

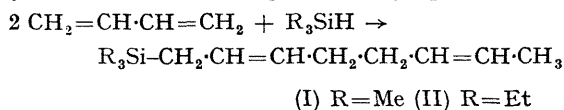
Novel Hydrosilylation of Butadiene catalysed by a Palladium Complex

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LOW-VALENT PALLADIUM COMPLEXES catalyse the linear dimerization of butadiene.¹ We now report the reaction of butadiene with silanes in the presence of palladium complex catalysts.

Low-valent palladium-phosphine complexes catalyse a novel hydrosilylation of butadiene on addition of silicon hydrides to butadiene dimer. Dried butadiene (6.5 g.), trimethylsilane (6.4 g.), benzene (20 ml.), and bis(triphenylphosphine)(maleic anhydride)palladium (219 mg.)² (85°, 4.5 hr.) gave a single, easily separable product (g.l.c.), (I) (98%, colourless liquid, b.p. 125—127°/95 mm., n_D^{20} 1.4543), a 1:2 trimethylsilane-butadiene adduct (elemental analysis and molecular weight). The proposed structure,



1-trimethylsilylocta-2,6-diene, completely satisfied all the spectroscopic observations: i.r., $\nu_{\text{C}=\text{C}}$ 1655 cm^{-1} ; $\delta_{\text{Si-Me}}$ 1247 cm^{-1} , no band attributed to the terminal vinyl group; n.m.r. τ 4.5—4.9 (—CH=); 7.8—8.1 (=C—CH₂—CH₂—C=); 8.38 (d, $J = 5$ c./sec., CH₃—C=); 8.5—8.7 (Si—CH₂—C=); 9.98 (s, Si—CH₃); ratio 4:4:3:2:9.

Bis(triphenylphosphine)(*p*-benzoquinone)palladium² was also found to be effective, but tetrakis(triphenylphosphine)-palladium³ and -platinum⁴ were much less effective.

Butadiene with triethylsilane gave selectively also

triethylsilylocta-2,6-diene [(II), b.p. 107—110°/4 mm. n_D^{20} 1.4690), 84%], but trichlorosilane and dimethylphenylsilane gave only the normal hydrosilylation products (butadiene-silane 1:1 adducts).

Dependence of yield of (I) on reaction temperature

Solvent	Temp.	Time (hr.)	Yield of (I)
C ₆ H ₆	65°	5.0	85%
C ₆ H ₆	85	4.5	98
C ₆ H ₆	110	6.5	74
THF	85	4.5	96

It is known⁵ that the metal complexes catalyse the hydrosilylation of olefins, dienes, and acetylenes. The palladium catalysts give the 1:2 adduct silane-butadiene to the complete exclusion of the 1:1 adduct; the reaction is thought to proceed by a mechanism different from that proposed¹ for the dimerization of butadiene with alcohols, since the former gave selectively octa-2,6-diene derivatives, while the latter gave octa-2,7-diene derivatives. The complex Pt(Ph₃P)₄ reacts⁶ with silicon hydrides to form the hydride complexes, PtH(SiR₃)(Ph₃P)₂. This suggests that the novel hydrosilylation of butadiene catalyzed by the palladium complex proceeds through a palladium hydride intermediate, by insertion of butadiene into the palladium-hydrogen bond.

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³ L. Malatesta and M. Angoletta, *J. Chem. Soc.*, 1957, 1186.

⁴ L. Malatesta and C. Cariello, *J. Chem. Soc.*, 1958, 2323.

⁵ See, for example, J. F. Harrod, and A. J. Chalk, *J. Amer. Chem. Soc.*, 1965, **87**, 1133.

⁶ J. Chatt, C. Eaborn, and P. N. Kapoor, *J. Organometallic Chem.*, 1968, **13**, 21.