Addition Reactions of Butadiene Catalyzed by Palladium Complexes

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Remarkable advances have been made in the last 20 years in organic synthesis by using transition-metal complexes. Many novel synthetic transformations have been discovered which seemed impossible by conventional methods.

Among the several transition metals commonly used in organic synthesis, palladium occupies a unique position. Palladium compounds are versatile reagents or catalysts for organic synthesis, as has been made apparent by the many new synthetic reactions discovered since the invention of the famous Wacker process in the late 1950's.

In the last 10 years, extensive synthetic studies have been carried out involving palladium compounds and mainly olefinic and aromatic substrates. A particular feature of many of these reactions is oxidation with divalent palladium, and nucleophilic substitution and addition reactions of olefins are typical examples. A previous Account by the author treated mainly this type of reaction.[1]

On the other hand, recently a different type of reaction catalyzed by palladium complexes has been discovered which involves oligomerization, mainly dimerization, and telomerization of butadiene. Oligomerization reactions of butadiene catalyzed by transition-metal complexes, particularly nickel complexes, which give various cyclic and linear oligomers, have been studied extensively and quite thoroughly, especially by Wilke.[2,3] However, studies on the oligomerization and telomerization of butadiene using palladium catalysts were initiated only recently. They show that palladium-catalyzed reactions of butadiene are both unique and useful.

Palladium complexes catalyze cocyclization of butadiene with heteropolar double bonds and telomerization with nucleophiles. These reactions, which are impossible or difficult to achieve by other transition-metal complexes, constitute the principal substance of this Account.

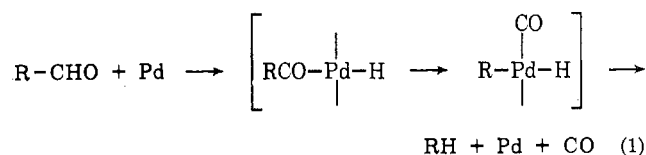## Cocyclization Reactions of Butadiene with Heteropolar Double Bonds

A novel reaction of butadiene catalyzed by palladium complexes is the cocyclization of 2 mol of butadiene with a heteropolar double bond to form a six-membered heterocyclic compound, which is expressed by the following general scheme.
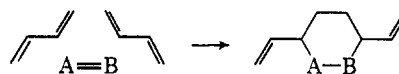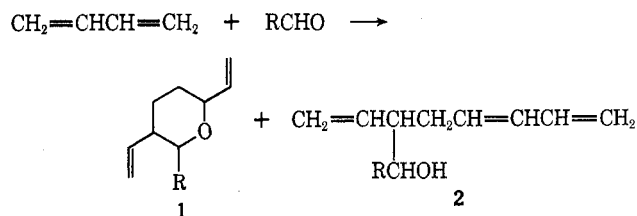

Cocylizations of butadiene catalyzed by nickel complexes are known, but they involve only olefinic and acetylenic bonds.[4,5] The palladium-catalyzed reaction is a unique example of metal-catalyzed cocyclization involving unsaturated bonds to hetero atoms.

The first example of the cocyclization involved 2 mol of butadiene and 1 mol of aldehyde to give 2-substituted 3,6-divinyltetrahydropyrans. In addition to the pyrans, 1-substituted 2-vinyl-4,6-heptadien-1-ols are also formed. Four research groups independently found this reaction.[6-9]

Palladium is an active catalyst for decarbonylation of aldehydes.[10] It is assumed that the first step in decarbonylation is an oxidative addition of the aldehyde to the palladium catalyst to form the acyl-palladium complex (eq 1). Generally, acyl-metal com-

$$R-CHO + Pd \longrightarrow \left[RCO-\overset{|}{\underset{|}{Pd}}-H \longrightarrow R-\overset{\overset{CO}{|}}{\underset{|}{Pd}}-H \right] \longrightarrow$$

$$RH + Pd + CO \quad (1)$$

plexes undergo olefin insertion.[11] In our attempt to synthesize ketones by the insertion of olefins into the acyl-palladium bonds formed from aldehydes, reactions of butadiene with aldehydes in the presence of the palladium complex of $(C_6H_5)_3P$ were carried out. The products isolated were not the expected ketones, but rather 2-substituted 3,6-divinyltetrahydropyrans

$$CH_2{=}CHCH{=}CH_2 \ + \ RCHO \ \longrightarrow$$

Jiro Tsuji was born in Shigaken, Japan, in 1927. He received his B.S. at Kyoto University and then came to this country as a Fulbright Exchange student, where he obtained his Ph.D. at Columbia, with Gilbert Stork. His main research interests have been in organic synthesis, especially of natural products, and in organotransition metal chemistry. Dr. Tsuji is presently a Senior Research Associate at Basic Research Laboratories, Toray Industries, Inc.

(1) J. Tsuji, *Accounts Chem. Res.*, 2, 144 (1969).
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(3) G. Wilke, B. Bogdanovic, P. Hardt, P. Heimbach, W. Keim, M. Kroner, W. Oberkirch, K. Tanaka, E. Steinrucke, D. Walter, and H. Zimmermann, *Angew. Chem.*, 78, 157 (1966).
(4) P. Heimbach and W. Brenner, *Angew. Chem.*, 78, 983 (1966).
(5) W. Brenner, P. Heimbach, K. J. Ploner, and F. Thomel, *Angew. Chem.*, 81, 744 (1969).
(6) K. Ohno, T. Mitsuyasu, and J. Tsuji, *Tetrahedron Lett.*, 67 (1971).
(7) R. M. Manyik, W. E. Walker, K. E. Atkins, and E. S. Hammack, *Tetrahedron Lett.*, 3813 (1970).
(8) P. Haynes, *Tetrahedron Lett.*, 3687 (1970).
(9) H. A. Jung, *British Patent*, application Feb 25, 1970.
(10) J. Tsuji and K. Ohno, *J. Amer. Chem. Soc.*, 90, 94 (1968).
(11) R. F. Heck, *Accounts Chem. Res.*, 2, 10 (1969).

(1) and 1-substituted 2-vinyl-4,6-heptadien-1-ols (2), in high yields.

