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THE REACTION OF SMALL RING COMPOUND WITH CARBON MONOXIDE
THE CARBONYLATION OF OXIRANE

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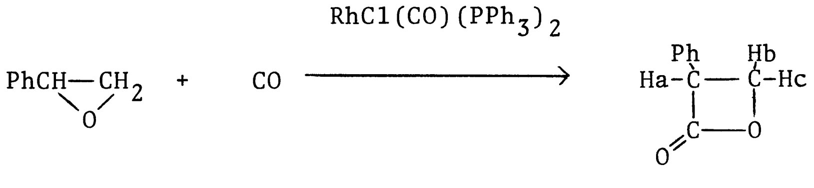
Summary: The carbonylation of oxiranes catalyzed by rhodium complex afforded β-lactones. Various factors which control the above reaction are presented.

There has been considerable attention on the interaction between highly strained organic molecules and transition metal complexes.[1,2] The insertion of metal complex into a αbond and the skeletal rearrangement of the strained molecule are well documented reactions. We have been interested in the activation of carbon monoxide in the system which is constituted of small ring compounds and transition metal complexes, and the recent paper[3] prompted us to report our preliminary results on the carbonylation of oxiranes to yield β-lactones.[4]

Oxirane, methanol, and trans-chlorocarbonyl bis(triphenylphosphine)rhodium(I) were placed in a stainless steel autoclave, and were reacted under carbon monoxide atmosphere. The results under various reaction conditions are summarized in the table.

As run 3 shows, following reaction takes place.



(II)

(V)

mp. 51.5-52.5°C

Table Carbonylation of Oxiranes under Various Conditions

Run	1	2	3	4	5	6	7	8	9
Oxirane	I	I	II	II	II	II	III	IV	II
Oxirane(mmol)	148	296	220	220	220	220	160	110	220
Methanol(mmol)	160	328	330	330	330	330	330	330	330
Rh Complex(mmol)^{a}	1.5	1.4	4.6	3.2	3.7	3.4	3.1	3.2	3.1
CO Pressure(kg/cm^2)	28	30	28	100	100	100	100	100	50
Reaction Time(h)	170	14	20	20	20	2	20	56	10
Reaction Temp.(°C)	20	110	110	60	110	110	110	110	120
Absorbed CO(mmol)	80	40	220	10	58	27	8	2	38
Oxirane/Abs.CO(x100)	54	13	100	4.5	76	12	5.0	1.8	17
β-Lactone(%)	5.3	4.0	67^{c}		3.2^{d}	2.7^{d}			N.D.^{b}

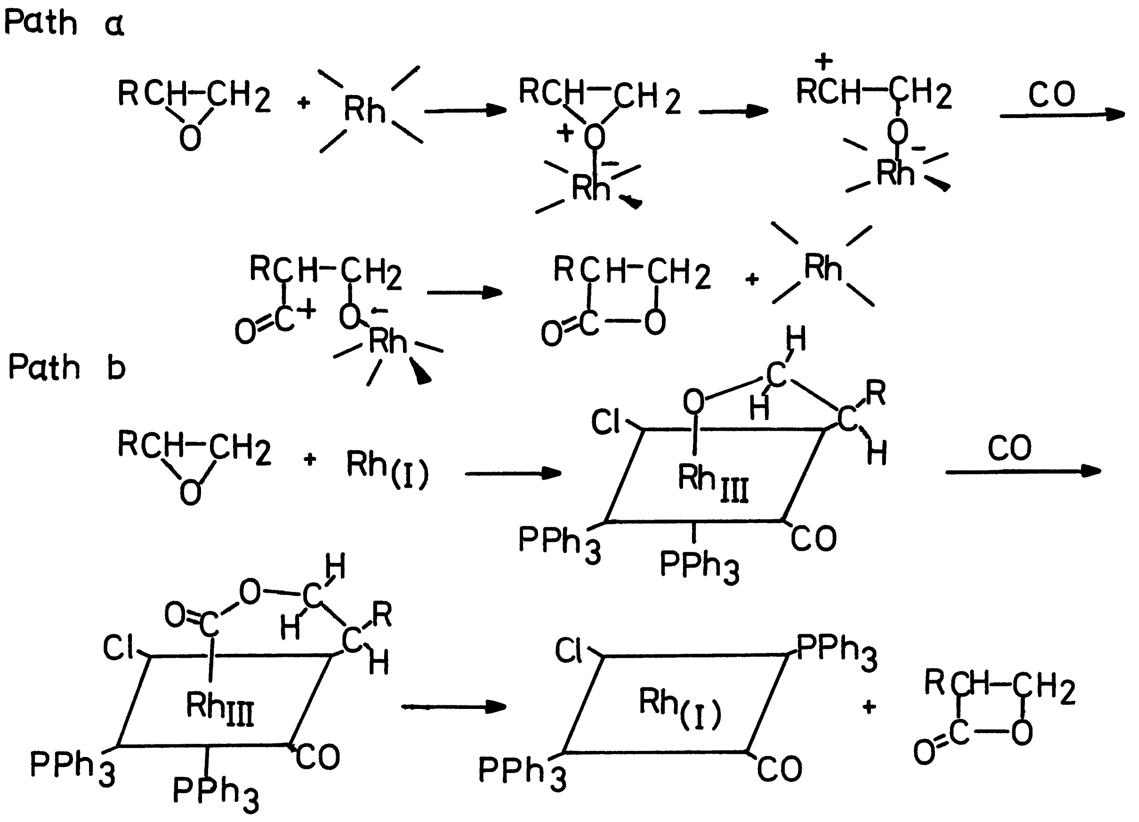
Oxirane: I Propylene Oxide II Styrene Oxide III Cyclohexene Oxide
IV trans-Stilbene Oxide

