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Regioselective Synthesis of Terminal Olefins from Alkanes via Rhodium-Catalyzed C-H Activation

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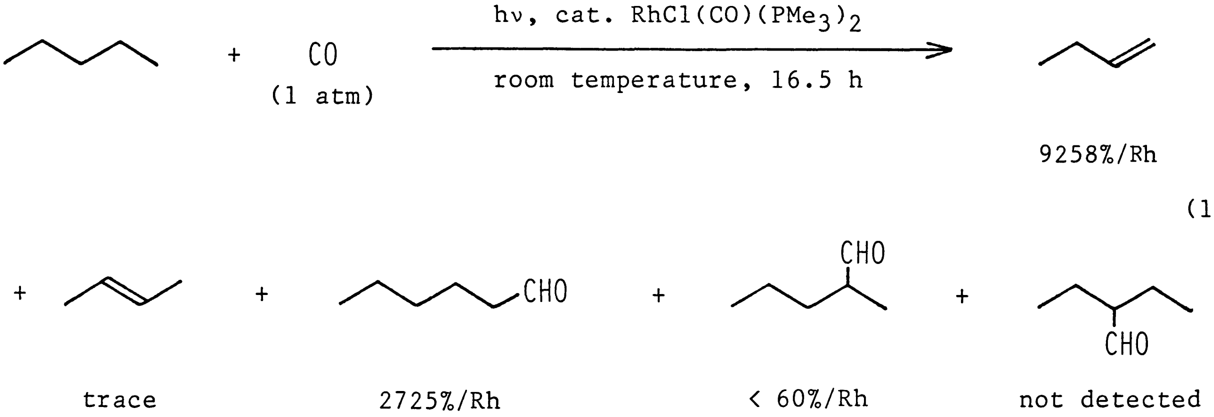
Pentane and decane were regioselectively transformed into 1-butene and 1-nonene with the simultaneous formation of acetaldehyde by photocatalysis in the presence of $RhCl(CO)(PMe_3)_2$ under carbon monoxide.

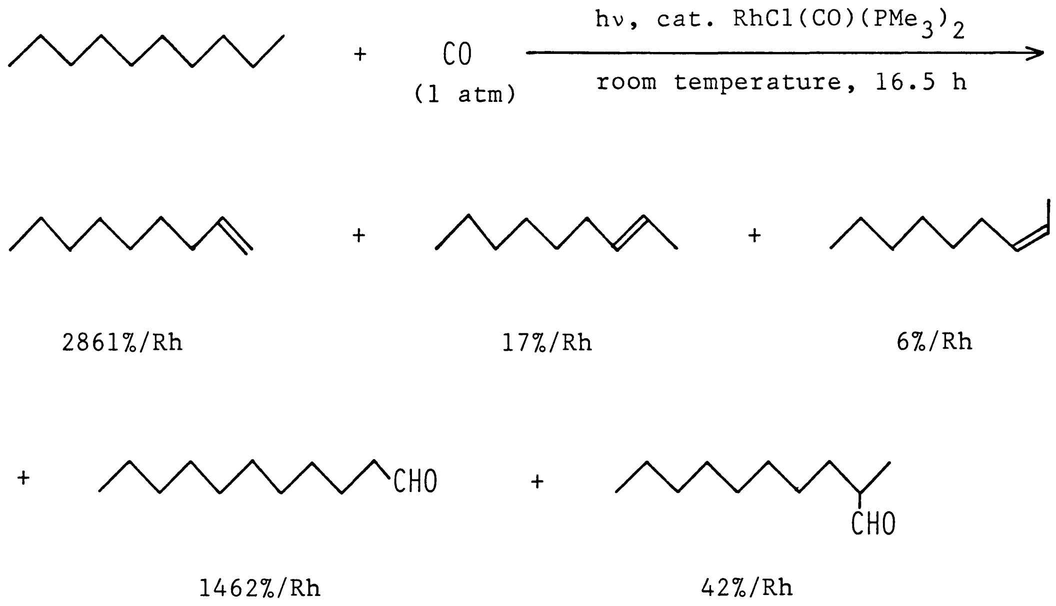
Regioselective functionalization of alkanes under mild conditions by transition metal complexes is of great interest,$^{1)}$ because it enables us to directly utilize various alkanes as raw materials in chemical industry. Although it is known that some transition metal complexes selectively attack the terminal methyl groups of alkanes,$^{2)}$ there have been few catalytic reactions which involve C-H activation. The transfer hydrogenations of t-butylethylene with alkanes in the presence of iridium hydrides occurred catalytically. They resulted, however, in the preferential formation of internal olefins, presumably because of the rapid double bond isomerization.$^{3,4)}$ We recently reported the efficient and regioselective carbonylation of benzene$^{5)}$ and alkanes$^{6)}$ by photocatalysis in the presence of rhodium carbonyl complexes. We now report the first example of the regioselective formation of the terminal olefins from alkanes via C-H activation catalyzed by transition metal complexes.