The reaction of benzaldehyde with butadiene at 80° for 10 hr in the presence of a catalytic amount of palladium acetate (Pd(OCOCH₃)₂) and (C₆H₅)₃P gave 1-phenyl-2-vinyl-4,6-heptadien-1-ol and 2-phenyl-3,6-divinyltetrahydropyran (*ca.* 90% yield), which were separated by distillation. Gas chromatographic assay of the pyran showed the presence of four stereoisomers, and three of them were isolated by column chromatography and characterized by nmr spectra.[12] They were 2-phenyl-*trans*-3,*cis*-6-divinyltetrahydropyran (3), 2-phenyl-*cis*-3,*cis*-6-divinyltetrahydropyran (4), and 2-phenyl-*cis*-3,*trans*-6-divinyltetrahydropyran (5). The nmr studies revealed that the large 2-phenyl group takes an equatorial conformation in the preferred structure, and the rate of inversion of the pyran ring is very slow. For example, in the nmr spectrum of 4, when H₅ was irradiated, the H₂ proton became a quartet. If rapid inversion took place, the quartet would collapse to a triplet.[13] On the other hand, rapid inversion was observed with 2-methyl-3,6-divinyltetrahydropyran.
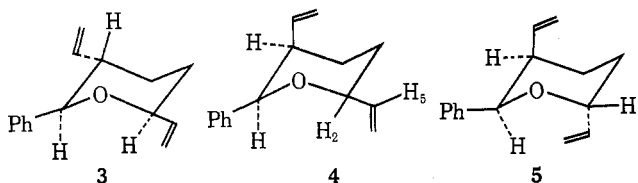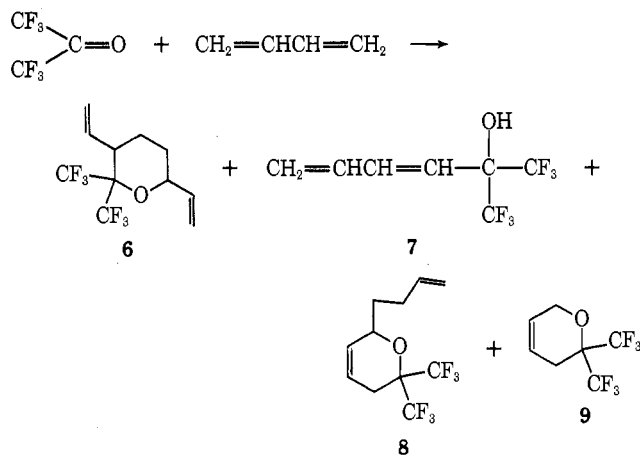

Various palladium–phosphine complexes can be used as effective catalysts. Most simply, Pd(O-COCH₃)₂ or palladium acetylacetonate can be used with (C₆H₅)₃P. Also π-allylpalladium chloride and [(C₆H₅)₃P]₂PdCl₂ are active catalysts in the presence of an excess of bases which remove the chloride ions from the coordination sphere of palladium. Zerovalent complexes such as [(C₆H₅)₃P]₄Pd and bis(triphenylphosphine)(maleic anhydride)palladium are also active. As the ligand, (C₆H₅)₃P is most conveniently used. Trialkylphosphines and triarylarsines are less active. The reaction can be carried out even at room temperature in solvents such as tetrahydrofuran, benzene, and dimethylformamide.

It was found that the ratio of the two products (1:2) can be controlled by changing the molar ratio of triphenylphosphine to palladium in the system. The unsaturated alcohol was obtained as a main product when the ratio was near unity. By increasing the amount of (C₆H₅)₃P, the relative amount of the pyran increased and the pyran was formed nearly selectively when the ratio was above 2. Also it was observed that triarylarsines tend to increase the relative amount of the unsaturated alcohol.[14]

Aromatic aldehydes, furfural, and aliphatic aldehydes, including formaldehyde, take part in the reaction. On the other hand, attempted reactions with common ketones such as acetone were not successful, and only 1,3,7-octatriene was formed. Some specific ketones, however, were found to take part in the reaction.[12] Perfluoroacetone gave 2,2-bis(trifluo-

romethyl)-3,6-divinyltetrahydropyran (6). In addition, other products (7, 8, 9) were obtained. Dihydropyrans 8 and 9 were formed by a Diels–Alder-type reaction. 1,1,1-Trifluoro-2-trifluoro-

methyl-*trans*- 3,5-hexadien-2-ol (7) was formed by the 1:1, rather than 2:1, addition of butadiene to the ketone. A similar 1:1 product was obtained by the
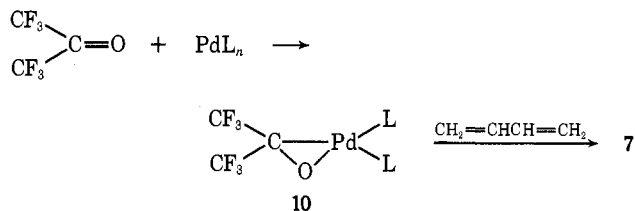
reaction of butadiene and acetone in the presence of nickel complex, which was consumed stoichiometrically.[15] Other active ketones like α-diketones, such as biacetyl and benzil, gave the corresponding pyrans (11).
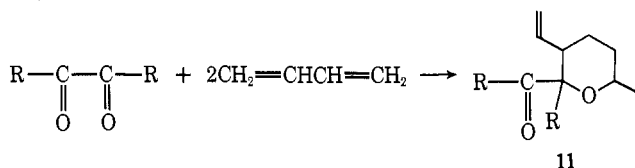
The reactivity of perfluoroacetone and α-diketones is attributed to their ability to coordinate with the catalyst. For example, complex 10 has been reported.[16] Simple ketones show no such reactivity toward palladium, and hence they are inert.

The mechanism of the reaction of aldehydes with butadiene is the following. σ,π-Diallylpalladium complex (12), coordinated by phosphine, was suggested as an intermediate in the dimerization of butadiene.[17] This intermediate seems to play an important role in the reaction of aldehydes. In the presence of aldehyde, insertion of the carbonyl group into the palladium–σ-allyl bond takes place giving an alkoxide-type complex (13). This intermediate has an equilibrium between π-allyl (13) and σ-allylpalladium (14) structures depending on the concentration of the phosphine. The former complex is expected to decompose through hydrogen transfer from the 4 po-

(12) K. Ohno, T. Mitsuyasu, and J. Tsuji, *Tetrahedron*, 28, 3705 (1972).

(13) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, p 218.

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(15) P. Heimbach, P. W. Jolly, and G. Wilke, *Advan. Organometal. Chem.*, 8, 39 (1970).

(16) B. Clark, M. Green, R. B. L. Osborn, and F. G. A. Stone, *J. Chem. Soc. A*, 168 (1968).

(17) S. Takahashi, H. Yamazaki, and N. Hagihara, *Mem. Inst. Sci. Ind. Res. Osaka Univ.*, 25, 125 (1968).
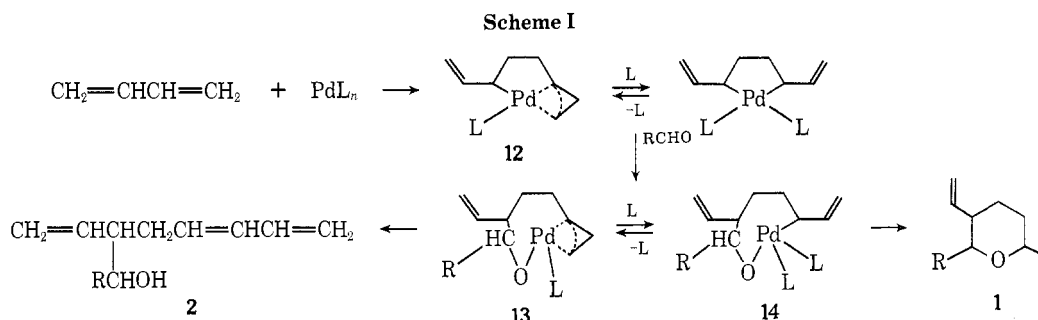
Scheme I

sition of the π-allyl moiety to the oxygen to give the unsaturated alcohol **2**. The pyran **1** is formed from the latter complex through ligand coupling (Scheme I). Existence of the postulated equilibrium between σ-allyl- and π-allylpalladiums is supported by the fact that the product distribution varies markedly with the molar ratio of $(C_6H_5)_3P$ to Pd. The relative extent of reaction by each pathway depends mainly on the relative ratio of the two catalytic components.

