

FORMATION OF BENZOIC ACID IN THE PALLADIUM(II) CATALYZED CLEAVAGE OF
PHENYL-ANTIMONY AND PHENYL-PHOSPHORUS GROUPS OF Ph_3Sb AND Ph_3P

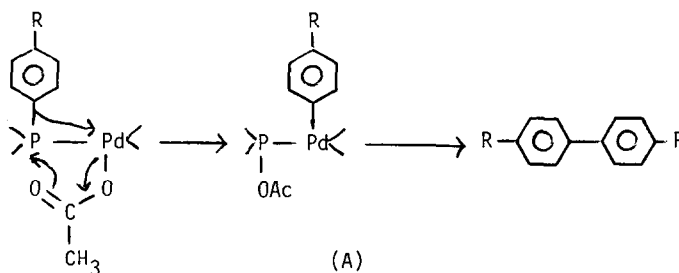
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ABSTRACT: Palladium (II) catalyzed cleavage of phenyl-antimony and phenyl-phosphorus groups of Ph_3Sb and Ph_3P under carbon-dioxide or CO/NO atmosphere leading to benzoic acid, has been demonstrated.

Studies concerning the process of catalyst degradation in the course of homogeneous transition metal catalyzed organic synthesis have become a very important field of research in recent years^{1,2}. Such a catalyst decay process generally occurs via an interaction of the metal with the ligands in some undesired manner leading to various by-products. Recently we reported a similar unexpected interaction of triphenylstibene with palladium (II) salts resulting in the cleavage of phenyl-antimony bonds². Now we wish to report here for the first time the formation of benzoic acid in the palladium (II) catalyzed cleavage of phenyl-antimony and phenyl-phosphorus groups of Ph_3Sb and Ph_3P under oxy-carbonylation conditions.

Similar to earlier reported reaction of Ph_3Sb with Pd(II) salts, the reaction of Ph_3P with $\text{Pd}(\text{OAc})_2$ in toluene at $>80^\circ\text{C}$ has been found to produce phenyl group containing organic products such as biphenyl, benzene and phenyl acetate in approximately 60, 18 and 5% yields (based on Pd). When tri(*p*-tolyl) phosphine was used instead of Ph_3P , the only coupling product was found to be 4,4'-dimethylbiphenyl. The absence of any 3,3'-dimethylbiphenyl, the expected product via the ortho-metalation process as proposed earlier in similar systems³, rules out the possibility of the phenyl group migration from phosphorus to palladium by the process of oxidative addition of the ortho C-H bond. In a reaction containing equimolar amounts of triphenyl phosphine and tri-*p*-tolylphosphine with $\text{Pd}(\text{OAc})_2$, three coupling products, i.e. biphenyl (homo-coupling of phenyl groups), 4,4'-dimethylbiphenyl (homo-coupling of tolyl groups) and 4-methylbiphenyl (hetero-coupling of phenyl and tolyl groups) were formed and the amounts of tolyl groups in these products were found to be approximately 10% higher than that of phenyl groups. These results suggest a possible mechanism outlined in Scheme 1 involving nucleophilic attack of acetate group on the coordinated phosphine for the migration of aryl groups from

Scheme 1

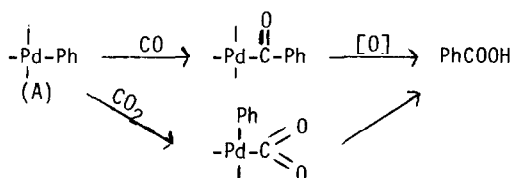


phosphorus to palladium. Formation of coupling product (or products) from an intermediate of the type (A) can be the result of a bimolecular mechanism or a radical process⁴.

When the above reaction of triphenylphosphine or triphenylstibene with palladium (II) salt was carried out in an atmosphere of CO₂ at 180-200°C formation of benzoic acid was observed to be the major product (15-40% yield based on Pd). Higher yields were obtained in the case of Ph₃Sb compared to that of Ph₃P suggesting a weaker Ph-Sb bond. Interestingly, when these reactions were carried out under the pressure of CO/NO/N₂, much higher (up to 6 times) yields of benzoic acid were obtained.

In a typical reaction, when Ph₃Sb (20 mmols) and PdCl₂ (10 mmols) dissolved in toluene (70 ml) were allowed to react in an autoclave (300 ml capacity) at 200°C under an atmosphere of CO/NO/N₂ (approximately 1:1:3) at 2300 psig (final pressure) for 3 hrs, about 50 mmols of benzoic acid were produced along with some benzophenone and anthraquinone. Although, a mixture of CO and NO under the above reaction conditions is known to generate CO₂ along with several other molecules, much higher amounts of benzoic acid formed in this reaction compared to that of with CO₂ alone, might suggest that the majority of the product in the former case is forming via the CO insertion into the Ph-Pd of intermediate (A) (Scheme 2) rather than the CO₂ insertion. Furthermore the formation of benzophenone and anthraquinone in the reaction with CO + NO supports the CO insertion over CO₂ insertion.

Scheme 2



Efforts are being made to confirm the above proposed mechanism and various experiments are in progress to determine whether or not other group VIII metal salts also catalyze the cleavage of C-P bonds of the tertiary phosphines.

REFERENCES:

- 1 D.R. Coulson, *J. C. S. Chem. Commun.*, 1530 (1968); R. Cramer and D.R. Coulson, *J. Org. Chem.*, **40**, (1975); C.W. Bradford, R.S. Nyholm, G.J. Gainsford, J.M. Guss, P.R. Ireland and R. Mason, *J. C. S. Chem. Commun.*, 87 (1972); C.W. Bradford and R.S. Nyholm, *J. Chem. Soc., Dalton Trans.*, 529 (1973); D.R. Fahey and J.E. Mahan, *J. Am. Chem. Soc.*, **98**, (1976); J.R. Blickensderfer and H.D. Kaesz, *J. Am. Chem. Soc.*, **97**, 2681 (1975); T. Yamane, K. Kikukawa, M. Takagi and T. Matsuda, *Tetrahedron*, **29**, 955 (1973); K. Kikukawa, T. Yamane, Y. Ohbe, M. Takagi and T. Matsuda, *Bull. Chem. Soc. Jpn.*, **52**, 1187 (1979).
- 2 A.B. Goel, H.J. Richards and J.H. Kyung, *Inorg. Chim. Acta*, **76**, L95 (1983).
- 3 A.D. Ryabov and A.K. Yatsimirsky, *J. Mol. Cat.*, **4**, 449 (1978).
- 4 P.M. Henry, "Palladium Catalyzed Oxidation of Hydrocarbons", Vol. 2, p. 312, D. Reidel Publication, Boston, USA (1981).

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