In the previous paper,$^{6)}$ we reported the selective formation of hexanal from pentane and carbon monoxide catalyzed by $RhCl(CO)(PMe_3)_2$ under irradiation. Our further investigation revealed that the reaction mixture contained a large amount of 1-butene, while only a trace amount of 2-butene was detected (Eq. 1).$^{7,8)}$ The typical reaction conditions were as follows; 0.7 mM solution of the catalyst ($RhCl(CO)(PMe_3)_2$ 6.7 mg (0.021 mmol) in pentane as a solvent (30 cm^3)) placed in a Pyrex flask was irradiated by a 100 W high pressure mercury lamp (UVL-100H, Riko Corp.) at room temperature under an atmospheric pressure of carbon monoxide (balloon). The products were characterized by the GC retention



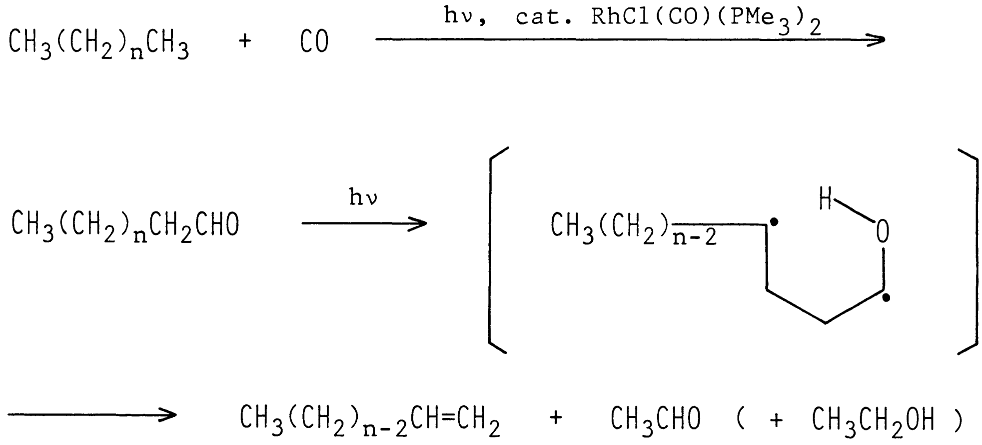
(1)

time and GC-MS. When decane was treated under the same conditions, 1-nonene was obtained as the main product accompanied with undecanal (Eq. 2). The isomerization of the terminal olefin to internal olefins was negligible.



(2)

The terminal olefin formation is presumably ascribed to the Norrish Type II photoreaction of the aldehyde formed as the initial product (Scheme 1).$^{9)}$ Although the reactions were conducted in a Pyrex flask which cuts off the light shorter than 300 nm, the broadness of the absorption peak of alkanals (λ_{max} 290 nm)9) allows the occurrence of the Norrish Type II reaction. As a matter of fact, acetaldehyde (2176%/Rh) and ethanol10) (1506%/Rh) were detected in the mixture of the pentane reaction. Very little formation of propylene and ethylene, which should be the main products in the Norrish Type II reaction of 2-methylpentanal and 3-ethylbutanal respectivly, is consistent with the regioselective formation of hexanal. In addition, the irradiation of hexanal (2.5 mmol) in pentane (30 cm^3) without the rhodium catalyst under carbon monoxide as a control experiment afforded 1.1 mmol of 1-butene after 16.5 h. In the reaction of decane, a substantial amount of acetaldehyde (798%/Rh) and ethanol (671%/Rh) was also detected, and the amount of octene was very small (55%/Rh).



Scheme 1.

In summary, this paper offers a novel procedure for the regioselective synthesis of terminal olefins from alkanes, whose carbon number was less by one than that of starting alkanes. As compared with the conventional cracking method of alkanes, the new procedure has the great advantages of the mildness of the reaction conditions and the remarkably high terminal selectivity. The control of the selectivity toward olefins against aldehydes by regulating the wavelength of the irradiation (λ_{max} of $RhCl(CO)(PMe_3)_2$ in benzene, 360 nm), as well as the improvement of the catalytic activity is now under investigation.

References

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7) The yields were represented on the basis of the rhodium catalyst. The conversions of the pentane in the reaction of Eq. 1 was 1%.

8) A small amount of decane (168%/Rh) was also detected. The dehydrogenative coupling of hydrocarbons via C-H activation will be published separately; see also Ref. 5.

9) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John-Wiley and Sons, New York (1967).

10) Ethanol seemed to be the reduction product of acetaldehyde; see Ref. 5. 1-Hexanol (920%/Rh) and 1-undecanol (284%/Rh) were also formed in the reaction of pentane (Eq. 1) and decane (Eq. 2), respectively.

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