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

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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.

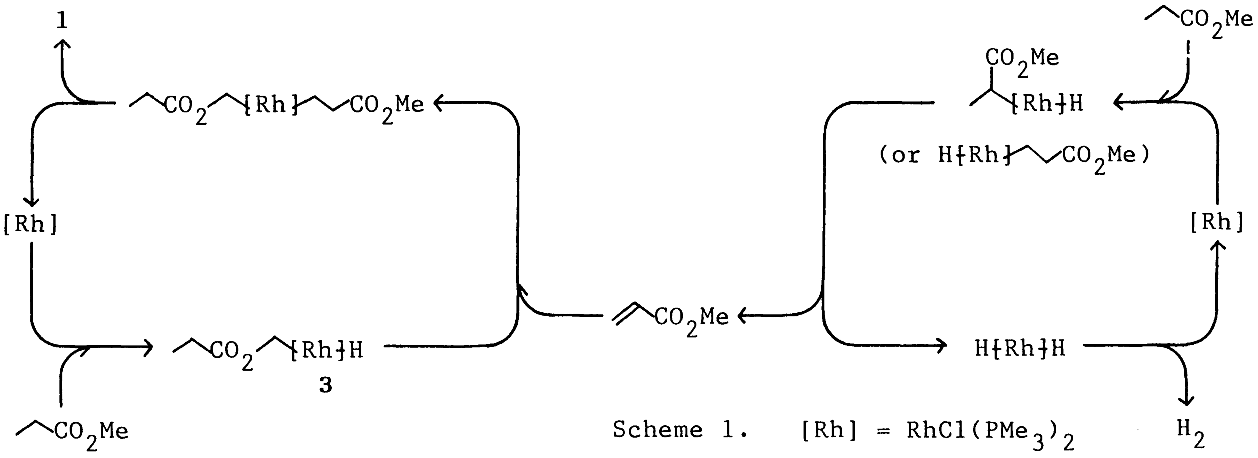
We have already reported various catalytic transformations of hydrocarbons in the presence of $RhCl(CO)(PMe_3)_2$ under irradiation.$^{1-9)}$ One of particular value among them is the dehydrogenation to produce olefins and biaryls from alkanes$^{9)}$ and arenes,$^{5)}$ respectively. Since it appeared 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.

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

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] = $RhCl(PMe_3)_2$

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

(v/v = 29/1) 1191%/Rh 4 718%/Rh 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.

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