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REGIOSELECTIVE C-O BOND CLEAVAGE OF ALLYLIC PHENYL CARBONATES PROMOTED BY GROUP 8 TRANSITION METAL HYDRIDO COMPLEXES

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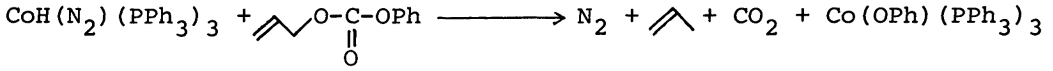
Carbon-oxygen bonds in allylic phenyl carbonates are selectively cleaved by hydrido complexes of Co, Ru and Rh to give $Co(OPh)L_3$, $RuH(OPh)L_2$ and $Rh(OPh)L_3$ with liberation of propylene and CO_2. An intermediate complex $RuH(O_2COEt)L_3$ has been isolated in the reaction of $RuH_2(PPh_3)_4$ with allyl ethyl carbonate. Reaction mechanisms are also discussed.

The allyl-O bond cleavage of organic substrates promoted by palladium to form π-allyl complexes and the subsequent attack of the π-allyl moiety by nucleophiles have been extensively applied to organic synthesis.$^{1)}$ Particularly, Pd-catalyzed C-O bond cleavage of allylic carbonates has been effectively utilized by Tsuji and others for synthesis of natural products. However, utility of transition metal complexes other than palladium to this type of reactions has been scarcely explored. Palladium(0) and nickel(0) complexes probably induce the C-O bond cleavage of allylic-O bonds by direct oxidative addition of the substrates to the metal as established in certain cases.$^{2)}$ On the other hand, hydrido- and alkyl-transition metal complexes may take a different course in their reactions with allylic compounds because of somewhat anionic nature of the hydrido or alkyl ligand.$^{3)}$ We now report the first evidence that the allylic C-O bond cleavage promoted by cobalt, rhodium and ruthenium hydrido triphenylphosphine complexes takes clearly different course from that promoted by palladium complexes.

The reaction of $CoH(N_2)(PPh_3)_3$, **1**, with allyl phenyl carbonate smoothly proceeds at 20 °C to give phenoxotris(triphenylphoshine)cobalt(I), **2**, accompanied by evolution of equimolar amounts of dinitrogen, carbon dioxide and propylene per mol of **1**.

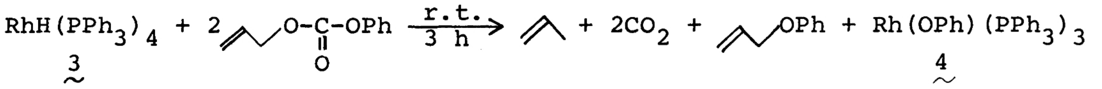


(1)

1 **2**

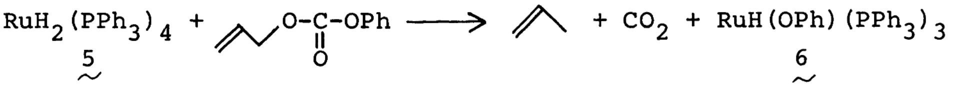
Complex 2 was fully characterized by elemental analysis, IR spectroscopy, magnetic susceptibility, X-ray structural analysis[4)] and chemical reactions. 2: mp (decomp); 178 °C. Found: C, 76.5; H, 5.4; Co, 6.4%. Calcd: C, 76.8; H, 5.4; Co, 6.3%. Complex 2 can be also prepared through an independent route by the reaction of 1 with phenol. Magnetic susceptibility of 2 (3.3 B.M.) suggests a high spin d^8 tetrahedral structure with two unpaired electrons. IR spectrum of 2 shows a strong ν(C-O) band at 1280 cm^{-1}, characteristic of transition metal phenoxide. Acidolysis of 2 with dry HCl liberates a quantitative yield of phenol per Co.

Similar C-O bond cleavage reaction takes place in the reaction of RhH(PPh$_3$)$_4$, 3, with allyl phenyl carbonate at room temperature. In this case, a decarboxylation reaction of allyl phenyl carbonate catalyzed by 3 partly takes place in the same reaction system to give allyl phenyl ether (ca. 1 mol/3), carbon dioxide (ca. 2 mol/3), propylene and Rh(OPh)(PPh$_3$)$_3$, 4, according to the following equation.

