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C-O BOND CLEAVAGE IN ALLYL PHENYL ETHER INDUCED BY THE PHOTOREACTION OF A HYDRIDOCOBALT COMPLEX

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C-O bond cleavage in allyl phenyl ether giving propylene has been found to proceed *via* an identical intermediate with that for catalytic double-bond migration giving propenyl phenyl ether by means of laser flash photolysis and product analysis for continuous irradiation.

We have reported that laser pulse excitation of hydridotetrakis(diethyl phenylphosphonite)cobalt(I) ($HCoP_4$: P = $(EtO)_2PPh$) induces the dissociation of P to give a transient coordinatively unsaturated species ($HCoP_3$),[1)] which is none other than a catalytic species for the double-bond migration of olefins.[2,3)] The photochemical double-bond migration was shown to proceed *via* following steps: 1) the coordination of an olefin to $HCoP_3$; 2) the insertion of the coordinated olefin into H-Co bond; 3) the elimination of β-hydrogen and CoP_3 leading to $HCoP_3$.[3)] We describe here the results of attempted catalytic double-bond migration in allyl phenyl ether.

A benzene solution (10 ml) of allyl phenyl ether (1.00 mmol) and $HCoP_4$ (0.100 mmol) was irradiated under anaerobic conditions at ambient temperature for 2 h using a super-high pressure mercury lamp and a Pyrex optical system. Main reaction products were found to be derived from C-O bond cleavage in allyl phenyl ether, i.e., propylene (0.079 mmol) and phenol (0.091 mmol).[4)] The catalytic double-bond migration leading to propenyl phenyl ether (0.021 mmol) took place a little, but it can be considered to be negligible as compared with the fact that almost all allylbenzene (1.00 mmol) and a half of 1-hexene (0.548 mmol) isomerized to β-methylstylene and 2-hexene, respectively, in the same conditions. Rather good material balances of $HCoP_4$ and phenol (or propylene) suggest that $HCoP_3$ was consumed in a path giving phenol and propylene.

Table 1 shows second order rate constants (k_2) for the coordination of olefins to $HCoP_3$ obtained by means of laser flash photolysis.[3)] k_2 for allyl phenyl ether is even lager than that for allylbenzene (1.3×10^8 $M^{-1}s^{-1}$) and 1-hexene (1.2×10^8 $M^{-1}s^{-1}$), that is, the ether oxygen does not have any inhibitory effects on the coordination. Moreover, by refering k_2 for propyl phenyl ether, it is obvious that a possibility for the coordination of an ether oxygen to $HCoP_3$ can be excluded.

The observations can, therefore, be cleary explained by Scheme 1. The elimination of $HCoP_3$ (Path A) from intermediate <u>3</u>, which arised from the insertion of coordinated allyl phenyl ether to H-Co bond, gives propenyl phenyl ether, and the catalytic cycle can be maintained. On the other hand, the elimination of $PhOCoP_3$ (Path B) from <u>3</u> yields propylene. Though double-bond migration did occur in this case too, $PhOCoP_3$ could not maintain any catalytic cycles and may react with P to afford $PhOCoP_4$.[5)]

Hayashi *et al.*, have reported that C-O bond cleavage in the derivatives of allyl alcohol occurred in the dark reactions with some cobalt, ruthenium, and rhodium complexes.[6)] In order to explain the regioselectivity of those reactions, they assumed an S_N2' type mechanism as shown in Scheme 2, in which the coordination of an allylic compound through oxygen to metal seems to have an important role. At least in our case, however, the S_N2' type mechanism appears not to be reasonable, because k_2 for propyl phenyl ether is negligibly small, namely, the coordination of allyl phenyl ether must take place through the double-bond leading to 3, if not the case, $HCoP_3$ will disappear by the re-coordination of P ($1.4\times10^8\ M^{-1}s^{-1}$).[3)]

Intermediate 3 can be derived from propenyl phenyl ether. Indeed, *cis*- and *trans*-propenyl phenyl ether gave propylene (0.084 and 0.078 mmol, respectively) and phenol (0.069 and 0.071 mmol, respectively) in the same conditions as the continuous irradiation. It should be noted that intermediate 4 is impossible for propenyl phenyl ether.

In conclusion, the present results strongly suggest that both the C-O bond cleavage and the catalytic double-bond migration proceed *via* an identical intermediate 3 and the competitive elimination of a β-hydrogen or a phenoxy group from 3 decides the direction realized. The fact that CoP_3 preferentially sellected a phenoxy anion as the fourth ligand indicates that cobalt(I) bearing only three phosphorus-ligands has a deficit in electron dencity.

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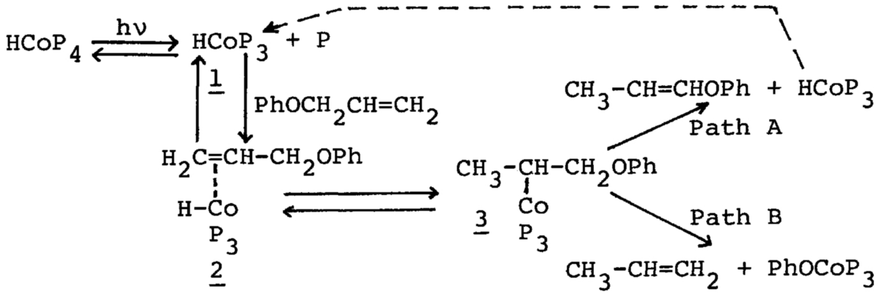
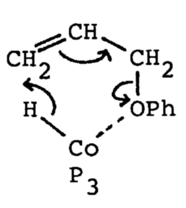
Table 1. Absolute second order rate constant for the coordination of olefins to $HCoP_3$ obtained by means of laser flash photolysis.

PhO-R R:	$-CH_2CH_2CH_3$	$-CH_2CH=CH_2$	$-CH=CHCH_3$ (*cis*)	$-CH=CHCH_3$ (*trans*)
k_2 $M^{-1}s^{-1}$	$<10^2$	1.9×10^8	9.5×10^7	2.0×10^7



Scheme 1.



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Scheme 2.

References
1) S. Oishi, K. Tajime, A. Hosaka, and I. Shiojima, J. Chem. Soc. Chem. Commun., 1984, 607. 2) M. Onishi, K. Hirai, M. Matsuda, and T. Fukunaga, Chem. Lett., 1983, 261. 3) S. Oishi, N. Kihara, and A. Hosaka, J. Organomet. Chem., 276, C33 (1984). 4) No reaction has occurred in the dark within 72 h. Phenol was determined after the treatment of mixtures with 0.5 M sulfuric acid. ,5) The isolation of $PhOCoP_4$ has been so far unsuccessful, probably because of further degradation induced by irradiation. 6) Y. Hayashi, S. Komiya, T. Yamamoto, and A. Yamamoto, Chem. Lett., 1984, 977.

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