CHEMISTRY LETTERS, pp. 683-684, 1988.

Double C-H Activation. Dimerization of Esters Catalyzed by $RhCl(CO)(PMe_3)_2$ under Irradiation

Toshiyasu SAKAKURA, Touru SODEYAMA, and Masato TANAKA*
National Chemical Laboratory for Industry, Tsukuba, Ibaraki 305

Dehydrogenation of methyl propionate yielded methyl 4-propionyloxybutyrate (head-to-tail dimer) by photocatalysis in the presence of $RhCl(CO)(PMe_3)_2$ at room temperature. Methyl acrylate is presumed to be an intermediate.

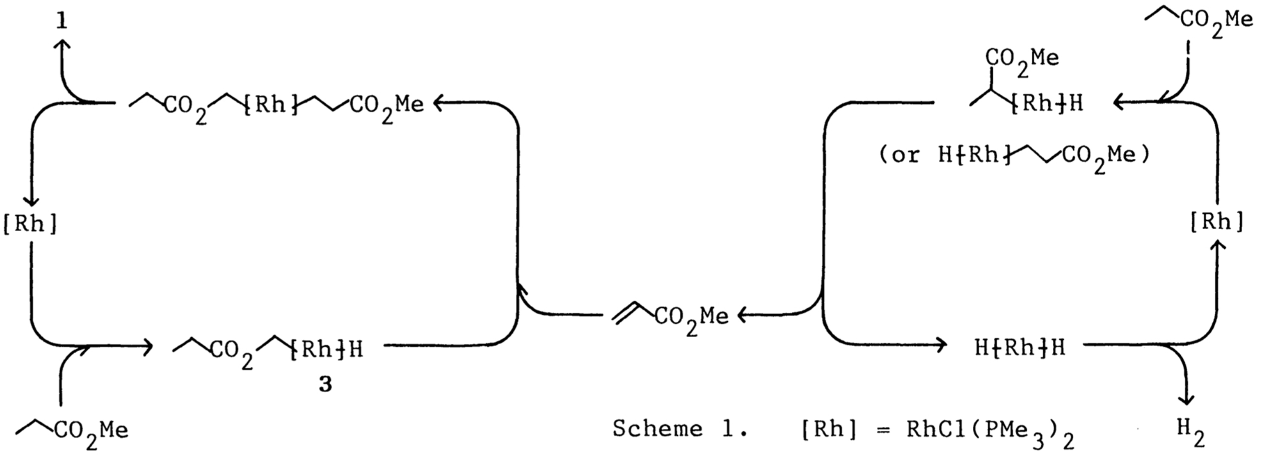
We have already reported various catalytic transformations of hydrocarbons in the presence of $RhCl(CO)(PMe_3)_2$ under irradiation.[1-9] One of particular value among them is the dehydrogenation to produce olefins and biaryls from alkanes[9] and arenes,[5] respectively. Since it appeared useful to apply this dehydrogenation to functionalized substrates in order to synthesize bifunctional products, we examined the reaction of esters.

A 0.7 mM solution of $RhCl(CO)(PMe_3)_2$ in methyl propionate (30 cm^3) was irradiated by a 100 W high pressure mercury lamp (UVL-100HA, Riko) through a Pyrex flask at room temperature for 6 h. The results are summarized in Eq. 1.

$$\begin{array}{l} CH_3CH_2CO_2CH_3 \xrightarrow[\text{cat. RhCl(CO)(PMe}_3)_2]{h\nu,\ 6\ \text{h, room temp}} \\ \qquad CH_3CH_2CO_2(CH_2)_3CO_2CH_3 \quad + \quad H_3COCO(CH_2)_4CO_2CH_3 \\ \qquad\qquad 2035\%/\text{Rh} \quad \mathbf{1} \qquad\qquad\qquad 116\%/\text{Rh} \quad \mathbf{2} \end{array} \qquad (1)$$

Main product was methyl 4-propionyloxybutyrate (**1**) (head-to-tail dimer). A small amount of dimethyl adipate (**2**) (head-to-head dimer) was also formed. The yields of methyl-branched isomers were less than 50%/Rh for each dimer. Distillation of the reaction mixture gave an almost pure sample of **1**. Very little residue observed after the distillation denied the formation of polymers. The structure of **1** was confirmed by the comparison of NMR, IR, and MS spectra with an authentic sample synthesized from γ-butyrolactone.

A tentative reaction mechanism is illustrated in Scheme 1. Although methyl acrylate was not detected in the reaction of Eq. 1 (less than 100%/Rh), the formation of **1** is presumably due to the addition of C-H bond of methyl propionate to methyl acrylate formed as an initial intermediate through dehydrogenation via C-H activation of another molecule of methyl propionate (double C-H activation). As a matter of fact, the reaction of methyl acetate with methyl acrylate under the same conditions yielded methyl 4-acetoxybutyrate (**4**) and dimethyl glutarate (**5**) (Eq. 2). The high **5**/**4** ratio in Eq. 2 as compared with **2**/**1** ratio is presumably ascribed to the absence of β-hydride elimination in the reaction of methyl acetate. The insertion of methyl acrylate seems to occur at the rhodium-hydrogen bond rather than the rhodium-carbon one; otherwise unsaturated esters also should have been formed via β-hydride elimination of the intermediate.[10] The addition of the radical formed from **3** to methyl acrylate is another feasible mechanism to afford the dimer.



Scheme 1. [Rh] = $\mathrm{RhCl(PMe_3)_2}$

$$\mathrm{AcOCH_3} \;+\; \mathrm{CH_2{=}CHCO_2CH_3} \xrightarrow[\mathrm{Rh}]{h\nu} \mathrm{AcO(CH_2)_3CO_2CH_3} \;+\; \mathrm{H_3COCO(CH_2)_3CO_2CH_3} \qquad (2)$$

$$(v/v = 29/1) \qquad 1191\%/\mathrm{Rh} \;\; \mathbf{4} \qquad 718\%/\mathrm{Rh} \;\; \mathbf{5}$$

In summary, this paper showed the possibility to synthesize bifunctional compounds through the intermolecular dehydrogenative coupling of C-H bonds. Further extensions of the reaction to various substrates are now under investigation.

References

1) T. Sakakura and M. Tanaka, Chem. Lett., 1987, 249.
2) T. Sakakura and M. Tanaka, J. Chem. Soc., Chem. Commun., 1987, 758.
3) T. Sakakura, T. Hayashi, and M. Tanaka, Chem. Lett., 1987, 859.
4) T. Sakakura and M. Tanaka, Chem. Lett., 1987, 1113.
5) T. Sakakura, T. Sodeyama, Y. Tokunaga, and M. Tanaka, Chem. Lett., 1987, 2211.
6) M. Tanaka, T. Sakakura, Y. Tokunaga, and T. Sodeyama, Chem. Lett., 1987, 2373.
7) T. Sakakura, Y. Tokunaga, T. Sodeyama, and M. Tanaka, Chem. Lett., 1987, 2375.
8) T. Sakakura, K. Sasaki, Y. Tokunaga, K. Wada, and M. Tanaka, Chem. Lett., 1988, 155.
9) T. Sakakura, T. Sodeyama, Y. Tokunaga, and M. Tanaka, Chem. Lett., 1988, 263.
10) The insertion of C=C double bonds to C-H bonds of hydrocarbons resulting in the formation of olefinic compounds will be published separately.

(Received February 4, 1988)