Organic Synthesis by Means of Noble-metal Compounds. The Mechanism of Simultaneous Formation of Isocyanate and π-Allylpalladium Chloride from Sodium Chloropalladate, Allyl Chloride, Primary Amine, and Carbon Monoxide[1]

By J. TSUJI and N. IWAMOTO
(Basic Research Laboratories, Toyo Rayon Co., Kamakura, Japan)

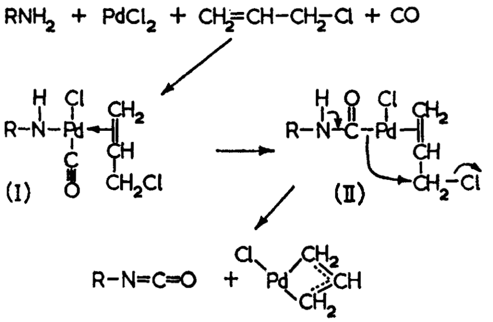
RECENTLY Shaw *et al.*, showed quite ingeniously the reaction mechanism of π-allylpalladium chloride formation from sodium chloropalladate, allyl chloride, water, and carbon monoxide.[2] In this mechanism, the essential reaction is the oxidative hydrolysis of carbon monoxide to carbon dioxide.

We have been investigating the interaction of carbon monoxide with amines in the presence of palladium chloride or metallic palladium, and have reported that urea or oxamide is formed. The palladium catalyst abstracts hydrogen from the amine.[3] Recently Stern and Spector have shown without giving a definite mechanism that isocyanate can be formed from primary amine, carbon monoxide, palladium chloride and sodium phosphate.[4] Certainly the isocyanate formation is an oxidative carbonylation of the amine.

A consideration of the mechanism of the π-allylpalladium chloride formation led us to investigate the reaction of primary amine, carbon monoxide, allyl chloride, and palladium chloride, and we find that both π-allylpalladium chloride and isocyanate can be formed together by the reaction. Thus n-butylamine, allyl chloride, palladium chloride, and sodium chloride were mixed in benzene, and carbon monoxide was passed for 2 hr. at 60° with stirring. Brown palladium chloride went into solution slowly. Examination of an infrared spectrum of the reaction mixture showed that the intensity of a band at 2270 cm.$^{-1}$ due to isocyanate increased with the reaction time. Finally the isocyanate was isolated as dibutylurea by the addition of an excess of butylamine. After evaporation of the solvent under reduced pressure, π-allylpalladium chloride was obtained.

In methanol, the reaction proceeded homogeneously and smoothly. Sodium chloride (4·5 g.) and palladium chloride (3·5 g.) were dissolved in methanol (150 ml.) by warming. Then butylamine (4·4 g.) and allyl chloride (16·5 g.) were added. Carbon monoxide was passed at room temperature for 1 hr. until the brown solution turned yellow. By distillation under reduced pressure, methyl n-butylcarbamate was obtained (1·3 g., 50%). From the residue, π-allylpalladium chloride was collected and recrystallized from chloroform (2·3 g., 62·4%). Only a negligible amount of metallic palladium was deposited.

The following mechanism is suggested for the reaction. Palladium chloride and amine form a complex when mixed, which is then transformed by the action of carbon monoxide and allyl chloride to the complex (I). The next step is carbon monoxide insertion into the palladium–nitrogen bond to form aminocarbonyl complex (II). Finally (II) collapses to form isocyanate and π-allylpalladium chloride. The net result is the abstraction of two hydrogen atoms from the amine by the oxidative action of palladium chloride. The stabilization of the reduced palladium by the formation of π-allylpalladium chloride is the driving force of the reaction. The mechanism of the isocyanate formation reported by Stern can be explained analogously; in this case, sodium phosphate certainly helps the abstraction of hydrogen from the amine.



(*Received, October 24th, 1966; Com.* 820.)

---

[1] Previous Paper, J. Tsuji and K. Ohno, *Tetrahedron Letters*, 1966, 4713.

[2] J. K. Nicholson, J. Powell, and B. L. Shaw, *Chem. Comm.*, 1966, 174.

[3] J. Tsuji and N. Iwamoto, *Chem. Comm.*, 1966, 380.

[4] E. W. Stern and M. L. Spector, *J. Org. Chem.*, 1966, **31**, 596.