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Aromatic Substitution of Olefins. XX. Reactions of Triphenylamine, -phosphine, -arsine, -stibine, and -bismuth with Styrene in the Presence of Palladium(II) Salts

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We reported[1–3] that direct substitution of benzene derivatives with olefins can take place in the presence of palladium(II) salts, and that nonbenzenoid aromatic compounds such as ferrocene, furan and thiophene can also react with olefins to give alkenyl-derivatives. In continuation of these studies we wish to determine the reactivity of triphenylphosphine, which has both aromatic ring and donor P atom, toward olefins. Extensive studies on reactions of triphenylphosphine with transition metals have been carried out. It is well known that phosphine metal halide complexes form an internal metal-carbon bond.[4] However, little is known about the reaction of triphenylphosphine in the presence of transition metal compounds involving the cleavage of the phosphorus-carbon bond.[5] In this paper we report a study of the reaction of styrene with triphenylamine, -phosphine, -arsine, -stibine, or -bismuth.

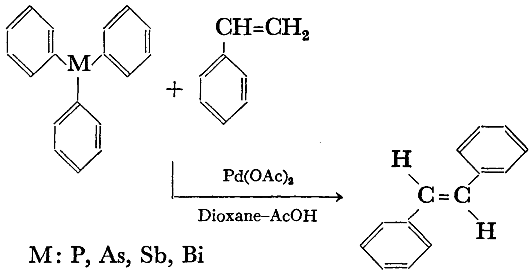
Table 1. Reaction of styrene with group V triphenyl-compounds by palladium (II) acetate[a]

Triphenyl-compound	Product and yield, %[b]	
NPh_3	*trans-p*-Diphenylaminostilbene	41
PPh_3	*trans*-Stilbene	64
	Methyldiphenylphosphine oxide	22
$AsPh_3$	*trans*-Stilbene	99
	Biphenyl	14
$SbPh_3$	*trans*-Stilbene	67
	Biphenyl	108
$BiPh_3$	*trans*-Stilbene	7
	Biphenyl	108
	trans, trans-1,4-Diphenylbutadiene	11
$BiPh_3$[c]	Biphenyl	3
	Benzene	
$P(p\text{-}CH_3C_6H_4)_3$	*trans-p*-Methylstilbene	41
	p,p'-Dimethylbiphenyl	3
	Methyldi-*p*-tolylphosphine oxide	10
$PdCl_2(PPh_3)_2$[d]	*trans*-Stilbene	3

a) Equimolar amounts of the triphenyl-compound, styrene, and palladium (II) acetate were used. All the reactions were carried out under reflux for 6 hr. b) Yields are based on palladium (II) acetate. c) The reaction was carried out in the absence of palladium (II) acetate. d) Dichlorobis (triphenylphosphine) palladium (II) was used in place of triphenylphosphine and palladium (II) acetate.

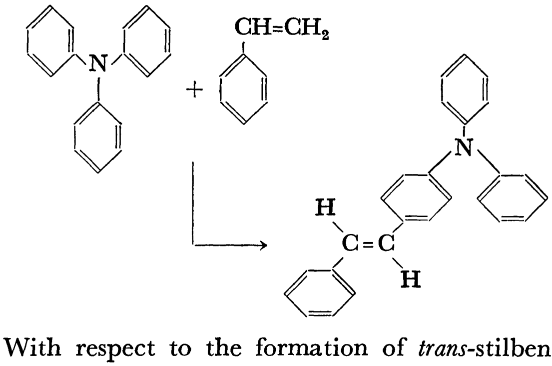
Results and Discussion

A solution of styrene, triphenylphosphine (1 mol equiv.), palladium(II) acetate (1 mol equiv.) in acetic acid and dioxane was stirred under relux for 6 hr, to give *trans*-stilbene (64%) with methyldiphenylphosphine oxide and metallic palladium. Reactions with other group V triphenyl-compounds such as triphenylamine, -arsine, -stibine, and -bismuth were carried out under similar reaction conditions. The results are given in Table 1. It is evident that these triphenyl-compounds can easily react with styrene to give *trans*-stilbene involving the cleavage of the M–C bond except for the case of triphenylamine (Eq. (1)).



(1)

In the reaction of triphenylamine with styrene, the product is not *trans*-stilbene but *trans-p*-diphenylaminostilbene which is the normal substitution product (Eq. (2)). This may be due to the higher energy of the N–C bond.



(2)

With respect to the formation of *trans*-stilbene, the reactivity is in the order triphenylarsine>triphenylstibine≃triphenylphosphine>triphenylbismuth>triphenylamine. The donor ability decreases in the order $NPh_3>PPh_3>AsPh_3>SbPh_3\gg BiPh_3$,[6] and the M–C bond energy increased in the same order $M=Bi<Sb<As<P<N$.[7] The yields of *trans*-stilbene for the tri-

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[3] R. Asano, I. Moritani, Y. Fujiwara, and S. Teranishi, This Bulletin, **46**, 663 (1973).

[4] G. W. Parshall, *Accounts Chem. Res.*, **3**, 139 (1970).

[5] K. Kikukawa, T. Yamane, M. Takagi, and T. Matsuda, *Chem. Commun.* **1972**, 695.

