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# Incorporation of $CO_2$ in Butadiene Dimerization Catalyzed by Palladium Complexes. Formation of 2-Ethylidene-5-hepten-4-olide

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Reaction of carbon dioxide with butadiene catalyzed by palladium–phosphine complexes was studied. When the reaction was carried out in certain polar, aprotic solvents, such as dimethylformamide (DMF), 2-ethylidene-5-hepten-4-olide was formed in about 5% yield by the incorporation of $CO_2$ together with the formation of butadiene linear dimers. The main dimer was 1,3,7-octatriene. The ditertiary phosphines, $R_2PCH_2CH_2PR_2$ where R is methyl or phenyl, were found to be suitable as the ligand for the olide synthesis. A possible mechanism involving the intermediate of $\pi$-allyl, $\sigma$-allyl form from two moles of butadiene and the palladium complex is proposed.

There has been much attention in recent years to the fixation of $CO_2$, but catalytic reaction is rare. In a preliminary communication[1] we have reported that $CO_2$ can react with butadiene in the presence of plladium–phosphine complexes to give a small amount of 2-ethylidene-5-hepten-4-olide together with butadiene oligomers in certain polar, aprotic solvents such as DMF. This is the first example of the catalytic formation of a new C–C bond between $CO_2$ and an organic compound.

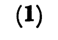
The dimerization of butadiene catalyzed by transition metal complexes is well known and it has been shown recently that not only the catalytic activity of metal complexes but also the catalytic properties can be altered when the dimerization reaction is carried out under $CO_2$ pressure.[2–5] For example, $Pt(PPh_3)_3$ converts butadiene to 4-vinylcyclohexene in 90—97% yield under nitrogen or argon atmosphere, however with $CO_2$ present, the product is mainly 1,3,7-octatriene with higher conversion of butadiene.[2] Though the role of $CO_2$ in these reactions is not clear yet, a direct effect on the catalyst has been suggested.

In this paper we wish to report the studies of the factors which affect the incorporation of $CO_2$ in butadiene dimer catalyzed by palladium–phosphine complexes.

## Results and Discussion

The catalytic activity of the following transition metal complexes on butadiene–$CO_2$ reaction was examined at 120 °C in DMF; $Pd(dpe)_2$, $Pt(dpe)_2$, $Ni(dpe)_2$, $HCo(dpe)_2$, $H_2Fe(dpe)_2$, $Pt(PPh_3)_4$, $RhCl(PPh_3)_3$, $H_2Ru(PPh_3)_4$, and $H_3Ir(PPh_3)_3$, where dpe stands for 1,2-bis(diphenylphosphino)ethane [$Ph_2PCH_2CH_2PPh_2$]. Among these complexes, only the $Pd(dpe)_2$ system afforded a $CO_2$-incorporated product, *i.e.*, 2-ethylidene-5-hepten-4-olide. Henceforth the catalytic activity of the palladium complex was examined in detail.

When butadiene was reacted with $CO_2$ in the presence of $Pd(dpe)_2$, butadiene linear dimers (**1**), (**2**), and (**3**) were obtained as the main products together with a small amount of the lactone (**4**).

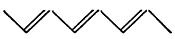

(**1**)

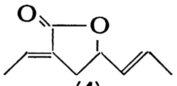

(**2**)

TABLE 1. EFFECT OF SOLVENT
Solvent 10 ml, $Pd(dpe)_2$ 0.2 mmol, butadiene 7.3 g, $CO_2$ 50 atm; 120 °C, 20 h.

| Solvent | Product yield (%) | | | | |
|---|---|---|---|---|---|
| | **1** | **2** | **3** | **4** | Others[b] |
| None | 2.4 | 3.6 | 58.0 | trace | 18.5 |
| DMF | 26.8 | 21.9 | 13.9 | 4.0 | 15.1 |
| DMSO | 55.7 | 12.3 | 4.5 | 4.2 | 9.3 |
| *t*-Butylalcohol | 44.3 | 17.9 | 6.6 | 0.5 | 15.0 |
| Triethylamine | 74.8 | 8.2 | trace | 0.5 | 7.7 |
| Tetramethylurea | 35.5 | 22.5 | 12.0 | 1.6 | 11.9 |
| 1-Methyl-2-pyrrolidone | 41.1 | 16.4 | 5.0 | 5.4 | ND[a] |
| Benzonitrile | 51.0 | 17.6 | 5.7 | 1.9 | ND |
| HMPA | 2.9 | trace | 0 | 0 | ND |
| Dichloromethane | 0.8 | trace | 0 | 0 | 1.3 |
| Anisole | 24.6 | 3.6 | 0 | 0.5 | 2.2 |
| Toluene | ND | ND | trace | 1.8 | 8.5 |
| Benzene | 35.7 | 21.8 | 17.7 | 0.4 | 18.1 |
| Chlorobenzene | 33.5 | 7.0 | 0 | 0.2 | 1.9 |
| Nitrobenzene | 60.9 | 2.2 | 0 | 0 | ND |