Isocyanates also take part in the cocyclization with butadiene.[18] The isocyanate C=N bond, rather than C=O bond, is involved in the reaction to give divinylpiperidones in high yield and selectivity. Use of a catalytic amount of the palladium complex suffices. For example, a benzene solution of phenyl isocyanate and isoprene in the presence of bis(triphenylphosphine)(maleic anhydride)palladium was shaken at 100° for 20 hr, and crystalline *trans*-3,6-diisopropenyl-1-phenyl-2-piperidone (**15**) as well as oily *cis*-3,6-diisopropenyl-1-phenyl-2-piperidone (**16**) were obtained. In this reaction, tail-to-tail coupling of isoprene takes place selectively.

$$CH_2=\overset{\underset{\displaystyle CH_3}{|}}{C}-CH=CH_2 \;+\; C_6H_5N=C=O \;\longrightarrow$$

15   16
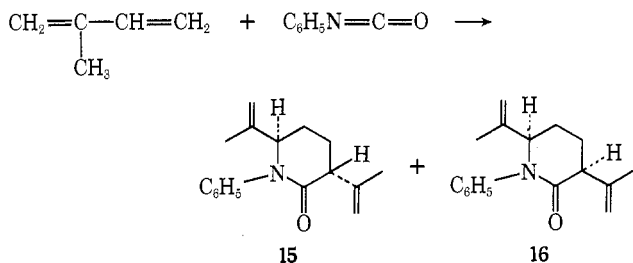
Butadiene and phenyl isocyanate gave equal amounts of (*Z*)-3-ethylidene-1-phenyl-6-vinyl-2-piperidone (**17**) and its *E* isomer **18** in 75% yield. In the reaction of butadiene, double-bond migration to the conjugated position took place.

$$CH_2=CHCH=CH_2 \;+\; C_6H_5N=C=O \;\longrightarrow$$

17   18
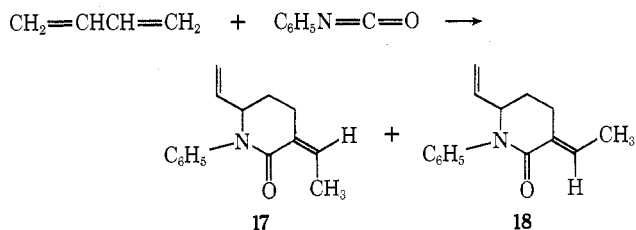
For this reaction, $Pd(OCOCH_3)_2$ and palladium acetylacetonate are most conveniently used with $(C_6H_5)_3P$ as the catalyst. Platinum complexes of phosphine have the same activity for the piperidone synthesis, although they are less active in the pyran formation reaction.

(18) K. Ohno and J. Tsuji, *Chem. Commun.*, 247 (1971).

Dimerization and Telomerization of Butadiene

Formation of *n*-dodecatetraene from butadiene in 30% yield by using bis(π-allyl)palladium is the first report of the palladium-catalyzed oligomerization of butadiene.[3] Later studies revealed that palladium-catalyzed reactions of butadiene proceed quite differently from reactions catalyzed by other transition-metal complexes. Linear dimerization is the main reaction with palladium catalysts, and no cyclodimerization or cyclotrimerization is possible.

The most interesting and important feature observed in the palladium-catalyzed dimerization of butadiene is the formation of telomers with various nucleophiles. As is well known, simple olefins coordinated to divalent palladium compounds react with nucleophiles to give vinylic compounds.[1] These reactions are oxidations with divalent palladium. The nucleophiles so far known to react with olefins are water,[19] alcohols,[19] carboxylic acids,[19] amines,[20-23] ammonia,[24] enamines,[25] active methylene compounds with two negative groups,[26] azides,[24] and cyanide.[27] Also CO reacts with olefin complexes of palladium.[28] It has been found that butadiene dimerizes with efficient incorporation of the same nucleophiles mainly at a terminal position to give 1-substituted 2,7-octadienes.

$$2CH_2=CHCH=CH_2 + YH \rightarrow$$
$$CH_2=CHCH_2CH_2CH_2CH=CHCH_2Y$$
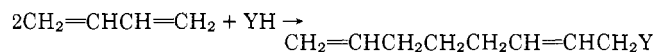
In this sense, the dimerizations catalyzed by palladium complexes are somewhat different from oligomerization reactions of butadiene catalyzed by other transition-metal complexes. With nickel, cobalt, iron, and other catalysts, it is generally not possible to introduce functional groups efficiently into oligomers. Recently, it was reported that alcohols,[29] amines,[30,31] and active methylene compounds[32] can

(19) J. Tsuji, *Advan. Org. Chem.*, **6**, 109 (1969).

(20) G. Paiaro, A. De Renzi, and R. Palumbo, *Chem. Commun.*, 1150 (1967).

(21) R. Palumbo, A. De Renzi, A. Panunzi, and G. Paoaro, *J. Amer. Chem. Soc.*, **91**, 3874 (1969).

(22) E. Stern and M. L. Spector, *Proc. Chem. Soc. London*, 370 (1961).

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(24) M. Tada, Y. Kuroda, and T. Sato, *Tetrahedron Lett.*, 2871 (1969).

(25) J. Tsuji, H. Takahashi, and M. Morikawa, *Tetrahedron Lett.*, 4387 (1965).

(26) H. Takahashi and J. Tsuji, *J. Amer. Chem. Soc.*, **90**, 2387 (1968).

(27) Y. Odaira, T. Oishi, T. Yukawa, and S. Tsutsumi, *J. Amer. Chem. Soc.*, **88**, 4105 (1966).

(28) J. Tsuji, M. Morikawa, and J. Kiji, *J. Amer. Chem. Soc.*, **86**, 4851 (1964).

(29) T. C. Shields and W. E. Walker, *Chem. Commun.*, 193 (1971).

(30) P. Heimbach, *Angew. Chem., Int. Ed. Engl.*, **7**, 882 (1968).

(31) R. Baker, D. E. Halliday, and T. N. Smith, *Chem. Commun.*, 1583 (1971).

(32) R. Baker, D. E. Halliday, and T. N. Smith, *J. Organometal. Chem.*, **36**, C61 (1972).

be introduced into butadiene and its dimers by using some specific nickel complexes to give butenyl and octadienyl ethers and corresponding compounds. However, the selectivity of the reactions is not high, and a mixture of telomers is obtained.

Furthermore, it should be pointed out that this reaction of butadiene is not an oxidation, which consumes divalent palladium, but catalytic. In contrast to the reactions of ethylene and other monoolefins, which reduce divalent palladium stoichiometrically and are catalytic only when used with a $Cu(II)-O_2$ cooxidation system, this type of reaction of butadiene represents true catalysis by palladium. Thus no metallic palladium is deposited during the reaction carried out under appropriate conditions.