[6] S. Murahashi, "Yūkikinzoku Handobukku," Asakura Shoten, Tokyo (1967), p. 706.

[7] T. Saito, "Kaisetsu Yūkikinzoku Kagaku," Hirokawa Shoten, Tokyo (1970), p. 4.

phenyl-compounds are shown as a function of the M–C bond energies in Fig. 1. The results suggest that the formation of *trans*-stilbene depends on donor ability and M–C bond energy. Increase in donor ability and decrease in bond energy result in the ease with which the M–C bond cleavage takes place. Triphenylarsine which has the desired donor ability and M–C bond energy is found to be the most reactive.

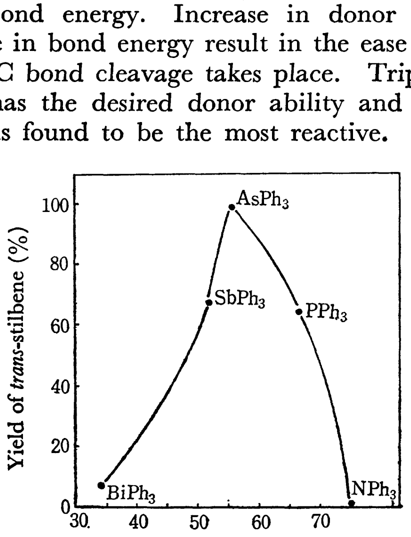
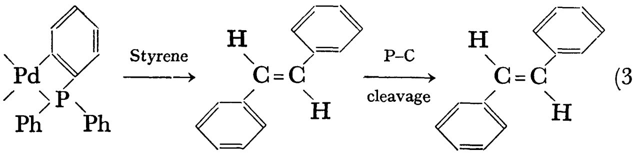


Fig. 1. Relation between the M–C bond energy of MPh_3 and yield of *trans*-stilbene.

Concerning the reaction of triphenylbismuth having less donor ability, biphenyl is formed as a major product accompanied by a small amount of *trans*-stilbene. When the reaction of triphenylbismuth with styrene is carried out in the absence of palladium(II) acetate, benzene is formed exclusively with a small amount of biphenyl.

It is well known that an *ortho*-metallation takes place in the reaction of transition metals and triphenylphosphine.

In order to examine whether the reaction proceeds *via* the *ortho*-metallation (Eq. (3)), the reaction of tri-*p*-tolylphosphine with styrene was carried out, producing *trans*-*p*-methylstilbene in 41% yield. This indicates that the Pd–C bond would be formed after the P–C bond fission, and that Eq. (3) might not be the case.



(3)

Experimental

Infrared spectra were recorded on an IR-E spectrometer (Japan Spectroscopic Co.). NMR spectra were obtained with a JEOL C-60HL spectrometer, with tetramethylsilane as an internal standard. Mass spectra were obtained with a Hitachi RMS-4 spectrometer.

Materials. Palladium(II) acetate was prepared according to the procedure of Wilkinson *et al.*[8] Dichlorobis(triphenylphosphine)palladium(II) was obtained by treating palladous chloride with a saturated benzene solution of triphenylphosphine. Triphenylamine, -phosphine, -arsine, -stibine, -bismuth, and tri-*p*-tolylphosphine were of commercial grade. Commercial styrene was purified. Acetic acid was dried over phosphorus pentoxide for 1 week and distilled. Dioxane was refluxed with sodium metal and distilled. Light petroleum refers to a fraction of bp 38—60 °C.

General Procedure for the Reaction of the Group V Triphenyl Compounds with Styrene. Solutions containing equimolar amounts of palladium(II) acetate, styrene, and the triphenyl compound in acetic acid and dioxane, were stirred for 6 hr under reflux. The resulting mixture was filtered to remove palladium metal. The filtrate was poured into water, and the mixture was extracted with chloroform. The extract was washed with aqueous sodium bicarbonate and water, dried (Na_2SO_4) and evaporated. The products were isolated by alumina column or gas chromatography and identified by comparison (mixed mp, IR, and NMR spectra) with authentic samples. A specific example of the reaction is as follows.

Reaction of Triphenylphosphine with Styrene. To a solution of styrene (1.56 g, 15 mmol), triphenylphosphine (3.93 g, 15 mmol), and palladium(II) acetate (3.37 g, 15 mmol) in dioxane (160 ml) was added acetic acid (40 ml) and the mixture was stirred for 6 hr under reflux ($CaCl_2$ guard tube). After work-up the residue was chromatographed on a column of alumina (100 g). Elution with light petroleum (1200 ml) gave *trans*-stilbene (1.57 g, 64%). Elution with ether (700 ml) gave triphenylphosphine oxide (1.13 g). Further elution with chloroform (900 ml) and recrystallization from light petroleum gave 0.72 g (22%) of methyldiphenylphosphine oxide, mp 110.5—111.5 °C (lit,[9] 109—111 °C). Finally elution with methanol (300 ml) gave tarry material (0.13 g) which was not further examined.

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9) H. Hoffmann, R. Grünewald, and L. Horner, *Chem, Ber.*. **93**, 861 (1960).