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Catalytic C-H Activation of Olefins. Dehydrogenative Dimerization to Dienes Catalyzed by $RhCl(CO)(PMe_3)_2$ under Irradiation

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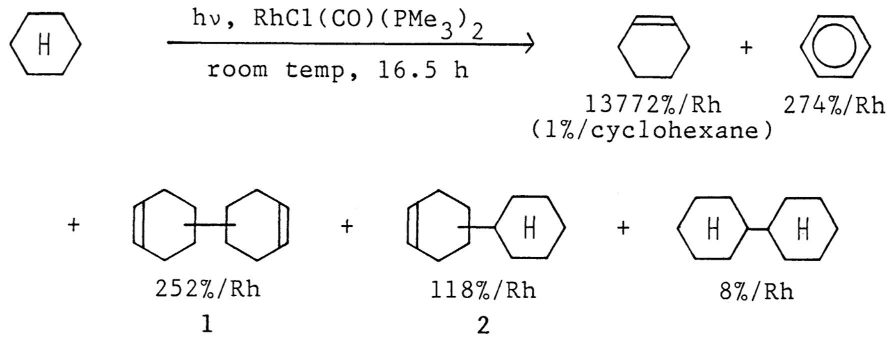
Dienes were formed by the dehydrogenative coupling of olefins via the photocatalyzed C-H activation in the presence of $RhCl(CO)(PMe_3)_2$ at an ambient temperature.

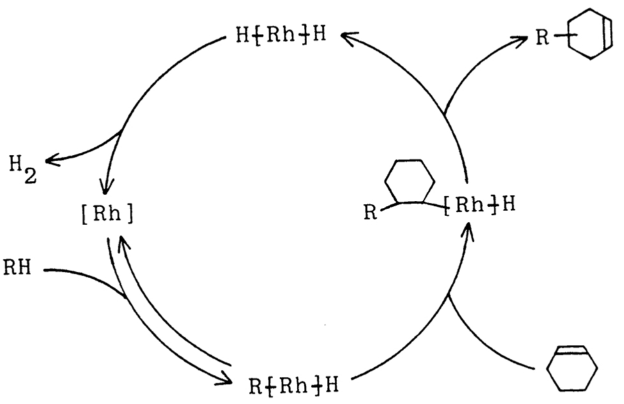
We have recently reported a wide range of transformations of alkanes or arenes catalyzed by $RhCl(CO)(PMe_3)_2$ under irradiation; carbonylation,1) isocyanide insertion,2) silylation,3) dehydrogenation,4) and olefin insertion.5) The key step of these reactions is considered to be an oxidative addition of C-H bonds of alkanes or arenes to $RhCl(PMe_3)_2$. The oxidative addition of sp^2 or allylic sp^3 C-H bonds of alkenes, however, has not yet been utilized in this catalytic system. We now wish to report dehydrogenative dimerization of olefins to dienes via the C-H activation catalyzed by $RhCl(CO)(PMe_3)_2$ under irradiation. Although many reactions have been reported as for monoene dimerization catalyzed by transition metal complexes, the example of diene formation is quite rare.6)

In the previous paper,4b) we reported the dehydrogenation of cyclohexane to cyclohexene. Further investigation of the reaction solution revealed that the intermolecular dehydrogenation also occurred to give a mixture of regio-isomeric bicyclohexenyls (**1**'s) and cyclohexylcyclohexenes (**2**'s) (Eq. 1). These isomers were characterized by capillary GC-MS (CI): **1**'s (M^+, 162), **2**'s (M^+, 164), and bicyclohexyl (M^+, 166). The carbon skeleton of the dimers was further confirmed by the fact that **1**'s and **2**'s were transformed into bicyclohexyl when treated with hydrogen in the presence of $RhCl(PPh_3)_3$. However, the position of C=C double bonds in **1**'s and **2**'s has not yet been determined. Very little occurrence of further oligomerization was confirmed by the analysis of the residue obtained



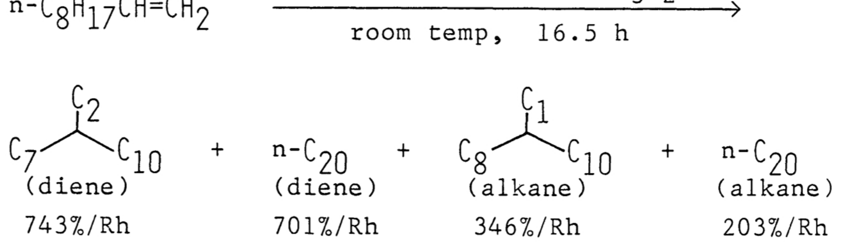
(1)

