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Cobalt-catalysed Photochemical Methoxycarbonylation of Olefins under Ambient Conditions

Yu-Tai Tao,* Tashin J. Chow, Jiann-T'suen Lin, Ching-Cheng Lin, Ming-Ta Chien, and Chu-Chieh Lin

Institute of Chemistry, Academia Sinica, Nankang, Taipei, 11529 Republic of China

Yuan L. Chow,*† and Gonzalo E. Buono-Core

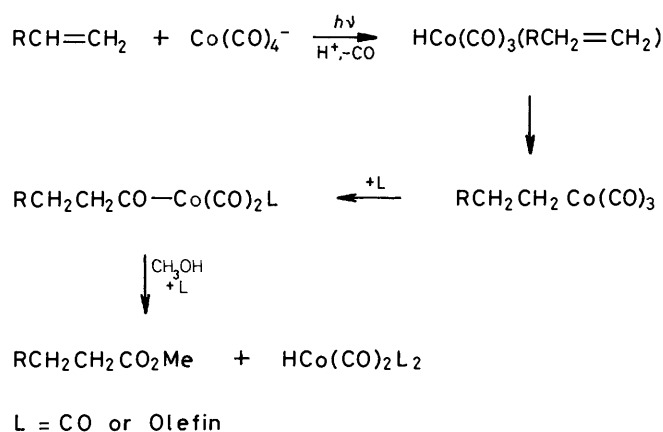
Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6

Photolysis of a solution containing catalytic amounts of bis(pentane-2,5-dionato)cobalt(II) and an olefin in methanol-acetone under carbon monoxide (1 atm) at room temperature caused methoxycarbonylation of the olefin yielding the corresponding methyl carboxylates.

The incorporation of CO into olefins is an important basic chemical process¹⁻⁴ that is commonly carried out by means of homogeneous catalysis with transition metal complexes in the presence of H₂ or an alcohol as co-substrates. Its applicability is limited by the high pressures and temperatures necessary, or by the costs of precious metals. Carbonylation catalysed by [Co₂(CO)₈] can proceed with reasonable rates at temperatures and pressures higher than 150 °C and 100 atms.⁵ The carbonylation of, for example, propene in the presence of [PdCl₂(PPh₃)₂] can be accomplished under more moderate conditions, *i.e.* 80–110 °C and 35 atm.^{6a} However, recently Alper and co-workers have demonstrated that the methoxycarbonylation of olefins catalysed by PdCl₂-CuCl₂ in acidic solution can occur at ambient temperature and pressure.^{6b} In 1981, Mirbach *et al.* demonstrated that the cobalt catalysed carbonylation of olefins can occur under milder conditions (80 °C and 80 atm of CO/H₂) if the solution is irradiated.⁷ We report here light promoted methoxycarbonylation catalysed by cobalt under ambient conditions, *i.e.*, under 1 atm of CO at room temperature. Photo-initiated carbonylations in the presence of transition metal catalysis are a recent interest.⁸

Typically, a Pyrex test tube containing an olefin (*ca.* 0.04M) and 10 mol% of bis(pentane-2,5-dionato)cobalt(II), [Co(acac)₂], in MeOH-Me₂CO (4:1, v/v) solution was irradiated under slow purging of CO (4–5 ml/min.) at room temperature to give a yellow photolysate. The corresponding methoxycarbonylation products (Table) started to form after a short induction period (0.5 h) and increased slowly and steadily as shown by g.c. analysis. Conversion of the olefin into product stopped on interruption of irradiation but resumed when illumination recommenced. The presence of PBu₃ retarded the photoinitiated methoxycarbonylation of oct-1-ene seriously; this could arise from competitive ligation of the Co centre by the better ligand, PBu₃. The major products shown in the Table were isolated and characterized by spectroscopy. The identities of the minor products were deduced from g.c.-m.s. data. All the isolated major products exhibit pertinent i.r. absorptions, at 1 730–1 740 cm⁻¹ and n.m.r. signals at 3.6 p.p.m. (3 H, s) and 2.2–2.4 p.p.m. (m), for a methoxycarbonyl group. The m.s. spectra of these products show the expected molecular ions and fragmentation patterns.

It was significant that all four possible methoxycarbonylation products (3)–(6) were obtained and that (3) and (4) were the major products regardless of whether oct-1-ene (1) or oct-4-ene




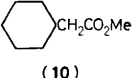

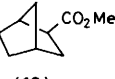

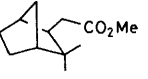

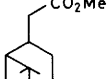
Scheme 1.

