

PHOTOCHEMICAL CARBONYLATION OF ALKYL IODIDES IN THE PRESENCE OF VARIOUS METAL CARBONYLS

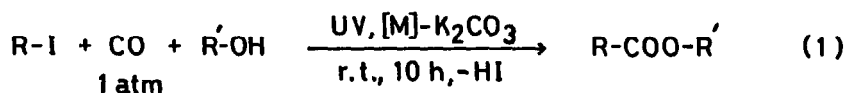
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Summary: Various transition metal complexes including group VII and VIII metal carbonyls are highly active catalyst precursors for the photochemical carbonylation of organic iodides at room temperature under an atmospheric pressure of carbon monoxide. Primary, secondary and tertiary alkyl iodides which have β -hydrogens on sp^3 -carbons were smoothly carbonylated by this catalyst system without β -hydride elimination to give the corresponding esters in yields of 63 - 88 %.

Photochemical behavior of transition metal carbonyls has been well studied and photogeneration of catalytically active species is of current interest in homogeneous catalysis.¹⁾ Recently, significant progress was made on the photochemical carbonylation by transition metal complexes,²⁾ since Mirbach and coworkers have reported the photochemical hydroformylation of olefins with cobalt and rhodium catalysts.³⁾

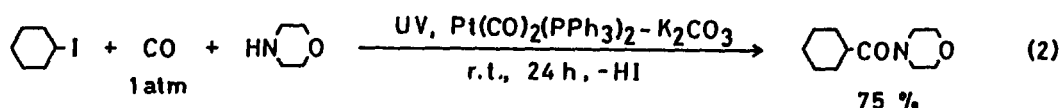
On the other hand, we have recently reported the first example of platinum complex-catalyzed thermal (120 °C) carbonylation of organic iodides with β -hydrogens on sp^3 -carbons under 70 kgcm⁻² of carbon monoxide.⁴⁾ It was considered that this novel reaction would be characteristic of platinum complexes because of the unusual stability of a σ -alkyl platinum intermediate.⁵⁾ In the course of further study, we found that not only platinum complexes but also group VII and VIII metal carbonyls catalyze the photocarbonylation of organic iodides under extremely mild conditions (at room temperature under an atmospheric pressure of carbon monoxide; eq. 1). We now report the preliminary results.



R = alkyl, [M] = Group VII, VIII metal carbonyl



A typical reaction procedure was as follows; A mixture of alkyl iodide (5 mmol), methanol (30 mmol), metal carbonyl (0.1 - 0.25 mmol), K₂CO₃ (3 mmol) and THF (7.5 ml) was placed in a Pyrex flask and irradiated by a 200 W high pressure mercury lamp for 10 h at room temperature under an atmospheric pressure of carbon monoxide (balloon). All products were isolated by column chromatography or distillation in vacuo. Satisfactory spectroscopic and analytical data for them were obtained.

Representative results are listed in Table 1. Primary, secondary and even tertiary alkyl iodides were smoothly carbonylated by the present catalyst system (Runs 7-11). In this carbonylation, the iodine was directly replaced by the alkoxy carbonyl group, and no other isomeric products were formed. Alkyl bromides and chlorides, however, were not carbonylated under the same reaction conditions. Among the platinum complexes, $\text{Pt}(\text{CO})_2(\text{PPh}_3)_2$ is most effective (Run 7). $\text{PtCl}_2(\text{PPh}_3)_2$, $\text{PtCl}_2(\text{P}(i\text{-Pr})_3)_2$ and $\text{PtCl}_2(\text{AsPh}_3)_2$ also showed catalytic activity (Runs 4-6). When 2-propanol and 2,2,2-trifluoroethanol were used instead of methanol, corresponding esters were obtained in good yields (cyclo- $\text{C}_6\text{H}_{11}\text{COOCH}(\text{CH}_3)_2$, 87 % (by GLC); cyclo- $\text{C}_6\text{H}_{11}\text{COOCH}_2\text{CF}_3$, 40 % (isolated)). When amines were employed as a nucleophile in our previous system,⁴⁾ they formed the quaternary ammonium salts. However, in the present reaction, amines could be used and gave the corresponding amides in good yields (eq. 2).



Without the irradiation, no reaction occurred (Run 2) and catalytic activity was quite low with visible light irradiation (Run 3). Furthermore, when the UV light was turned off, the reaction ceased completely. It indicates that continuous irradiation is necessary to maintain the catalytic activity.