a. $RhClCO(PPh_3)_2$ b. Not determined c. Isolated yield d. Based on IR

α-Phenyl-β-propiolactone (V)[5] was isolated by continuous chromatographic separation and identified by its characteristic IR (1818, 1170, 1070 cm^{-1}) and PMR δ4.23(d,d, 1H, Hb, Jba=7.8, Jbc=8.4 Hz), 4.72(d,d, 1H, Hc), 5.62(t, 1H, Ha, Jab$\approx$Jbc=7.8 Hz), 7.34(s, 5H, aromatic) spectra. Further, alkaline treatment of (V) afforded α-phenyl-β-hydroxy propionic acid; mp. 60-61°C, IR 3200, 1700, 1080, 1040 cm^{-1}, PMR δ3.60(d, 2H, J=6.2 Hz, $-CH_2-$), 4.71(t, 1H, -CH-), 7.28(s, 5H, aromatic), thus supporting the structure of (V). It is noteworthy that the formation of β-lactone is the main reaction, since the previous reports describe only the production of β-hydroxy ester in the carbonylation of oxirane.[4,6]

Several factors affect the product distribution.[7] (1) Effect of carbon monoxide pressure: At the initial pressure of 28-50 kg/cm^2, no hydroxy ester formation(IR, 1735 cm^{-1}) was observed in the reaction mixture, and this fact shows that β-lactone was selectively formed. However, at higher pressure, both β-lactone and hydroxy ester were produced irrelevant to the reaction time. (2) Effect of temperature:[8] For the β-lactone formation, preferable reaction temperature exists around 100°C (run 3,4), although β-lactone is formed slowly even at room temperature for a certain oxirane (run 1).10) (3) Effect of solvent: It was found that methanol is a suitable solvent, and the use of benzene or the reaction without solvent did not afford β-lactone. (4) Reactivity and the structure of oxirane: Propylene oxide and styrene oxide react in a similar manner to give β-lactone, but the absorption of carbon monoxide was very slow for trans-stilbene oxide and cyclohexene oxide, and β-lactone was not produced.11) (5) Effective catalysts for the carbonylation:1) Besides reported $Co_2(CO)_8$4a), and $K_2Fe(CO)_4$4c), catalytic reactivity of $PdCl_2$, $Pd(OAc)_2$, $CoCl(PPh_3)_3$, $Pt(CO)_2(PPh_3)_2$, and $RhH(CO)(PPh_3)_3$ were investigated for the carbonylation of oxirane (II).12) Among them, only the rhodium complex was effective for β-lactone formation, while other catalysts afforded hydroxy ester, or acid anhydride.13)

Two paths are presumed for β-lactone formation ; the first is that rhodium catalyst is acting as a Lewis acid and interacts with the oxirane oxygen (path a), and the second is the oxidative addition of Rh(I) to the oxirane C-O bond (path b). Reaction schemes are shown below.



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References and Footnotes

1. K. G. Powell, and F. J. McQuillin, Chem. Comm., 931 (1971).
2. L. Cassar, P. E. Eaton, and J. Halpern, J. Am. Chem. Soc., 92, 3515 (1971).
3. The carbonylation of cyclopropane catalyzed by rhodium complex was recently reported. M. Hidai, M. Orisaku, and Y. Uchida, Chem. Lett., 1980, 753.
4. The carbonylation of oxirane to give β-hydroxy esters is reported.
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   b. R. F. Heck, J Am. Chem. Soc., 85, 1460 (1963).
   c. Y. Takegami, Y. Watanabe, T. Mitsudo, and H. Masada, Bull. Chem. Soc. Jpn., 41, 158 (1968).
5. Very small amounts of the isomer of (V), β-phenyl-β-propiolactone, have been obtained, which was indicated by similar IR with that of (V) but showed different TLC values.
6. In some cases, β-hydroxy ester (IR 1735, 1215 cm^{-1}) was also detected in the reaction mixture.
7. Mass balance and other products were not investigated precisely. One of the side reactions is the addition of methanol to oxirane catalyzed by metal complex under the reaction conditions.
8. The reaction temperature higher than 120°C was not examined, since other rhodium-catalyzed reactions of oxiranes are known to occur at an elevated temperature.[9)]
9. J. Blum, B. Zinger, D. Milstein, and O. Buchman, J. Org. Chem., 43, 2961 (1978).
10. On prolonged reaction, propylene oxide reacted to afford α-methyl-β-propiolactone, while other oxiranes failed. Different reactivity of oxiranes related to their structures is discussed in the literature.[4c)]
11. This fact suggests that 1,2-disubstituted oxirane does not react under the employed reaction conditions.
12. Concentration of each catalyst was 2-3mol% of the oxirane.
13. Detailed study will be reported later.

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