Another noteworthy feature is that $PdCl_2$, widely used to catalyze reactions of simple olefins, is not an effective catalyst of oligomerization; $Pd(OCOCH_3)_2$ and palladium acetylacetonate can be used conveniently. That is, palladium complexes without coordinated halogen can be used as satisfactory catalysts. When $PdCl_2$ is used, bases must also be added in order to eliminate the coordinated chloride ion from the coordination sphere of palladium. Zerovalent palladium complexes such as $[(C_6H_5)_3P]_4Pd$ or bis(triphenylphosphine)(maleic anhydride)palladium are also used.
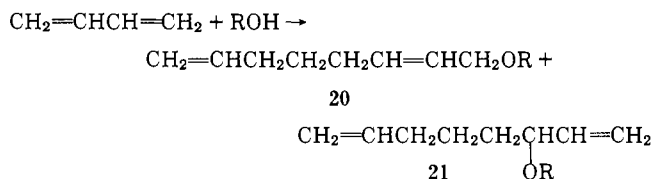
Dimerization of butadiene to form 1,3,7-octatriene (19) proceeds in aprotic solvents in a high yield using, for example, the above zerovalent palladium complexes as catalysts.[33,34] The reaction is faster in isopropyl alcohol.
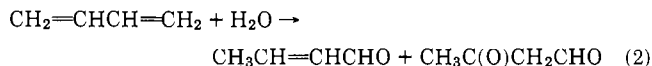
$$2CH_2=CHCH=CH_2 \rightarrow CH_2=CHCH_2CH_2CH=CHCH=CH_2$$
$$19$$
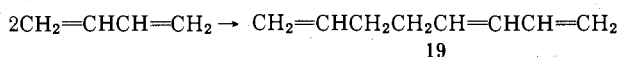
Telomerization of butadiene with carboxylic acids in the presence of palladium salts and alkali phenoxide was first claimed in patents.[35] Also the reaction of phenol and butadiene, catalyzed by $PdCl_2$ under basic conditions, gave a small amount of phenoxybutene. When pyridine was added, 1-phenoxyoctadiene was obtained in a low yield.[36,37] These studies showed that palladium is a catalyst of telomerization of butadiene, but it seems likely that the activity of the palladium catalyst is low in the absence of proper ligands. A major breakthrough was the discovery that ligands are very important in the palladium-catalyzed telomerization. Especially, $(C_6H_5)_3P$ has a profound effect on the reaction, increasing selectivity and activity of the palladium catalyst. In the following, telomerizations with various nucleophiles are surveyed.

Reactions of Alcohols, Phenols, and Water. Butadiene reacts with alcohols to form 1-alkoxy-2,7-octadiene (20) as a main product, accompanied by a small amount of 3-alkoxy-1,7-octadiene (21).[38-40]
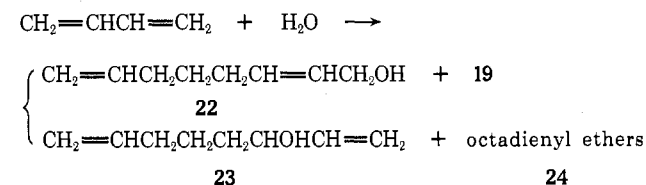
Methanol is the most reactive alcohol. Steric effects seem to have a large influence on the reaction, and secondary alcohols react to only a small extent. Almost no ether formation was observed with tertiary alcohols. Very facile reaction takes place with phenols to give phenyl octadienyl ether in high yield.[37,41]

$$CH_2=CHCH=CH_2 + ROH \rightarrow$$
$$CH_2=CHCH_2CH_2CH=CHCH_2OR +$$
$$20$$
$$CH_2=CHCH_2CH_2\overset{|}{C}HCH=CH_2$$
$$21 \qquad OR$$

From the standpoint of industrial application, the most promising process which might be developed by the telomerization of butadiene is synthesis of *n*-octanol. For this purpose, telomerization with water is most desirable. It is well known that simple olefins react with water very easily in the presence of $PdCl_2$ to give carbonyl compounds. Actually the reaction of water with olefins is responsible for the rapid emergence of the modern organic chemistry of palladium. The oxidative reaction of butadiene with water using $PdCl_2$ and $CuCl_2$ gives crotonaldehyde and 3-ketobutyraldehyde[42] (eq 2). The telomerization of butadiene with water catalyzed by palladium complexes,

$$CH_2=CHCH=CH_2 + H_2O \rightarrow$$
$$CH_3CH=CHCHO + CH_3C(O)CH_2CHO \quad (2)$$

however, is rather tricky, and it was only recently that water was shown to be incorporated into the dimer. Under the usual conditions, reaction of water with butadiene takes place only to a small extent. Efficient telomerization with water was found to occur in the presence of a considerable amount of CO_2 in solvents like butyl alcohol, acetone, and acetonitrile, as follows.[43]

$$CH_2=CHCH=CH_2 + H_2O \rightarrow$$
$$\begin{cases} CH_2=CHCH_2CH_2CH_2CH=CHCH_2OH + 19 \\ \qquad\qquad\qquad 22 \\ CH_2=CHCH_2CH_2CH_2CHOHCH=CH_2 + \text{octadienyl ethers} \end{cases}$$
$$23 \qquad\qquad\qquad\qquad\qquad\qquad 24$$

The effect of CO_2 is remarkable. For example, reaction of butadiene (1 mol), water (2 mol), and CO_2 (0.5 mol) in acetone (1.8 mol) for 2 hr gave the following yields of the above compounds: 22 (69%), 23 (7%), 19 (13%), and 24 (10%). The role of CO_2 in facilitating the telomerization with water is not clear. Also CO_2 showed some effect on the simple dimerization of butadiene catalyzed by palladium or platinum catalysts.[44]

In an attempt to synthesize 1-octanol, the reaction of trimethylsilanol with butadiene was carried out and 1-trimethylsiloxy-2,7-ocatdiene was obtained, which was hydrolyzed very easily to give 2,7-octadienol (22).[45]

(33) S. Takahashi, T. Shibano, and N. Hagihara, *Tetrahedron Lett.*, 2451 (1967).

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(39) Mitsubishi Chemical Industries, Netherlands Patent, 68,16008.

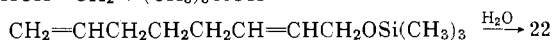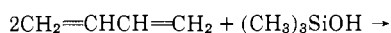(40) British Petroleum Co., Netherlands Patent, 69,15738, 69,15582.

(41) E. J. Smutny, U. S. Patent, 3,518,318 (1970), 3,518,315 (1970).

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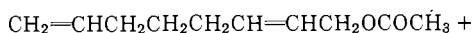(44) J. F. Kohle, L. H. Slaugh, and K. L. Nakamaye, *J. Amer. Chem. Soc.*, 91, 5905 (1969).

