

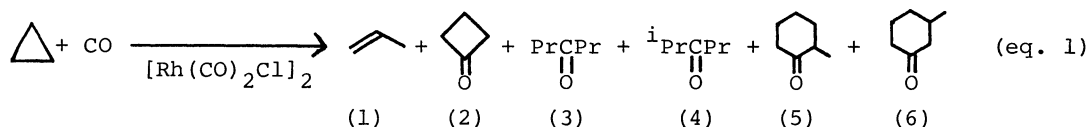
RHODIUM CATALYZED CARBONYLATION REACTIONS OF CYCLOPROPANES

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Cyclopropane was carbonylated by $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ under carbon monoxide pressure to give cyclobutanone, dipropyl ketone, propyl isopropyl ketone, and 2- or 3-methylcyclohexanone. Some other cyclopropane derivatives were also examined. Norcarane gave a small amount of bicyclo[4.2.0]octa-7-one, though phenylcyclopropane did not give any carbonylation products. The formation of polyketone was efficient in the case of methylenecyclopropane.

A number of carbonylation reactions by transition metal complexes have been known.¹⁾ However, the carbonylation of cyclopropane has rarely been reported.²⁾ Here we report the first example of the catalytic carbonylation reactions of cyclopropanes.

Cyclopropane reacted with carbon monoxide under pressure in the presence of catalytic amount of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ in benzene to give the carbonylated products (2)~(6), together with propylene(1) which is the isomerization product of cyclopropane.³⁾ (eq.1)



The products were identified by comparing the G.C.-M.S. spectra with those of authentic samples. The G.C.-M.S. analysis also gave the evidence for the presence of some diketones such as octane-4,5-dione and other cyclohexanone derivatives such as 2-(2-oxopentyl)cyclohexanone in the mixed products.

The results of cyclopropane carbonylation are summarized in Table 1. At ca. 160°C for 15 hours, cyclobutanone(2) and dipropyl ketone(3) were obtained(run 1). Above ca. 200°C, the selectivity of the product(2) was lost and the isomerization to propylene(1) became faster(run 2). When ethylene was added, the yield and the selectivity of cyclobutanone(2) increased significantly(run 3). Addition of σ -donor ligands such as PPh_3 inhibited the isomerization to propylene(1) but showed no effect on carbonylation(run 4). For the formation of (3) and (4), two hydrogen atoms are formally required besides cyclopropane and carbon monoxide. Addition of hydrogen, however, did not increase the yields of (3) and (4), and propylene(1) formed underwent hydroformylation to give butyraldehyde(7) and isobutyraldehyde(8) (run 5). We must await further investigation to elucidate the mechanism for the formation of the ketones.

The metallacyclopentane complexes of titanium and nickel are known to react with carbon monoxide to give cyclopentanone.⁴⁾⁵⁾ However the reactions are stoichiometric. Wilkinson et al. reported that cyclopropane reacts with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ at 40°C to give a rhodacyclopentanone complex.⁶⁾ When this metallacycle $[(\text{C}_3\text{H}_8\text{CO})\text{Rh}(\text{CO})\text{Cl}]_2$ was employed as a catalyst in the above carbonylation reaction, almost the same result as

Table 1. $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ catalyzed carbonylation of cyclopropane^{a)}

run	Δ (mmol)	temp. (°C)	time (hrs.)	conv. (%)	product yield (mmol)							
					(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
1	66	160	15	26	9.5	2.4	1.7	0.2	tr.	tr.	tr.	tr.
2	90	200	15	85	51.3	0.5	3.2	0.3	0.1	0.1	tr.	tr.
3 ^{b)}	47	165	15	42	5.5	4.1	0.3	tr.	0.1	tr.	0	0
4 ^{c)}	56	150	15	28	2.7	1.4	0.1	0.1	0.1	0.1	1.0	0.4
5 ^{d)}	47	140	18	42	tr.	0.9	0.6	0.1	0	0	15.1	3.0
6	84	160	60	73	14.6	2.3	2.0	0.8	0.2	0.1	tr.	tr.

a) $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ 0.2 mmol, benzene 10 ml, initial CO pressure 50 kg/cm²

b) Ethylene (7 kg/cm²) was added. c) PPh_3 (0.2 mmol) was added.

c) Hydrogen (5 kg/cm²) was added.

with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ was obtained. We believe our results are the first example of catalytic ring closure of metallacycle by carbon monoxide. It may be reasonable to consider that 2- or 3-methylcyclohexanone are formed via further insertion of propylene to the rhodacyclopentanone.

Carbonylation of some other cyclopropanes was also investigated. Phenylcyclopropane did not undergo carbonylation even at 220°C. The carbonylation of norcarane, bicyclo[4.1.0]heptane, gave a small amount of bicyclo[4.2.0]octa-7-one,⁷⁾ which is a carbon monoxide insertion product to the cyclopropane ring of norcarane. On the other hand, polyketone was obtained in a good yield in the case of methylenecyclopropane. G.P.C. analysis showed that the polyketone consists of three parts of polymers whose average molecular weights are <10,000, ca. 10,000, and $2\sim 3 \times 10^4$. The structure of this polyketone was supposed to contain the unit $\text{[-CH}_2\text{-C(CH}_3\text{)=CH-C-C(CH}_3\text{)=CH-CH}_2\text{-]}$

based on i.r., ¹H-n.m.r., and ¹³C-n.m.r. spectra. The copolymerization of carbon monoxide and ethylene by γ -irradiation⁸⁾ and peroxide⁹⁾ has previously been reported.

References and Notes

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