after the distillation of the reaction mixture; the amount of oligomers larger than the dimers, if any, was less than half of the dimers. Similarly, dimers were formed in the dehydrogenation of cyclooctane, in which the major components were also diene-type dimers. Since the mechanism of the diene formation in the dehydrogenation of cyclohexane was presumably ascribed to the C-H activation of the primarily-formed cyclohexene followed by C=C bond insertion as represented in Scheme 1, we investigated dehydrogenative dimerization of an olefin (1-decene). In a typical reaction, a 0.7 mM solution of $RhCl(CO)(PMe_3)_2$ in 1-decene (30 cm^3) was irradiated by a 100 W high pressure mercury lamp at room temperature under nitrogen for 16.5 h. The products were characterized by GC and GC-MS. Diene-type dimers were formed catalytically as anticipated, accompanied by some saturated dimers (Eq. 2).$^{7)}$ Intramolecular dehydrogenation products (decadienes, cyclodecane, and cyclodecene) were less than 50%/Rh for each isomer. The sequence of the carbon skeleton of the dienes was established by the conversion to saturated forms via the hydrogenation with $RhCl(PPh_3)_3$ followed by the comparison with the authentic samples.$^{7,8)}$ The dimer formation did not proceed without the irradiation even at 100 °C. As was the case for the other C-H activation reactions,$^{1-5)}$ the performance of $RhCl(CO)(PPh_3)_2$ and



R: cyclo-C_6H_9
[Rh]: $RhCl(PMe_3)_2$

Scheme 1.

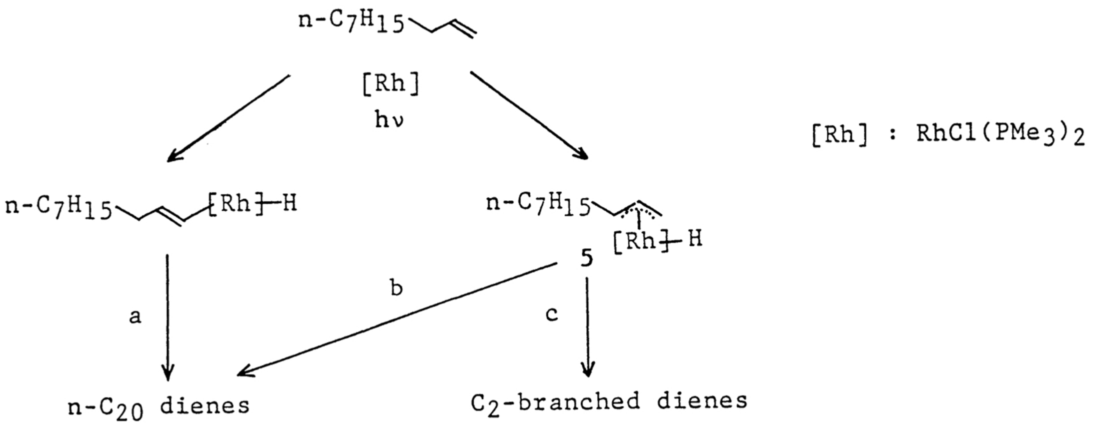


3 4

(2)

$IrCl(CO)(PMe_3)_2$ was inferior to $RhCl(CO)(PMe_3)_2$; the yield of the dimers was very small (eicosadiene **4**'s; 42%/Rh and 33%/Ir, respectively). A similar mechanism to Scheme 1 is also likely for the dimerization of 1-decene.

In the C-H activation of an olefin, selectivity for different type C-H bonds within the molecule (sp^2, sp^3, and allylic sp^3 C-H bonds) is a matter of interest. The present dimerization of 1-decene most likely proceeds via the activation at the terminal sp^2 and/or allylic C-H bonds according to the following consideration (Scheme 2).



Scheme 2.

The formation of the n-C_{20} dienes (**4**'s in Eq. 2) is possibly rationalized by C-H activation at the terminal sp^2 C-H bond of 1-decene (path a). In respect to the reactivity in C-H activation, sp^2 C-H bonds are usually more reactive than sp^3 bonds as reported by Field et al. that the reaction of 1-pentene with $Fe(dmpe)_2$ selectively gave 1-pentenyliron complex.$^{9)}$ This trend seems to be valid with the present $RhCl(CO)(PMe_3)_2$ system; in order to estimate the difference in the reactivity between sp^3 and sp^2 C-H bonds of 1-decene, we exposed a mixture of decane and 1-decene (1/1) to the same conditions as in Eq. 2. The amount of C_{20}-monoenes (the cross-dimers formed via sp^3 C-H bond activation of decane), if any, was less than 2% of the homo-dimers derived from 1-decene.

Another possible pathway leading to the formation of the n-C_{20} dienes (**4**'s) is the dimerization at the terminal position of the π-allylic intermediate **5** formed via the activation at the allylic C-H bond (path b). The formation of the dienic dimers with branching C_2 units (**3**'s in Eq. 2) is also rationalized by the participation of the π-allylic intermediate **5** (path c).$^{10)}$ The formation of the C_2-branched dimers (**3**'s) may also be explainable by the mechanism involving the 1-alkenyl complexes formed from 2- or 3-decene resulting from double bond isomerization. However, this mechanism seems less likely because the amount of 2-decene after the reaction was only 4% of 1-decene.

In summary, this paper offers the first example of olefin functionalization through the C-H activation by $RhCl(CO)(PMe_3)_2$ to give diene-type dimers. The position of C=C double bonds in the dimeric products and further mechanistic details of the reaction are now under investigation.

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8) The mass spectral data of 8-ethyloctadecane were as follows; 282 (M^+, 1), 253 (M^+-Et, 84), 182 (26), 140 (45), 127 (14), 113 (20), 99 (35), 85 (100), 71 (99).
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