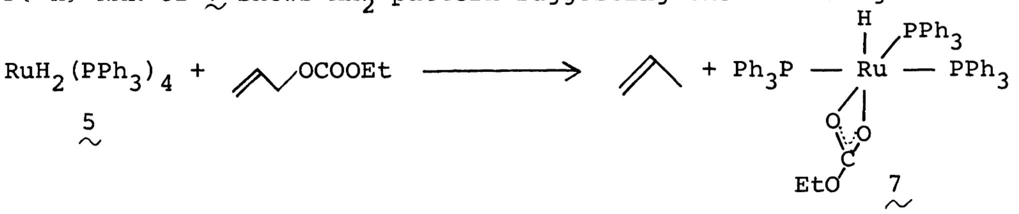

(2)

Prolonged rection time increases the yield of CO$_2$ and allyl phenyl ether. The isolated complex, 4, is characterized by elemental analysis as well as by comparing its IR data with those reported in the literature.[5)]

Reaction of RuH$_2$(PPh$_3$)$_4$, 5, with allyl phenyl carbonate also proceeded to afford RuH(OPh)(PPh$_3$)$_4$, 6,[6)] with liberation of quantitative amounts of C$_3$H$_6$ and carbon dioxide.


(3)

Generation of the phenoxide complexes on interaction of these hydrido complexes with allyl phenyl carbonate suggests the intermediate formation of phenylcarbonato complexes. Although the phenylcarbonato complex was not isolated in these reactions, probably owing to the rapid decarboxylation, an analogue of the supposed intermediate, RuH(O$_2$COEt)(PPh$_3$)$_3$ (7), was isolated in the reaction of RuH$_2$(PPh$_3$)$_4$ with allyl ethyl carbonate with concomitant evolution of one equivalent of propylene. Complex 7 was characterized by IR and NMR spectroscopy and elemental analysis. 7: Found: C, 69.9; H, 5.2%. Calcd: C, 70.0; H, 5.3%. ^{1}H-NMR (in CD$_2$Cl$_2$ at room temperature): δ: -18.66 (1H, q, J=28.3 Hz) for Ru-H; 0.86 (3H, t, J=6.8 Hz) for OCH$_2$CH$_3$; 3.55 (2H, q, J=6.8 Hz) for OCH$_2$CH$_3$. ^{31}P{^{1}H}-NMR of 7 shows AX$_2$ pattern suggesting the following structure.[7)]


(4)

In fact, thermolysis of ethylcarbonato complex 7 at 80 °C in toluene caused decarboxylation liberating CO$_2$ (100%) and CH$_4$ (82%). The resulting complex was characterized as $RuH_2(CO)(PPh_3)_3$ (75%) based on IR spectrum showing the ν(C≡O) band at 1940 cm^{-1}.[8)]

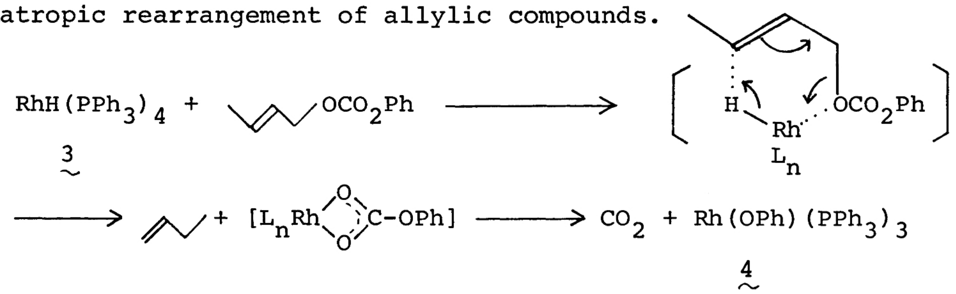
$$\underset{\mathbf{7}}{RuH(O_2COEt)(PPh_3)_3} \xrightarrow[\text{in toluene}]{80\ °C\ \text{for 3 h}} CO_2 + CH_4 + RuH_2(CO)(PPh_3)_3 \qquad (5)$$

The carbonyl complex $RuH_2(CO)(PPh_3)_3$ and methane have been probably formed by further thermolysis of an ethoxo complex formed by decarboxylation of 7.