(45) S. Takahashi, T. Shibano, and N. Hagihara, *Kogyo Kagaku Zasshi*, 72, 1798 (1969).

$$2CH_2=CHCH=CH_2 + (CH_3)_3SiOH \rightarrow$$

$$CH_2=CHCH_2CH_2CH_2CH=CHCH_2OSi(CH_3)_3 \xrightarrow{H_2O} 22$$

Reaction of Carboxylic Acids. The reaction of acetate anion with simple olefins in the presence of $PdCl_2$ or $Pd(OCOCH_3)_2$ has been studied extensively; vinylic acetates are the main products. On the other hand, the reaction of acetate with butadiene has received less attention. Butadiene reacts with acetate to give butadienyl monoacetate.[22] Also, formation of crotyl acetate and 3-acetoxy-1-butene in nearly equal amounts by using $PdCl_2$ and $CuCl_2$ was reported.[46] Further studies revealed that octadienyl acetate is formed by using $PdCl_2$ and a base as catalyst.[35]

$$CH_2=CHCH=CH_2 + CH_3CO_2H \rightarrow$$

$$CH_3CH=CHCH_2OCOCH_3 + CH_3CH(OCOCH_3)CH=CH_2$$
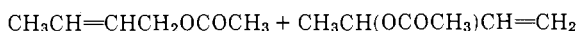
Later it was found that addition of acetate to butadiene to form 1-acetoxy-2,7-octaiene (25) as a main product and 3-acetoxy-1,7-octadiene (26) as a minor product proceeds more efficiently when a palladium catalyst is used combined with $(C_6H_5)_3P$ as a ligand.[33,47]

$$CH_2=CHCH=CH_2 + CH_3CO_2H \rightarrow$$

$$CH_2=CHCH_2CH_2CH_2CH=CHCH_2OCOCH_3 +$$
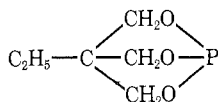
25

$$CH_2=CHCH_2CH_2CH_2CH(OCOCH_3)CH=CH_2$$

26

The reaction carried out without proper solvents is too slow to be satisfactory from a practical standpoint, but the reaction is faster under selected conditions. Selection of solvents and their relative amounts seems to be important.[48] A more remarkable effect was observed by addition of basic compounds. Sodium or potassium acetate accelerates the reaction especially at high concentrations.[49] A marked effect of addition of a molar quantity of tertiary amines such as 2-(N,N-diethylamino)ethanol has been reported.[50] For example, the reaction of butadiene, acetic acid, and 2-(N,N-diethylamino)ethanol(4.0 mol each) in the presence of palladium acetylacetonate and $(C_6H_5)_3P$ (3.0 mmol each) gave essentially complete conversion of butadiene after 2 hr at 90° to yield 25 (71%), 26 (21%), and 19 (8%).

$(C_6H_5)_3P$ is a good ligand for the reaction, and sometimes it is used in a large excess over palladium to secure prolonged life of the catalyst. Some phosphites such as trimethylol propanephosphite (27) have favorable effects on the rate and gave the high selectivity value of 25.[50] Reaction times of 2 hr at 50° with this ligand gave an 81% yield of 25 and 9% of 26 without forming octatriene. However, this ligand seems to be decomposed during the reaction.

$$C_2H_5-C\underset{CH_2O}{\overset{CH_2O}{\underset{\diagdown}{\diagup}}}P$$

27

Another possible application of the telomerization is synthesis of terpenes. Telomerization of isoprene with acetate or water, if carried out stereospecifically, would be an attractive synthetic method for terpene alcohols. However, so far it has not been possible to synthesize terpenes such as geranyl acetate with high selectivity from isoprene and acetic acid. A mixture of products is always obtained and separation of useful compounds is not easy.[51] Moreover, the reactivity of isoprene is much lower than that of butadiene.

Carboxylic acids other than acetic acid react similarly, but with somewhat different reactivity. An exception is formic acid, and formate ester is formed in only trace amount.[52] A reaction of formic acid with butadiene in the presence of triethylamine, catalyzed by $Pd(OCOCH_3)_2$, leads to the formation of 1,6-octadiene. When $(C_6H_5)_3P$ was added, a mixture of 1,7-octadiene and 1,6-octadiene (1:2) was obtained. CO_2 is released during the reaction and the stoichiometry is as in eq 3.

$$2CH_2=CHCH=CH_2 + HCO_2H \rightarrow$$

$$CH_2=CHCH_2CH_2CH_2CH=CHCH_3 + CO_2 \quad (3)$$
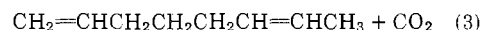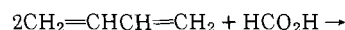
Reaction of Ammonia and Amines. Direct addition of ammonia to olefinic bonds would be an attractive method of amine synthesis if it could be carried out smoothly, but so far the facile addition of ammonia to simple olefins had not been reported. Like water, ammonia does not react with butadiene smoothly under usual conditions, and selection of proper conditions is important. A reaction of aqueous ammonia (28%, 5 g) with butadiene (32 g) in acetonitrile (60 ml) in the presence of $Pd(OCOCH_3)_2$ (63 mg) and $(C_6H_5)_3P$ (261 mg) at 80° for 10 hr gave tri-2,7-octatrienylamine (28) (29 g) as a main product, accompanied by a small amount of di-2,7-octadienylamine (29) (1.2 g). Also isomeric triamine 30 was formed as a by-product.[53]

$$CH_2=CHCH=CH_2 + NH_3 \longrightarrow$$

$$(CH_2=CHCH_2CH_2CH_2CH=CHCH_2)_3N +$$

28

$$(CH_2=CHCH_2CH_2CH_2CH=CHCH_2)_2NH +$$

29

$$(CH_2=CHCH_2CH_2CH_2CH=CHCH_2)_2-N$$
$$|$$
$$CH_2=CHCH_2CH_2CH_2CHCH=CH_2$$

30

Selection of proper solvents and their amounts are important. Acetonitrile, dimethylformamide and *tert*-butyl alcohol are most suitable. Water seems to have a favorable effect on the reaction, and aqueous ammonia is superior to pure ammonia.

Primary and secondary amines react smoothly with butadiene, and their hydrogens are replaced by 2,7-octadienyl groups to give secondary and tertiary amines.[33,34]

Reaction of Enamines. Enamines have dipolar double bonds and their cyclization to give four- and

(46) T. Inagaki, Y. Takahashi, S. Sakai, and Y. Ishii, *Bull. Jap. Petrol. Inst.*, 13, 73 (1971).

(47) D. R. Bryant and J. E. McKeon, U. S. Patent, 3,534,088 (1970).

(48) T. Arakawa and H. Miyake, *Kogyo Kagaku Zasshi*, 74, 1143 (1971).

(49) T. Mitsuyasu and J. Tsuji, German Offen., 2040,708 (1972).

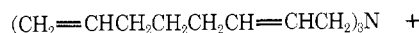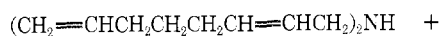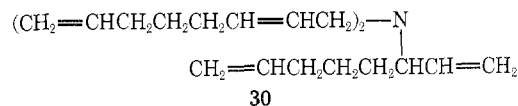(50) W. E. Walker, R. M. Manyik, K. E. Atkins, and M. L. Farmer, *Tetrahedron Lett.* 3817 (1970).

