, 10.8 ppm.

(13) $^1$H NMR (dioxane-$d_8$, 300 MHz): Ru(COD)($C_6H_6$) δ 5.30; Ru(*COD*)($C_6H_6$) δ 2.10–1.90 (multiplet); free $C_6H_6$, δ 7.35; free COD, δ 5.52, 2.32 ppm.

(14) A linear correlation was found between $[ACR]^{-1}$ and reaction time (39 h; *r* = 0.999).

(15) Experimental conditions with COD (without COD): ACR/Ru = 21 (26), [ACR] = 16.6 (19.9) vol %, COD/dioxane-$d_8$ = 1 vol ratio.

place to form **13**. (*E*)-dimer is obtained through the reaction of a second ACR molecule to form **14**, followed by reductive elimination regenerating **12**. Intermediates of the trimer have not yet been clarified. However, it is possible that **14** reacts with the third ACR molecule via an aldol-type reaction to form the trimer. (*E*)-dimer apparently is not the intermediate to the trimer.[16] The trimer easily oligomerizes into a complex mixture. When the reaction is carried out under high pressures of $H_2$, ruthenium dihydride complexes are probably formed, which will subsequently react with ACR to form $(ACR)_n(COD)RuHCH(CH_3)CHO$. This appears to react with the second ACR molecule to form (*E*)-3-hydroxy-2-methylpent-4-enal in a manner similar to the trimer formation through the reaction of **14** and ACR.

**Acknowledgment.** Thanks are due to Prof. Kenji Itoh, Toyohashi University of Technology, for fruitful discussions, and approval to present this work by Mitsubishi Petrochemical Co. is gratefully acknowledged.

OM940372E

---

[16] Selectivity for (*E*)-dimer is almost constant during the reaction period (see text). The dimerization reaction with initial addition of the (*E*)-dimer showed that TON's of (*E*)-dimer and trimer were comparable to those for the experiment without adding (*E*)-dimer.