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Visible Light-Assisted Dehydrogenation of Alkanes Catalyzed by the $RhCl(CH_2=CH_2)(PMe_3)_2$-hν System

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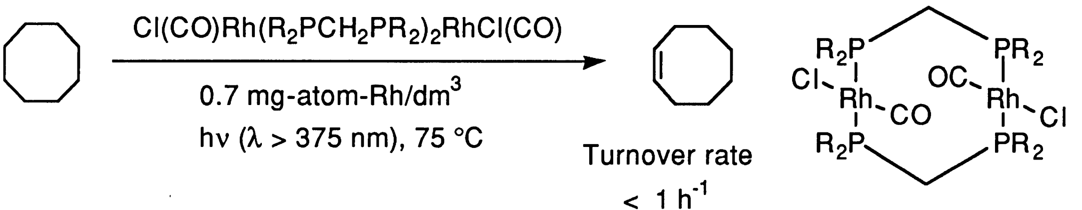
Alkanes are catalytically dehydrogenated to alkenes with $RhCl(CH_2=CH_2)(PMe_3)_2$ (λ_{max} 416 nm) under visible light irradiation in the presence of ethylene. The reaction proceeds smoothly even at room temperature; the quantum yield of cyclooctane dehydrogenation was 0.10 at 25 °C.

We have reported various functionalizations of hydrocarbons *via* C-H bond activation catalyzed by the $RhCl(CO)(PMe_3)_2$-hν system.[1] Especially, dehydrogenation of alkanes proceeds with high efficiency. However, since this system needs constant UV irradiation, development of visible-light assisted reactions has been strongly desired. Here we wish to report dehydrogenation of alkanes with a rhodium complex under visible light irradiation.

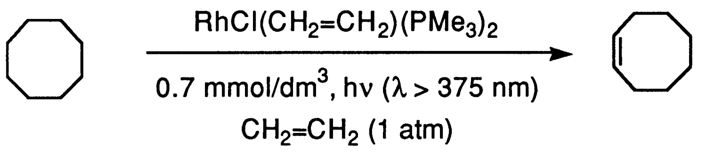
We first examined the catalytic activities of the bisphosphine-bridged analogues (**1** and **2**) of $RhCl(CO)(PMe_3)_2$ (**3**) in dehydrogenation of cyclooctane because the electronic absorptions of **1** and **2** appear at considerably longer wavelength as compared with **3** (λ_{max} 360 nm) owing to the rhodium-rhodium interactions.[2] However, these complexes hardly catalyzed the reaction under visible light irradiation (Eq. 1).[3,4]



(1)

1: R = Ph, λ_{max} 445 nm (CH_2Cl_2)
2: R = Me, λ_{max} 467 nm (CH_2Cl_2)

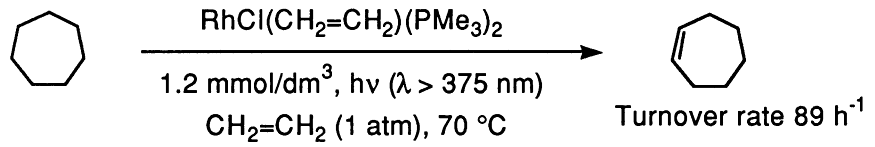
On the other hand, we have recently synthesized the ethylene analogue of **3**, $RhCl(CH_2=CH_2)(PMe_3)_2$ (**4**) from $[RhCl(PMe_3)_2]_2$.[5] Since **4** also shows an absorption in the visible region (λ_{max} 416 nm in cyclooctane), **4** is expected to catalyze dehydrogenation of alkanes under visible light irradiation. In practice, cyclooctane was smoothly converted to cyclooctene at 30 °C under ethylene, which was necessary to stabilize the complex (Eq. 2). The quantum yield was 0.10 at 25 °C.[6] The carbonyl complex **3** was almost inactive under the same reaction conditions. The analysis of gaseous products after the reaction at 25 °C for 0.25 h revealed the formation of ethane (turnover 18) with a small amount of dihydrogen (turnover 1); the corresponding amount of cyclooctene was detected in the liquid phase (turnover 20). Thus the present dehydrogenation is basically a transfer hydrogenation of ethylene with alkanes. Ethylene insertion products, such as ethyl- or vinylcyclooctanes and C_4 compounds formed *via* ethylene dimerization were not detected. Heating of the reaction mixture to 70 °C considerably accelerated the reaction. The dehydrogenation of cycloheptane proceeded in a similar manner to give cycloheptene without any formation of cyclooctene (Eq. 3). This clearly shows that cyclooctene in Eq. 2 did not come from cyclotetramerization of ethylene.



Temp/°C	Turnover rate/h^{-1}
70	160
30	77

(2)

(c.f. $RhCl(CO)(PMe_3)_2$, 30 °C: turnover rate = 1 h^{-1})



(3)

Although hydrogen transfer from alkanes to alkenes has already been reported by Crabtree and Felkin,[7] the present procedure is advantageous in the following points. i) The catalytic activity is much higher at a much lower temperature. ii) The hydrogen acceptor (ethylene) is much less expensive than t-butylethylene, the use of which is indispensable in both Crabtree's and Felkin's systems. iii) It shows the new possibility of the utilization of solar energy.

Since the catalytic activity of $RhCl(L)(PMe_3)_2$ under visible light irradiation varied depending upon the identity of L (CO or $CH_2{=}CH_2$), further improvement can be expected by suitably modifying the nature of the ligand.

References

1) M. Tanaka and T. Sakakura, *Pure Appl. Chem.*, **62**, 1147 (1990); T. Sakakura, T. Sodeyama, K. Sasaki, K. Wada, and M. Tanaka, *J. Am. Chem. Soc.*, **112**, 7221 (1990); T. Sakakura, T. Sodeyama, and M. Tanaka, *New J. Chem.*, **13**, 737 (1989) and references cited therein.

2) A. L. Balch, *J. Am. Chem. Soc.*, **98**, 8049 (1976).

3) The reactions of Eqs. 1 to 3 were carried out in 2.5 cm^3 scale under irradiation with a high-pressure mercury lamp (Ushio USH-500D) through a UV-cut filter (Toshiba L-39); transmittance is over 10% at λ > 375 nm.

4) Under UV irradiation through Pyrex (Riko UVL-100H), **1** catalyzed the dehydrogenation of cyclooctane (Rh 0.7 mg-atom/dm^3, 96 °C). The catalytic activity was increasing with the reaction time; turnover numbers at 1,3, and 6 h were 3, 37, and 118, respectively.

5) T. Sakakura, F. Abe, and M. Tanaka, submitted to this journal.

6) In the quantum yield measurement, mercury emissions at 405 and 436 nm of a high-pressure mercurry lamp were irradiated through a set of glass filters (Toshiba L-39 and V-42); relative transmittance is over 10% from 375 to 500 nm. Photon number was estimated by means of a thermopile photocalorimeter: Scientech Inc., Model 38-0405.

7) R. H. Crabtree, *Chem. Rev.*, **85**, 245 (1985); H. Felkin, T. Fillebeen-Khan, Y. Gault, R. Holmes-Smith, and J. Zakrzewski, *Tetrahedron Lett.*, **25**, 1279 (1984).

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