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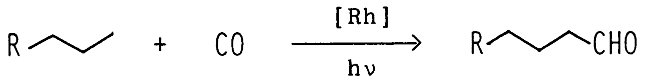
Remarkable Effect of the Wavelength in the Photoassisted Carbonylation of the C-H Bond of Decane in the Presence of $RhCl(CO)(PR_3)_2$ as the Catalyst

Toshiyasu SAKAKURA, Koushi SASAKI,[†] Yuko TOKUNAGA,
Keisuke WADA,[†] and Masato TANAKA[*]
National Chemical Laboratory for Industry,
Yatabe, Tsukuba, Ibaraki 305
[†]Research Center, Mitsubishi Chemical Industries,
1000 Kamoshida-cho, Midori-ku, Yokohama 227

$RhCl(CO)(PR_3)_2$-catalyzed and photoassisted carbonylation of decane leading to the formation of C_{11} aldehydes and/or 1-nonene was remarkably affected by the wavelength; irradiation with $\lambda >$ 295 nm was essential to the formation of 1-nonene and undecanal. By cutting off $\lambda <$ 325 nm, 1-nonene formation was completely suppressed, and a series of isomeric C_{11} aldehydes were obtained.

Recently, we have reported that photoassisted catalysis of $RhCl(CO)(PMe_3)_2$ promotes the direct carbonylation of the C-H bonds in hydrocarbons under mild conditions (room temperature, atmospheric pressure).[1-4] One of the unique features of these new type carbonylation reactions through C-H bond activation lies in the regioselectivity; substituted benzenes are carbonylated predominantly at the meta C-H bond.[2] In the reactions of alkanes (pentane and decane), linear aldehydes resulting from the carbonylation at the terminal C-H bonds are formed with an extremely high regioselectivity (> 97%, Eq. 1).[3,4] In the latter reactions, terminal olefins with one carbon missing (1-butene and 1-nonene, respectively) are also obtained with > 99% regioselectivities (Eqs. 1



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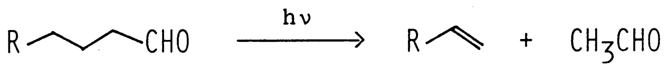

(2)

and 2). The formation of the terminal olefins is presumably due to the linear aldehyde products subsequently undergoing the Norrish type II reaction (Eq. 2) under the photo-carbonylation conditions. The Norrish type II reaction is triggered by the excitation of the carbonyl group (λ_{max} ca. 290 nm). On the other hand, $RhCl(CO)(PR_3)_2$ exhibits a metal-to-ligand charge transfer (MLCT) band at about 360 nm. Photolysis of the rhodium complex (R = Ph) with the light (> 315 nm) has been reported to result in the formation of the coordinatively unsaturated $RhCl(PR_3)_2$,5) which we believe is the key catalytic species for the carbonylation. With these considerations in mind, it appeared interesting to see if we could selectively obtain either the aldehyde or the olefin in the alkane carbonylation by regulating the irradiation wavelength. The results of the wavelength dependence herein reported are surprising; not only the aldehyde/olefin selectivity but also the regioselectivity of the aldehyde formation is significantly affected.

The reaction procedure was as follows: a 0.7 mM solution of $RhCl(CO)(PR_3)_2$ in decane (2 ml) placed in a Pyrex rectangular cell was irradiated with a 500 W high pressure mercury lamp (USH-500D, Ushio) at room temperature under an atmospheric pressure of carbon monoxide (balloon). The wavelength was regulated by means of Toshiba UV-D35, UV-35, and L-39 glass filters.

