

## Reaction of Co-ordinated Phosphines: Arylation of Olefins by Palladium(II) Acetate and Triarylphosphine

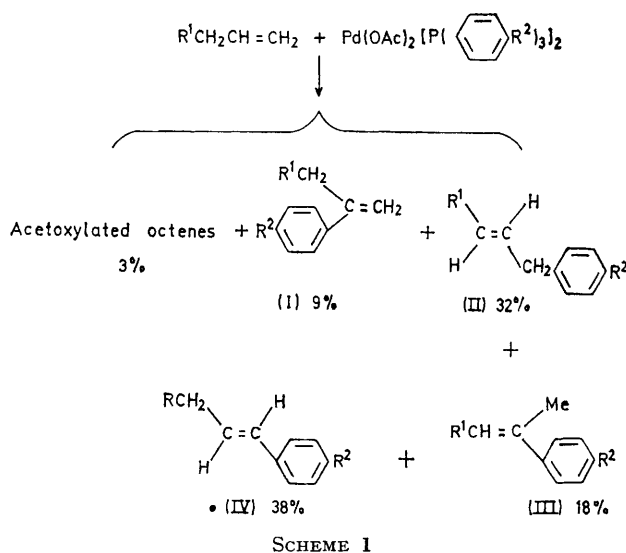
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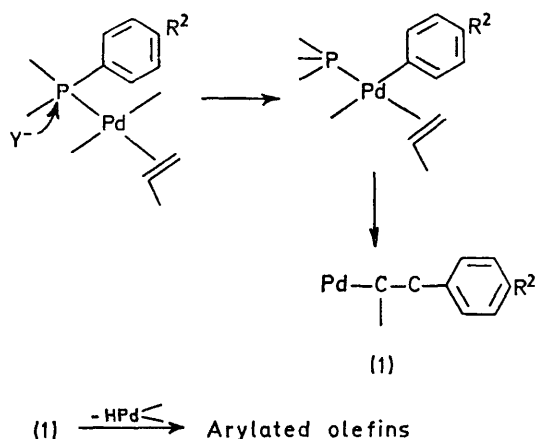
**Summary** Olefins are arylated by Pd(OAc)<sub>2</sub> and PAR<sub>3</sub>; a phenylpalladium complex is presumed to be an intermediate.

LITTLE is known about the reactivity of triarylphosphines co-ordinated to metal ions.<sup>1</sup> Here, we report a novel reaction of olefins with triarylphosphines co-ordinated to Pd(OAc)<sub>2</sub>.

The complex, Pd(OAc)<sub>2</sub>(PAR<sub>3</sub>)<sub>2</sub>, which on heating in acetic acid decomposes to biaryl and metallic palladium, reacted with olefins to produce the corresponding arylated olefins in good yield. A similar arylation occurred when a mixture of olefin and PAR<sub>3</sub> was added to Pd(OAc)<sub>2</sub> in acetic acid. However, excess of PAR<sub>3</sub> (> 2 moles per Pd atom) inhibited the arylation. The reaction between Pd(OAc)<sub>2</sub>[P(*p*-tolyl)<sub>3</sub>]<sub>2</sub> and oct-1-ene is formulated in Scheme 1.† The reaction of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>-NaOMe with oct-1-ene in methanol produced benzene (*ca.* 0.14 mole per mole of PPh<sub>3</sub>) instead of arylated octenes. These results suggest that a



† Little is known at present about the fate of the dearylated triarylphosphines, although a small amount of diphenylphosphinic acid was isolated.



SCHEME 2

nucleophilic substitution on phosphorus may be involved in the initiation of the reaction.<sup>2</sup>

The reaction was followed by g.l.c. and was complete in 1–2 h at 40 °C. With oct-1-ene (I), (II), and (IV) were produced. With cyclohexene the products were 3- and 4-phenylcyclohexene, while 1-phenylcyclohexene, the main product from the phenylation of cyclohexene with Pd(OAc)<sub>2</sub> and benzene,<sup>3</sup> was only detected in small amounts.† This is similar to the acetoxylation of cyclohexene and acyclic olefins by Pd(OAc)<sub>2</sub>.<sup>4</sup>

These observations strongly suggest a phenylpalladium intermediate (Scheme 2).

Other olefinic compounds such as styrene, hexa-1,5-diene, vinyl acetate, acrylonitrile, and ethyl acrylate are also arylated in good yield.

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† Considerable amounts (15–20%) of biphenyl were detected in both cases. The amount decreased as the reaction proceeded or on the addition of copper(II) acetate. Thus, it was probably produced during g.l.c. (ca. 250 °C).

<sup>1</sup> M. A. Bennett and L. L. Milner, *J. Amer. Chem. Soc.*, 1969, **91**, 6983.

<sup>2</sup> R. F. Hudson, 'Structure and Mechanism in Organo-Phosphorus Chemistry,' Academic Press, London, 1965.

<sup>3</sup> S. Danno, I. Moritani, and Y. Fujiwara, *Tetrahedron*, 1969, **25**, 4819.

<sup>4</sup> S. Wolfe and P. F. C. Campbell, *J. Amer. Chem. Soc.*, 1971, **93**, 1497.