(51) K. Suga, S. Watanabe, and K. Hijikata, *Aust. J. Chem.*, 24, 197 (1971).

(52) S. Gardner and D. Wright, *Tetrahedron Lett.*, 163 (1972).

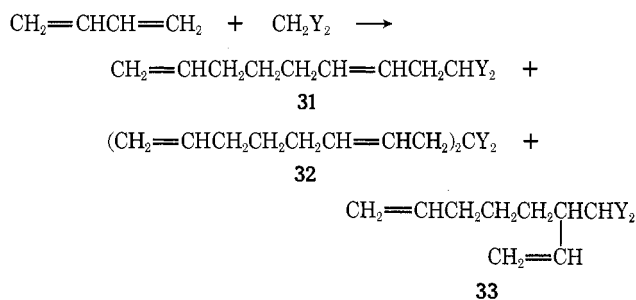(53) T. Mitsuyasu, M. Hara, and J. Tsuji, *Chem. Commun.*, 345 (1971).

six-membered rings is known. Also enamines are reactive nucleophiles. In view of these dual reactivities of enamines, the reaction of butadiene with enamines using palladium catalyst was investigated.

Reactions of the pyrrolidine enamines of cyclohexanone and cyclopentanone with butadiene proceed smoothly in acetonitrile in the presence of $Pd(O-COCH_3)_2$ and $(C_6H_5)_3P$.[54] The products isolated after hydrolysis were 2-(2,7-octadienyl)cyclohexanone accompanied by 2,6-di(2,7-octadienyl)cyclohexanone and the corresponding cyclopentanone derivatives.

$$2CH_2{=}CHCH{=}CH_2 \quad + \qquad \longrightarrow$$

$$CH_2{=}CHCH_2CH_2CH_2CH{=}CHCH_2$$
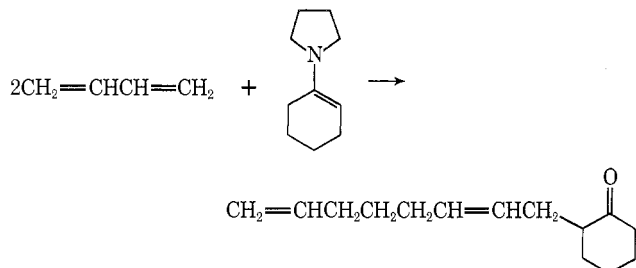
Reaction of Active Methylene Compounds.

Compounds with a methylene or methyne group to which are attached two electronegative groups, such as carbonyl, alkoxycarbonyl, formyl, cyano, nitro, and sulfonyl groups, react with butadiene smoothly and their acidic hydrogens are replaced with 2,7-octadienyl groups to give mono- and disubstituted compounds (31 and 32).[39,55] Also branched telomers (33) are formed as by-products.
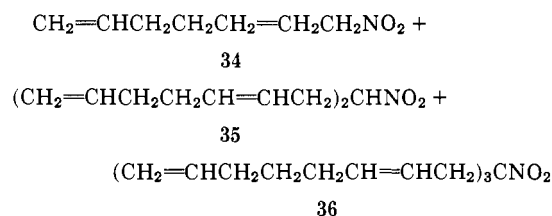
$$CH_2{=}CHCH{=}CH_2 \quad + \quad CH_2Y_2 \quad \longrightarrow$$

$$CH_2{=}CHCH_2CH_2CH_2CH{=}CHCH_2CHY_2 \quad +$$

31

$$(CH_2{=}CHCH_2CH_2CH_2CH{=}CHCH_2)_2CY_2 \quad +$$

32

$$CH_2{=}CHCH_2CH_2CH_2\underset{\underset{CH_2{=}CH}{|}}{C}HCHY_2$$

33

The reactions with β-diketones, α-formyl ketones, malonates, α-formyl, α-cyano, α-keto, and α-nitro esters, and related compounds have been carried out using mainly $[(C_6H_5)_3P]_2PdCl_2$ and sodium phenoxide as catalysts. In these reactions, when a bidentate ligand such as ethylenebis(diphenylphosphine) was used, 1 mol of butadiene reacted with 1 mol of active methylene compound to give butenyl derivatives.[56]

$$CH_2{=}CHCH{=}CH_2 + CH_2Y_2 \rightarrow$$

$$CH_3CH{=}CHCH_2CHY_2 \quad +$$

$$CH_2{=}CHCH(CH_3)CHY_2$$
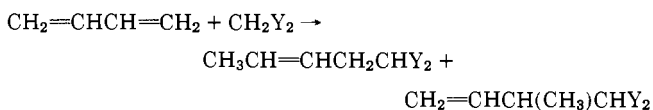
In general, methylene or methyne groups activated by one electronegative group are not active for the telomerization; simple ketones and esters, for example, are inert. However, nitroalkanes react with butadiene smoothly, and their α hydrogens are replaced with 2,7-octadienyl groups.[53] For example, a reaction

of nitromethane with butadiene in the presence of $[(C_6H_5)_3P]_2PdCl_2$ and sodium hydroxide in isopropyl alcohol at room temperature gave 9-nitro-1,6-nonadiene (34), 9-nitro-1,6,11,16-heptadecatetraene (35), and 9-nitro-9-(2,7-octadienyl)-1,6,11,16-heptadecatetraene (36), accompanied by a small amount of branched products. The relative amounts of these

$$CH_2{=}CHCH{=}CH_2 + CH_3NO_2 \rightarrow$$

$$CH_2{=}CHCH_2CH_2CH_2{=}CH_2CH_2NO_2 \quad +$$

34

$$(CH_2{=}CHCH_2CH_2CH{=}CHCH_2)_2CHNO_2 \quad +$$

35

$$(CH_2{=}CHCH_2CH_2CH_2CH{=}CHCH_2)_3CNO_2$$

36

products can be controlled by adjusting the reaction time and the ratio of reactants. The reaction is also applicable to other nitroalkanes. Hydrogenation of these unsaturated nitroalkanes gives corresponding long-chain amines, which are novel in that they have a primary amino group at the middle of the molecule, rather than at the terminal position as in common amines. Following is one example.

$$(CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2)_2CHNH_2$$
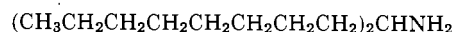
Transfer of Allylic Groups

