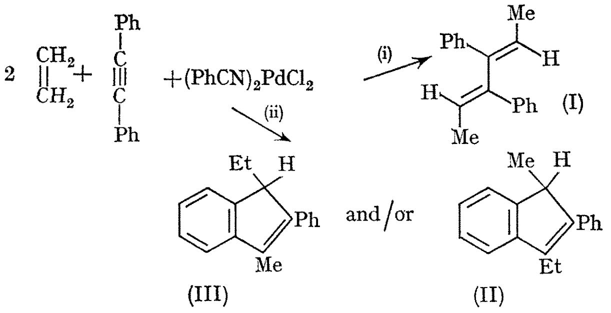
A Novel Palladium(II) Chloride-promoted Addition–Rearrangement Reaction of Terminal Olefins with Diphenylacetylene

By PAUL MUSHAK and MERLE A. BATTISTE*

(*Department of Chemistry, University of Florida, Gainesville, Florida* 32601)

Summary In the presence of palladium(II) chloride, ethylene and certain terminal olefins react with diphenylacetylene to give substituted alka-1,3-dienes derived from the symmetrical addition of two olefin units to the acetylenic reactant.

IN the course of a related study of the cycloaddition reactions of π-olefinic palladium(II) compounds, we have observed that ethylene and certain terminal olefins in the presence of palladium(II) chloride undergo reaction with diphenylacetylene (tolan) to furnish hydrocarbon products arising from addition, with rearrangement, of two olefin units to one of the acetylenic reactant. These transformations constitute a novel departure from documented palladium(II)-mediated processes of olefin dimerization[1] and tolan trimerization[2] as well as a one-step procedure for the synthesis of variously substituted alka-1,3-dienes.



Conditions: (i) heat, 4—6 hr.; (ii) heat, 24 hr.; heat, HCl, 3 hr

The reaction with ethylene has been carried out under a variety of experimental conditions. Treatment of a mixture of tolan and a frozen solution of dichlorobis(benzonitrile)palladium(II) in benzene with an excess (relative to tolan) of ethylene followed by heating at 80° for periods of 4—6 hr. furnishes as the main product (35—40% yield) *trans,trans*-3,4-diphenylhexa-2,4-diene (I), m.p. 100—101°, identified by n.m.r., i.r., and mass spectral analysis, as well as authentic-sample[3] comparison. G.l.c. analysis (10% hexamethylphosphoramide on Gas Chrom Q, 25°) of the gaseous reaction contents discloses that dimerization of ethylene to chiefly *trans*-but-2-ene also occurs. In addition, several metal-containing compounds were isolated, partial characterization of which suggests polymeric structures arising through competitive reaction(s) rather than intermediates leading to (I).

Reduction in the relative amount of metal reactant was without effect on the yield of (I), while prolongation of the reaction time to *ca.* 24 hr. led to isolation of reduced metal and a second compound of formula $C_{18}H_{18}$, characterized as the indene derivative, 3-ethyl-1-methyl-2-phenylindene (II).[4,5] Subsequent reactions carried out in this fashion provided variable data, in some cases a mixture of (II) and its isomer, 1-ethyl-3-methyl-2-phenylindene (III), being observed.

In view of the known[3] acid-catalysed rearrangement of (I) to (II), as well as the observed formation of HCl in the palladium chloride-catalysed dimerization reactions of ethylene,[1] it appears likely that HCl-promoted rearrangement of initially formed (I) to indene (II) is occurring on extended reaction. Thus, when benzene saturated with anhydrous HCl was used as solvent under conditions normally leading to formation of (I), exclusive formation of (II) resulted. On the other hand, formation of (I) or (II) does not occur when HCl or HCl–aluminium chloride, or simple heating of the reactants, is substituted for palladium(II) chloride. The latter observation clearly suggests the participation of palladium(II)-co-ordinated intermediates in the formation of (I).

The scope of this reaction, particularly with other olefins has been investigated. Propene, the isomeric butenes, and styrene react with tolan in the presence of palladium(II) chloride to furnish products (Table) structurally analogous to (I). However, variation of the reaction times in these cases provided no evidence for formation of the corresponding indene derivative(s). *cis*-But-2-ene yields the same product as but-1-ene, pointing to preferential reaction of the latter olefin subsequent to palladium(II)-promoted isomerization of the but-2-ene.[6]

Diene Products from the Pd^{II}*-promoted*[a] *reactions of olefins with diphenylacetylene*

Olefin	Diene product (*trans,trans*)[b]	M.p. (uncorr.)	% Yield
Propene	4,5-Diphenylocta-3,5-diene	65—66°	40
But-1-ene	5,6-Diphenyldeca-4,6-diene	78—79°	56
Isobutene	2,7-Dimethyl-4,5-diphenylocta-3,5-diene	177—179°	60
cis-But-2-ene	5,6-Diphenyldeca-4,6-diene	77—78°	50
Styrene	1,3,4,6-Tetraphenylhexa-2,4-diene	150—153°	26

[a] 2·1 : 1 Tolan–metal halide was employed in most cases.

[b] The *trans,trans*-product was the only isomer detected. Satisfactory analytical and spectral (n.m.r., i.r., and mass) data were obtained in all cases.

When vinyl bromide is employed as the olefin moiety, a complex mixture of at least six products is obtained, while other monosubstituted olefins bearing electron-withdrawing substituents, such as acrylonitrile, methyl acrylate, and vinyl acetate, gave no evidence for addition–rearrangement product formation. Similarly inert were acyclic

$\alpha\beta$-disubstituted ethylene derivatives such as stilbene and dichloroethylene, while cyclohexene as a representative cycloolefin, gave a mixture of two hydrocarbons. Although structure elucidation is not complete, spectral analysis rules out either being structural analogues of (I).

Financial support of this research by the Air Force Office of Scientific Research is acknowledged.

(*Received, July 22nd,* 1969; *Com.* 1117.)

---

[1] Y. Kusunaki, R. Katsuno, N. Hasegawa, S. Kurematsu, Y. Nagao, K. Ishii, and S. Tsutsumi, *Bull. Chem. Soc. Japan*, 1966 **39**, 2021.

[2] A. T. Blomquist and P. M. Maitlis, *J. Amer. Chem. Soc.*, 1962, **84**, 2329.

[3] G. A. Jeffrey, H. P. Koch, and S. C. Wyburg, *J. Chem. Soc.*, 1948, 1118.

[4] W. Hausmann and A. E. Wilder Smith, *J. Chem. Soc.*, 1949, 1030.

[5] A. A. Plentl and M. T. Bogert, *J. Amer. Chem. Soc.*, 1941, **63**, 989.

[6] (a) G. C. Bond and M. Hellier, *J. Catalysis*, 1965, **4**, 1; (b) M. B. Sparke, L. Turner, and A. J. M. Wenham, *ibid.*, 1965, **4**, 332. (c) S. V. Pestrikov and I. I. Moiseev, *Izvest. Akad. Nauk S.S.S.R., Ser. Khim.*, 1965, 349.