Table 1. Platinum Complex Catalysed Photocarbonylation of Alkyl Iodides.^a

Run	Alkyl iodide	Pt-complex	% Conv. ^b	% Product ^c	Light	
1	n-C ₆ H ₁₃ -I	-	0	-	0	UV
2	n-C ₆ H ₁₃ -I	PtCl ₂ (PPh ₃) ₂	0	-	0	-
3	n-C ₆ H ₁₃ -I	PtCl ₂ (PPh ₃) ₂	49	n-C ₆ H ₁₃ COOMe	15	visible
4	n-C ₆ H ₁₃ -I	PtCl ₂ (PPh ₃) ₂	64	n-C ₆ H ₁₃ COOMe	41	UV
5	n-C ₆ H ₁₃ -I	PtCl ₂ (P(i-Pr) ₃) ₂	93	n-C ₆ H ₁₃ COOMe	48	UV
6	n-C ₆ H ₁₃ -I	PtCl ₂ (AsPh ₃) ₂	92	n-C ₆ H ₁₃ COOMe	55	UV
7	n-C ₆ H ₁₃ -I	Pt(CO) ₂ (PPh ₃) ₂	90	n-C ₆ H ₁₃ COOMe	67(52)	UV
8	n-C ₁₀ H ₂₁ -I	Pt(CO) ₂ (PPh ₃) ₂	77	n-C ₁₀ H ₂₁ COOMe	76	UV
9	 -I	Pt(CO) ₂ (PPh ₃) ₂	87	 COOMe	84(62)	UV
10	n-C ₆ H ₁₃ CH(CH ₃)I	Pt(CO) ₂ (PPh ₃) ₂	75	n-C ₆ H ₁₃ CH(CH ₃)COOMe	(46)	UV
11	(CH ₃) ₃ C-I	Pt(CO) ₂ (PPh ₃) ₂	-	(CH ₃) ₃ CCOOMe	63	UV

^a A mixture of alkyl iodide (5 mmol), MeOH (30 mmol), K₂CO₃ (3 mmol), Pt complex (0.25 mmol) and THF (7.5 ml) was irradiated in a Pyrex flask by a 200 W high pressure Hg lamp for 10 h at room temperature under atmospheric pressure of carbon monoxide (balloon).

^b Conversion of alkyl iodide determined by GLC. ^c Determined by GLC based on the amount of alkyl iodide charged and figures in the parentheses are isolated yields.

Surprisingly, various group VII and VIII metal carbonyls also catalyze the present photocarbonylation. The results are summarized in Table 2. Stoichiometric reactions of group VI and VII metal carbonyls⁶⁾ and photochemistry of them⁷⁾ were extensively studied, but to our knowledge, effective catalytic carbonylation using them has not yet been reported. Group VI metal carbonyls such as $\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$, and $\text{W}(\text{CO})_6$ were not good catalyst for the present reaction. On the other hand, group VII metal carbonyls such as $\text{Mn}_2(\text{CO})_{10}$ and $\text{Re}_2(\text{CO})_{10}$ showed high catalytic activity and methyl cyclohexanecarboxylate was obtained in high yields. Among group VIII metal carbonyls, $\text{Co}_2(\text{CO})_8$, $\text{Ru}_3(\text{CO})_{12}$ and $\text{Os}_3(\text{CO})_{12}$ showed high catalytic activity. Material balance was always good indicating that no side reaction such as β -hydride elimination occurred. According to studies of photochemical behavior of d^8 square planar complexes and various transition metal carbonyls, almost all intermediates and observed transients are formed via initial photodissociation of CO .⁸⁾ Indeed, when $\text{Os}_3(\text{CO})_{12}$ was used in the present reaction, recently reported $\text{Os}_3(\text{CO})_{11}$ ⁹⁾ were detected by FT-IR absorption at 2097, 2066, 2027 and 1996 cm^{-1} . This result suggests that photochemical dissociation of CO to generate coordinatively unsaturated species is a key step in the present reaction.

Table 2. Activities of Various Transition Metal Carbonyls in Carbonylation of Cyclohexyl Iodide^a