Exchange of allylic groups was observed in the reaction of allyl acetate and sodium propionate in the presence of $PdCl_2$ to give allyl propionate.[57] During the course of studies on the telomerization of butadiene, it was found that the 2,7-octadienyl group can be transferred to other active hydrogen compounds. For example, 1-acetoxy-2,7-octadiene reacts with diethylamine under palladium catalysis to yield N,N-diethyl-2,7-octadienylamine by transfer of the allylic group.[50,58] The reaction can be extended to allylic functional moieties in general, including alcohols, ethers, esters, and amines. For example, allyl alcohol reacts with diethylamine in the presence of palladium acetylacetonate and $(C_6H_5)_3P$ at 50° for 30 min to yield allyldiethylamine[59] (eq 4). Allylic

$$CH_2{=}CHCH_2OH + (C_2H_5)_2NH \rightarrow CH_2{=}CHCH_2N(C_2H_5)_2 \quad (4)$$

ethers and esters react with acetylacetone to give carbon allylated products.[60] Allylation of enamines with allyl acetate is another example[54] (eq 5). Even

$$(5)$$
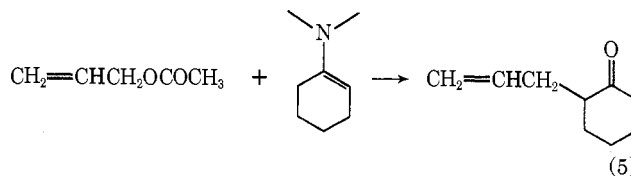
allyldiethylamine reacts with acetylacetone to give 3-allylacetylacetone and 3,3-diallylacetylacetone by C–N bond cleavage.[59]

In these allyl transfer reactions, C–O and C–N bonds are cleaved. Thus simple elimination of allylic

(54) J. Tsuji, special lecture presented at 23rd International Congress of Pure and Applied Chemistry, July 1971.

(55) G. Hata, K. Takahashi, and A. Miyake, *Chem. Ind.*, 1836 (1969); *J. Org. Chem.*, 36, 2116 (1971).

(56) K. Takahashi, G. Hata, and A. Miyake, *Chem. Ind.*, 488 (1971); *Bull. Chem. Soc. Jap.*, 45, 1183 (1972).

(57) A. Sabel, J. Smidt, R. Jira, and H. Prigge, *Chem. Ber.*, 102, 2939 (1969).

(58) T. S. Shryne, E. J. Smutny, and D. P. Stevenson, U. S. Patent, 3,493,617 (1970).

(59) K. E. Atkins, W. E. Walker, and R. M. Manyik, *Tetrahedron Lett.*, 3821 (1970).

(60) G. Hata, K. Takahashi, and A. Miyake, *Chem. Commun.*, 1392 (1970); *Bull. Chem. Soc. Jap.*, 45, 230 (1972).

groups is also possible in the absence of nucleophiles by using palladium catalyst. 1-Phenoxy-2,7-octadiene is converted into 1,3,7-octatriene by heating with palladium complexes of phosphine.[36,37] Similarly, acetic acid is eliminated from 1-acetoxy-2,7-octadiene by the catalysis of palladium.

$$CH_2=CHCH_2CH_2CH_2CH=CHCH_2OX \rightarrow$$

$$CH_2=CHCH_2CH_2CH=CHCH=CH_2 + XOH$$

$$X = CH_3CO, C_6H_5, CH_3$$
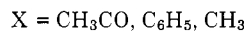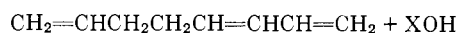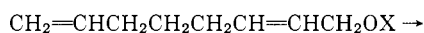
Reaction of Hydrosilanes

Telomerization with hydrosilanes, namely hydrosilation of butadiene, proceeds in the presence of palladium catalysts. This reaction is somewhat different from other palladium-catalyzed telomerizations discussed earlier. In the hydrosilation of butadiene, 1 or 2 mol of butadiene react depending on the kind of silane.[61-63] Trimethylsilane reacts with 2 mol of butadiene, catalyzed by bis(triphenylphosphine)(maleic anhydride)palladium, to give 1-trimethylsilyl-2,6-octadiene in 98% yield (eq 6). In this reaction, the 2,6-

$$2CH_2=CHCH=CH_2 + HSi(CH_3)_3 \rightarrow$$

$$CH_3CH=CHCH_2CH_2CH=CHCH_2Si(CH_3)_3 \quad (6)$$
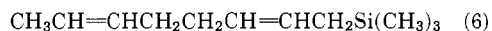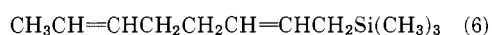
octadienyl rather than the 2,7-octadienyl derivative was formed. On the other hand, 1 mol of butadiene reacts with trichlorosilane at 100° for 6 hr to give 1-trichlorosilyl-2-butene in 93.5% yield.

$$CH_2=CHCH=CH_2 + HSiCl_3 \rightarrow CH_3CH=CHCH_2SiCl_3$$
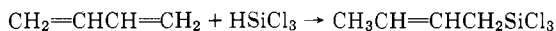
Unlike the telomerizations mentioned previously, the hydrosilation of butadiene is possible by using various palladium compounds including $PdCl_2$ without base, and even metallic palladium when combined with various aryl- and alkylphosphines.

Carbonylation of Butadiene

Palladium is an active catalyst for carbonylation of simple olefins.[1] In the carbonylation of butadiene, 1 mol of butadiene reacts with CO by using $PdCl_2$ as the catalyst to give 3-pentenoate.[64,65] Further studies revealed that the carbonylation of butadiene can be made to give 3,8-nonadienoate by using different palladium catalysts.[54,66,67]

$$CH_3CH=CHCH_2CO_2R \leftarrow CH_2=CHCH=CH_2 + CO + ROH \rightarrow$$
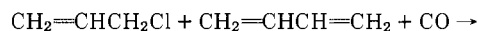
$$CH_2=CHCH_2CH_2CH_2CH=CHCH_2CO_2R$$
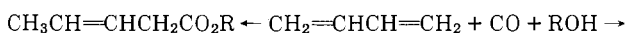
The essential factor which differentiates the monomeric and dimeric carbonylations is the presence or absence of a halide ion coordinated to palladium. With halide-free complexes, such as Pd(O-COCH$_3$)$_2$ and (C$_6$H$_5$)$_3$P, 3,8-nonadienoate is obtained almost selectively. In a typical run, a reaction of butadiene (20 g), isopropyl alcohol (30 ml), and CO (50 atm) at 110° for 16 hr gave isopropyl 3,8-nonadienoate (32.5 g). The reaction proceeds

smoothly even in *tert*-butyl alcohol to give the *tert*-butyl ester in a high yield.

In the carbonylation reaction, 2 mol of butadiene form the diallylic palladium complex and then CO insertion takes place to give 3,8-nonadienoate. When chloride ion coordinates with the palladium, formation of the diallylic complex is not possible, and only monomeric complex is formed, CO insertion to which gives 3-pentenoate.

$$CH_2=CHCH=CH_2 + CO + ROH$$

$$CH_3CH=CHCH_2CO_2R \qquad CH_2=CHCH_2CH_2CH=CHCH_2CO_2R$$
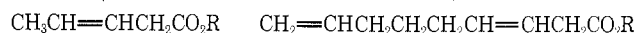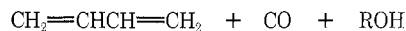
CO insertion into π-allylpalladium chloride is a well-established reaction.[68] Carbonylation of allyl chloride catalyzed by $PdCl_2$ gives 3-butenoyl chloride *via* the π-allylpalladium complex as an intermediate.[69,70] Carbonylation of allyl chloride in the presence of an excess of butadiene, catalyzed by π-allylpalladium chloride in benzene, produced a mixture of 3,7-octadienoyl chloride and 3-butenoyl chloride.[71] The former was formed by insertion of butadiene into π-allylpalladium bond, followed by CO insertion.