In order to obtain further insight into mechanism of the C-O bond cleavage of allyl phenyl carbonate, reaction of substituted allyl phenyl carbonates were examined. The reaction of 3 with an excess amount of 2-butenyl phenyl carbonate liberated CO_2 and only 1-butene.

(6)

The high regioselectivity in the product olefin in the C-O bond cleavage demonstrated in the present study strongly suggests involvement of the following S_N2' type reaction mechanism accompanying the double bond shift, similar to the sigmatropic rearrangement of allylic compounds.

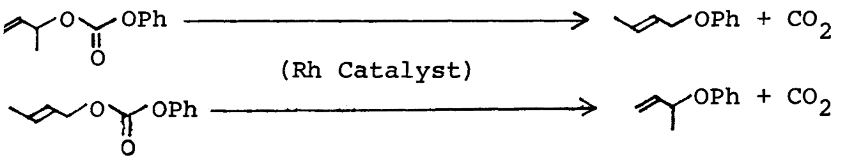


(7)

The actual reaction of 3 with the allylic phenyl carbonate may proceed through insertion of the allylic double bond into Rh-H bond followed by β-elimination of the phenylcarbonato entity by rhodium. Formation of 1-butene as the sole reaction product in the reaction of 3 with the allylic phenyl carbonate are not compatible with the direct oxidative addition of allylic phenyl carbonate to Rh(I) followed by reductive elimination of the hydrido-allylic lagands. The process would yield 2-butene from 2-butenyl phenyl carbonate in disagreement with the present result. The reaction of 3 with 1-methyl-2-propenyl phenyl carbonate liberated CO_2 and a mixture of 1-butene and 2-butene, the retio between 1-butene and 2-butene depending on reaction conditions. The formation of 2-butene in this reaction is elucidated by a similar S_N2' mechanism to that depicted above, whereas 1-butene seems to originate from the reaction of 3 with 2-butenyl phenyl ether which was formed by a $Rh(OPh)(PPh_3)_3$-catalyzed decarboxylation of 1-methyl-2-propenyl phenyl carbonate (vide infra, Eq. 8 and Mechanism). Actually, evolution of CO_2 prior to that of butenes was observed in the reaction of 3 with 1-methyl-2-propenyl phenyl carbonate, and a reaction of 3 with 2-butenyl phenyl ether gave 1-butene.

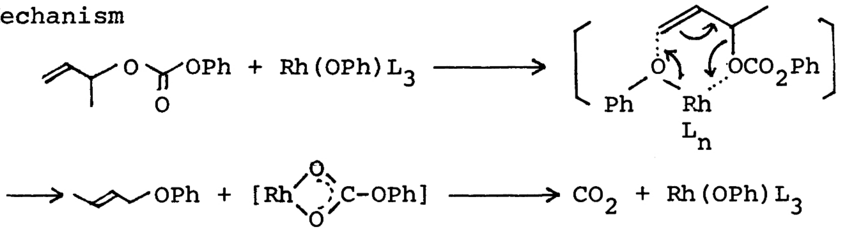
Similar reaction of 1 and 5 with the allylic phenyl carbonates with the CH_3-substituent have been less clear-cut than those of Eq. 6, and mixtures of 1-butene and 2-butene have been produced. The butenes may have been formed by isomerization of 2-butene and 1-butene, originally produced as in Eq. 6, catalyzed by the hydrido complexes 1 and 5 which are known to catalyze the double bond migration.[9)]

The regioselectivity in the allyl-O bond cleavage promoted by the cobalt, rhodium, and ruthenium complexes different from that promoted by palladium complexes provides an opportunity for synthetic applications. One example is the decarboxylative allylic ether formation from allylic carbonate catalyzed by rhodium complexes.



(8)

Mechanism



The details of these catalytic reactions will be reported separately.[10)]

References

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