(2) was the substrate, although the ratios of these products were slightly different depending on the particular octenes. In both cases, some octane (<10%) was also detected but the amounts of isomeric octenes were too small to be detected by g.c.-analysis. The regioselectivity was considerably improved with hindered olefins 3,3-dimethylbut-1-ene (7) and methylenecyclohexane (9), in which the terminal esters were obtained as the major products in addition to trace amounts of the alternative product. Camphene (13) and β-pinene (15) were methoxycarbonylated with good regioselectivity and stereoselectivity that suggested the effects of steric controls. In the methoxycarbonylation of the terminal olefin (7) in CH₃OD-(CD₃)₂CO, the ester (8) was analysed for deuterium distribution to show (i) that the ester sample contained [²H₁]-(**8**) (88%) and [²H₀]-(**8**) (12%) as shown by g.c.-m.s., and (ii) that ²H and ¹H n.m.r. spectra both demonstrated that one deuterium is equally distributed between the two CH₂ groups, *i.e.*, each contains 1.5 and 0.5 atom fractions of ¹H and ²H, respectively. The product [²H₀]-(**8**) might arise from isotope dilution in the photo-reduction stage to produce acacH.

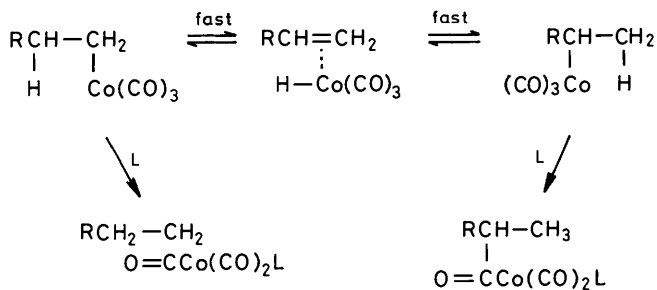
While [Co(OAc)₂] and [Co₂(CO)₈] could be substituted for [Co(acac)₂] to give comparable results, CoCl₂ under similar conditions gave a more complex mixture containing much smaller yields of the methyl esters. [Co(acac)₂] In methanol-acetone showed no visible changes under a CO atmosphere but on irradiation⁹ was rapidly converted into [Co(CO)₄]⁻, which could be detected by i.r. spectroscopy (1 900 cm⁻¹)¹⁰ and isolated as the (PPh₃)₂N⁺ salt in 35% yield. Na[Co(CO)₄]

† Visiting professor from Simon Fraser University, Burnaby, British Columbia, Canada, 1986–1987.

Table. Photochemical methoxycarbonylation of olefins in the presence of $\text{Co}(\text{acac})_2$ in $\text{MeOH}-\text{Me}_2\text{CO}^a$

Olefin	Irradiation time (h)	Products	Yield (%)	
$\text{Me}(\text{CH}_2)_5\text{CH}=\text{CH}_2$ (1)	20	$\left\{ \begin{array}{l} \text{Me}(\text{CH}_2)_7\text{CO}_2\text{Me} \quad (3) \\ \text{Me}(\text{CH}_2)_5\text{CH}(\text{Me})\text{CO}_2\text{Me} \quad (4) \\ \text{Me}(\text{CH}_2)_4\text{CH}(\text{Et})\text{CO}_2\text{Me} \quad (5) \\ \text{Me}(\text{CH}_2)_3\text{CH}(\text{Pr})\text{CO}_2\text{Me} \quad (6) \end{array} \right\}$	56 ^b	
$\text{PrCH}=\text{CHPr}$ (2)	30		67 ^b	
$\text{Bu}^i\text{CH}=\text{CH}_2$ (7)	10		$\text{Bu}^i\text{CH}_2\text{CH}_2\text{CO}_2\text{Me}$ (8)	45 ^c
	20			66 ^c
	20		48 ^d	
	20		50 ^{c,e}	
	20		67 ^{c,f}	

^a A test tube containing solution was placed near a Hanovia type cooling unit for irradiation, a 450 W lamp was used as the light source. ^b In the crude products, octane was detected. The ratio of 6:5:4:3 was 1:0.7:3.8:5.5 for oct-1-ene and 1:1.4:1.8:2.4 for oct-4-ene. ^c In the crude products, small amounts of the alternative regioisomers were detected by g.c.-m.s. analysis. ^d Only one product was obtained which was shown to be the *exo*-isomer. ^e Two products (the *endo*- and *exo*-isomers) were obtained in a 4:1 ratio. ^f The ratio of the two stereoisomer is 15:1.

**Scheme 2.**

($\text{pK}_a < 2$)^{10,11} generated from $[\text{Co}_2(\text{CO})_8]$ and NaH could catalyse the methoxycarbonylation of olefins in the presence of acetic acid (*ca.* 0.02M) under similar photolysis conditions. Incorporating the generally accepted step of addition of Co-H across an olefinic bond as a mechanistic component,¹¹⁻¹³ we propose $[\text{HCo}(\text{CO})_3(\text{olefin})]$ as the reactive intermediate (Scheme 1) which is derived from an unspecified photoexcitation step.¹⁴ While photoexcitation is definitely required, this step has not been identified. The pattern of deuterium distribution in ester (8) indicates that the reversible addition-elimination sequence must be much faster than the rearrangement of alkyl-Co complexes to give acyl-Co complexes and that such rearrangements are sensitive to steric hindrance (Scheme 2). The basic mechanism in Scheme 2 shows rapid migration of the double bond in the octene chain and affords the observed mixtures of esters (3)-(6).

Acknowledgements

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