The results are summarized in Table 1. Irradiation with $295 < \lambda < 420$ nm for 5 h led to the similar product selectivities to those obtained with a 100 W immersion-type lamp (UVL-100H, Riko Corp.);4) the main products were undecanal and 1-nonene with high terminal selectivities (Run 1).6) When short-wavelength light was cut off, the olefin formation was, as anticipated, completely inhibited (Runs 2 and 3)7) because of the lack of excitation of the aldehyde. Interestingly, the absence of short-wavelength light caused an entirely different regioselectivity. The terminal selectivity was lost, and a wide spectrum of isomeric aldehydes were formed with 2-methyldecanal being the main one.8) In the reaction of alkanes with $(\eta^5-C_5Me_5)Rh(PMe_3)$, Bergman et al. have reported that C-H activation occurs at both the terminal and internal C-H positions but that the internal activation product rearranges rapidly to the thermodynamically-favoured terminal C-H activation product.9) We speculate that the high terminal selectivity of our system attained with the irradiation involving the short-wavelength is presumably attributable to the photo-enhanced

Table 1. Effect of irradiation wavelength and phosphine ligands in the photoassisted carbonylation of decane by $RhCl(CO)(PR_3)_2$

Run	Wavelength[a)	R	Time	Yield / %/Rh				
	nm		h	$C_{9-n}\text{-}\underset{\text{CHO}}{\underset{\vert}{C}}\text{-}C_n$	(n = 0 : 1 : 2 : 3 : 4)	nonene 1-	nonene 2-trans	nonene 2-cis
1	295-420	Me	5	610	(86 : 5 : 4 : 2 : 3)	319	0	0
2	> 325	Me	5	126	(8 : 45 : 17 : 15 : 16)	0	0	0
3	> 325	Me	16.5	559	(6 : 44 : 17 : 16 : 17)	0	0	0
4	> 375	Me	16.5	32	(0 : 49 : 18 : 17 : 17)	0	0	0
5	> 325	n-Bu	16.5	281	(8 : 59 : 13 : 10 : 11)	0	0	0
6	> 325	i-Pr	16.5	194	(45 : 39 : 7 : 5 : 4)	0	0	0

$RhCl(CO)(PR_3)_2$ 0.7 mM, CO 1 atm, room temperature, irradiated with a 500 W high pressure mercury lamp.
a) Ranges where the transmittance is over 10%.

isomerization from the internal to the terminal activation species prior to the migratory CO insertion. The regioselectivities of the carbonylation could be controlled not only by irradiation wavelength but also by the bulkiness of phosphine ligands (Runs 3,5, and 6). When bulky triisopropylphosphine was used as a ligand in place of trimethylphosphine, a considerable increase in the terminal selectivity was obtained as anticipated; undecanal became the main product.

In addition to the selectivities, catalytic activity was also dependent on the wavelenth. Irradiation with $295 < \lambda < 420$ nm was favorable for a high catalytic activity as compared with the irradiation with $\lambda > 325$ nm. The effect is much larger than simply expected from the difference of the irradiation energy.[10)] A similar effect of the wavelength was observed in the carbonylation of benzene. The results seem to indicate that the MLCT band at about 360 nm may not play a crucial role. The stronger absorption band below 340 nm,[11)] the assignment of which is not clear, is possibly more important. Irradiation of the long-wavelength ($\lambda > 375$ nm) hardly promoted the carbonylation (Run 4).

In conclusion, the product selectivity (aldehyde vs. olefin), the regioselectivity, and the catalytic activity can be controlled by the regulation of the irradiation wavelength and/or the bulkiness of the phosphine ligand in the catalytic C-H bond carbonylation. Further studies on the control of the regioselectivity in arene carbonylation as well as the role of irradiation are under way.

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5) D. A. Wink and P. C. Ford, J. Am. Chem. Soc., 109, 436 (1987).
6) The high terminal selectivity in the present reaction is improbable to result from the different secondary photoreaction rates of undecanal and its regioisomers, because the high regioselectivity was obtained constantly from the very beginning of the reaction. In addition, the irradiation of a regioisomeric mixture of C_{11}-aldehydes in the absence of the rhodium complex gave similar consumption rates for each isomer.
7) Octene, which should have been formed from 2-methyldecanal through the Norrish type II reaction, was not detected, either.
8) The influence of the light of visible region in Runs 2 to 6 is small, because the same trend was observed even after cutting off that region.
9) R. A. Periana and R. G. Bergman, J. Am. Chem. Soc., 108, 7332 (1986).
10) The ratio of the UV irradiation energy in the use of UV-D35 filter to that of UV-35 is about 1.6.
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