$$CH_2=CHCH_2Cl + CH_2=CHCH=CH_2 + CO \rightarrow$$

$$CH_2=CHCH_2CH_2CH=CHCH_2COCl + CH_2=CHCH_2COCl$$

Mechanism of the Telomerization Reactions

Unlike nickel, the size of a palladium atom precludes cyclization, and a rapid hydrogen transfer occurs to give linear oligomers and telomers. The σ,π-diallylpalladium complex **12** coordinated by phosphine is postulated as the intermediate in the dimerization. 1-Substituted 2,7-octadienes are formed from this intermediate by 1,6 addition of nucleophiles (YH) to the allylic ligand. In other words, this intermediate is protonated at C$_6$ *via* σ-allylpalladium bond fission by protic medium (YH) and attacked by the nucleophiles at C-1 of the π-allylpalladium bond to yield the corresponding telomers. 3,6 addition gives rise to branched telomers. The fact that 1-methoxy-6-deuterio-2,7-octadiene was formed by the reaction of butadiene with CH$_3$OD can be explained by this mechanism.[38]

$$CH_2=CHCH=CH_2 + PdL_n \rightarrow$$

$$CH_2=CHCHDCH_2CH_2CH=CHCH_2OCH_3$$

$$CH_2=CHCHDCH_2CH=CHCH=CH_2$$
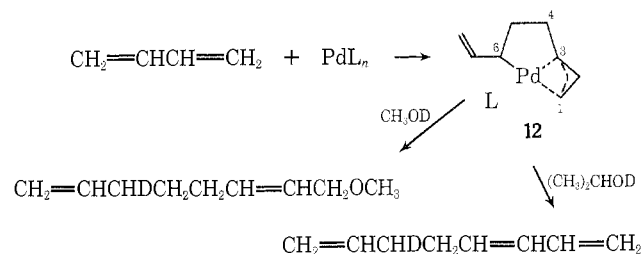
(61) S. Takahashi, T. Shibano, and N. Hagihara, *Chem. Commun.*, 161 (1969).
(62) S. Takahashi, T. Shibano, H. Kojima, and N. Hagihara, *Organometal. Chem. Syn.*, 1, 193 (1971).
(63) M. Hara, K. Ohno, and J. Tsuji, *Chem. Commun.*, 247 (1971).
(64) J. Tsuji, J. Kiji, and S. Hosaka, *Tetrahedron Lett.*, 605 (1964).
(65) S. Hosaka and J. Tsuji, *Tetrahedron*, 27, 3821 (1971).
(66) W. E. Billups, W. E. Walker, and T. C. Shields, *Chem. Commun.*, 1067 (1971).
(67) J. Tsuji, M. Hara, and Y. Mori, *Tetrahedron*, 28, 3721 (1972).

(68) J. Tsuji, J. Kiji, and M. Morikawa, *Tetrahedron Lett.*, 1811 (1963).
(69) J. Tsuji, J. Kiji, S. Imamura, and M. Morikawa, *J. Amer. Chem. Soc.*, 86, 4350 (1964).
(70) W. T. Dent, R. Long, and G. H. Whitefield, *J. Chem. Soc.*, 1588 (1964).
(71) D. Medema, R. van Helden, and C. F. Kohll, *Inorg. Chim. Acta*, 3, 255 (1969).

Formation of 1,3,7-octatriene is possible from the same intermediate complex by hydrogen migration from C-4 to C-6. When the reaction was carried out in $(CH_3)_2CHOD$, the octatriene obtained was thought to be monodeuterated at C-6.[34] From this result, it is reasonable to assume that the addition of a proton of isopropyl alcohol to the C-6 atom and the elimination of the proton from C-4 result in an increasing rate of hydrogen migration from C-4 to C-6, and hence enhancement of the rate of octatriene formation is possible.[17]

Stoichiometric reactions of π-allylpalladium chloride with nucleophiles are known. For example, the complex reacts with diethyl malonate to give diethyl allylmalonate. Also reactions of the complex with enamines of cyclohexanone produced 2-allylcyclohexanone.[25,72]

$$CH_2\!\!=\!\!CHCH_2CH(CO_2R)_2 + Pd + Cl^-$$
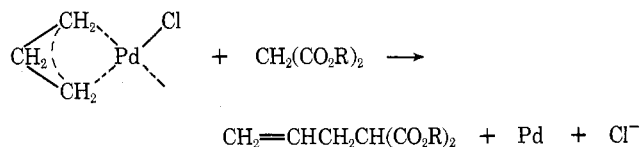
In the catalytic reactions of butadiene, the original π-allylic ligand comes off at the end of the cycle, and subsequent cycles involve formally a reversible oxidation–reduction between the palladium(0) complex and the π-allylic palladium(II) complex derived from butadiene. This is possible in the absence of the strongly coordinated chloride ion.

Related Reactions

Reaction of butadiene in benzene using π-allylpalladium acetate as the catalyst yielded the trimer, *n*-1,3,6,10-dodecatetraene, with selectivity of 70% and conversion of 30% in 22 hr.[73] A minor product was

1,3,7-octatriene. When the reaction was carried out in methanol, a mixture of octadienyl, dodecatrienyl, hexadecatetraenyl, and higher methyl ethers was obtained. π-Allylpalladium acetylacetonate is not an active catalyst for the trimerization. An acetate-bridged palladium complex (37) was isolated, which was found to be the active catalyst of the trimerization. Also stable chelate complexes of palladium (38) are catalysts for the trimerization of butadiene in dimethylformamide or Me_2SO (60% yield, 30% conversion) at 70°.[74] Salts of palladium with noncomplexing anions such as ClO_4^- and BF_4^- convert butadiene into a mixture of divinylcyclobutanes.[75]

37   **38**
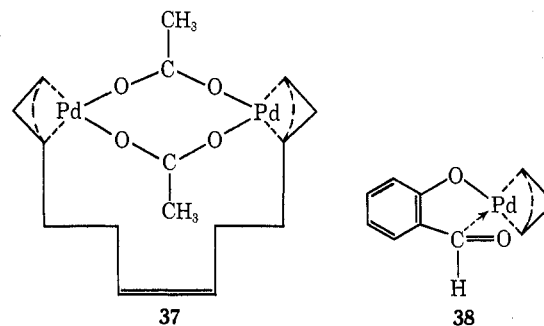
Stereoselective synthesis of 1,4-hexadiene from butadiene and ethylene has been reported.[76] The catalyst was prepared by the reaction of $[(C_6H_5)_3P]_2$-$PdCl_2$ with diisobutylaluminum chloride.

$$CH_2\!\!=\!\!CHCH\!\!=\!\!CH_2 + CH_2\!\!=\!\!CH_2 \rightarrow CH_2\!\!=\!\!CHCH_2CH\!\!=\!\!CHCH_3$$
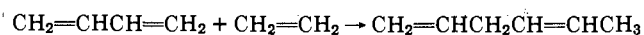
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