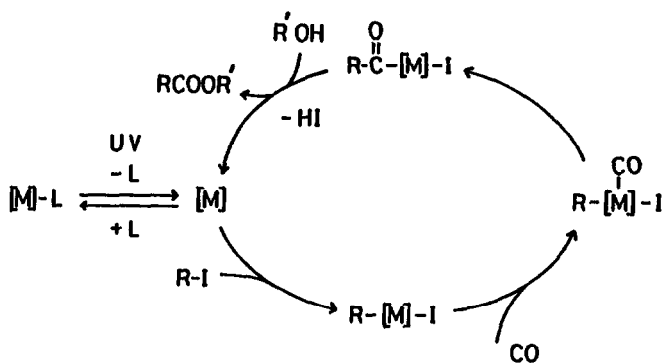
metal carbonyl	VI	VII	VIII				
	$\text{Cr}(\text{CO})_6$	$\text{Mn}_2(\text{CO})_{10}$	$\text{Fe}_3(\text{CO})_{12}^d$	$\text{Fe}_2(\text{CO})_9$	$\text{Fe}(\text{CO})_5$	$\text{Co}_2(\text{CO})_8$	$\text{Ni}(\text{CO})_4$
Conv.(%) ^b	12	100	51	44	48	88	49
Yield(%) ^c	5	88	33	21	36	76	47
	$\text{Mo}(\text{CO})_6$	—	$\text{Ru}_3(\text{CO})_{12}^d$	$\text{Rh}_6(\text{CO})_{16}^d$	$\text{RhCl}(\text{CO})(\text{PPh}_3)_2$	$\text{Pd}_3(\text{CO})_3(\text{PPh}_3)_4^d$	
Conv.(%) ^b	11	—	100	17	48		37
Yield(%) ^c	8	—	82	7	42		25
	$\text{W}(\text{CO})_6$	$\text{Re}_2(\text{CO})_{10}$	$\text{Os}_3(\text{CO})_{12}^d$	$\text{IrCl}(\text{CO})(\text{PPh}_3)_2$		$\text{Pt}(\text{CO})_2(\text{PPh})_2$	
Conv.(%) ^b	21	87	83	44		87	
Yield(%) ^c	8	77	67	42		84	

^a A mixture of cyclohexyl iodide (5 mmol), methanol (30 mmol), metal carbonyl (0.25 mmol), K_2CO_3 (3 mmol) and THF (7.5 ml) was placed in a Pyrex flask and irradiated by a 200 W high pressure mercury lamp for 20 h at room temperature under an atmospheric pressure of carbon monoxide (balloon). ^b Conversion of cyclohexyl iodide determined by GLC. ^c Yield of methyl cyclohexanecarboxylate determined by GLC based on the amount of cyclohexyl iodide charged. ^d Metal carbonyl (0.1 mmol) was used.

A tentative catalytic cycle is illustrated in Scheme I. Oxidative addition of alkyl iodide to a photochemically generated active catalyst center would afford the σ -alkyl metal intermediate. Insertion of CO into the alkyl metal bond followed by nucleophilic attack of alcohol provides the ester. Then, base assisted elimination of HI allows a catalytic cycle

to be closed with regenerating an active catalyst species. There seems to be some possibility of a radical chain reaction. However, addition of a radical scavenger such as 2,6-di-*t*-butylphenol (1 mmol was added to the present system) did not affect the reaction at all. Mechanistic study and application of the present reaction are now in progress.

Scheme I



$L = \text{CO or } \text{PR}_3$, $[\text{M}] = \text{Group VII, VIII metal carbonyl}$

References

- 1) G. L. Geoffroy, M. S. Wrighton, in "Organometallic Photochemistry", Academic Press, New York (1978).
- 2) A. J. Kunin, R. Eisenberg, *J. Am. Chem. Soc.*, **108**, 535 (1986). T. Sakakura, M. Tanaka, *J. Chem. Soc., Chem. Commun.*, 758 (1987).
- 3) M. J. Mirbach, M. F. Mirbach, A. Saus, N. Topalsavoglou, T. N. Psu, *J. Am. Chem. Soc.*, **103**, 7590 (1981). *idem.*, *ibid.*, **103**, 7594 (1981). A. Saus, T. N. Psu, M. Mirbach, M. F. Mirbach, *J. Mol. Catal.*, **18**, 117 (1983).
- 4) R. Takeuchi, Y. Tsuji, Y. Watanabe, *J. Chem. Soc., Chem. Commun.*, 351 (1986).
- 5) F. R. Hartley, in "The Chemistry of Platinum and Palladium", Applied Science, London, p. 330 (1973).
- 6) P. M. Treichel, in "Comprehensive Organometallic Chemistry", eds. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon Press, Oxford, Vol. 4, p. 1 (1982). N. M. Boag, H. D. Kaesz, in "Comprehensive Organometallic Chemistry", eds. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon Press, Oxford, Vol. 4, p. 161 (1982).
- 7) C. G. Kreiter, in "Advances in Organometallic Chemistry", eds. F. G. A. Stone and R. West, Academic Press, London, Vol. 26, p. 297 (1986).
- 8) For example. D. Wink, P. C. Ford, *J. Am. Chem. Soc.*, **107**, 5566 (1985).
- 9) J. G. Bentson, M. S. Wrighton, *J. Am. Chem. Soc.*, **109**, 4518 (1987).

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