a) Not determined. b) "Others" mainly consists of butadiene trimers.


(**3**)


(**4**)

It was found that the distribution of the products depends on the solvent used. The effects of the solvents are summarized in Table 1. In the solvent-free system, 2,4,6-octatriene was the main product whereas 1,3,7-octatriene was the main one in certain solvents. The isomerization of 1,3,7-octatriene to 2,4,6-isomer has been reported to be affected by several palladium(0) phosphine complexes under $CO_2$ atmosphere.[4] Table 1 shows that polar, aprotic solvents such as DMF, dimethyl sulfoxide (DMSO), and 1-methyl-2-pyrrolidone are suitable for the lactone formation. But in case of hexamethylphosphoric triamide (HMPA), which is a typical polar, aprotic solvent, the decomposition of the catalyst was observed. The yield of the lactone (**4**) was rather small in benzene.

The yield of the lactone (**4**) increased with the increase in the amount of solvent DMF as shown in

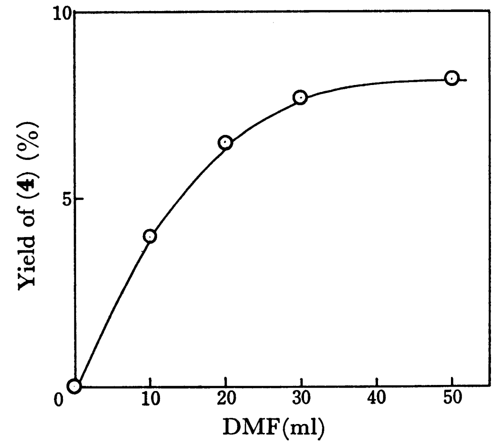


Fig. 1. Effect of the amount of DMF. Pd(dpe)$_2$ 0.2 mmol, butadiene 7.3 g, $CO_2$ 50 atm; 120 °C, 20 h.

Fig. 1. This may be ascribed to the increase in the relative concentration of $CO_2$ to butadiene, because $CO_2$ concentration in the solvent is almost constant whereas that of butadiene is lowered with the increase in the amount of the solvent.

When the reaction was carried out at temperature below 100 °C and terminated before the complete conversion of butadiene, then the organic acids, (**5**) and (**6**), were isolated in up to 10% together with the lactone (**4**). Both acids were easily converted into the lactone (**4**) under the conditions given in Table 1, indicating that these acids were the precursors of the lactone (**4**). The $CO_2$-incorporated products were obtained in the highest yield from the catalyst system involving Pd(dpe)$_2$ in DMF at 84 °C as shown in Fig. 2.

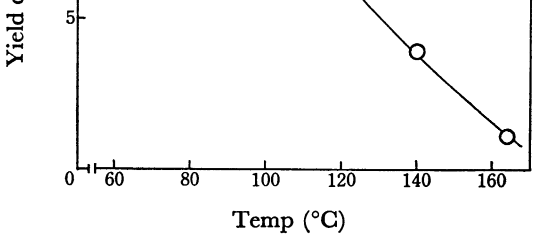


Fig. 2. Effect of temperature on the yield of **4**+**5**+**6** Pd(dpe)$_2$ 0.2 mmol, butadiene 7.3 g, DMF 20 ml, $CO_2$ 50 atm; 20 h.

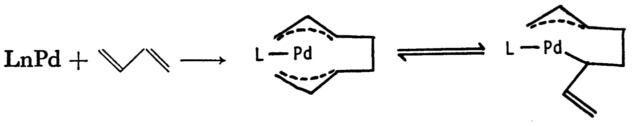
Table 2. Effect of ligand
Pd(dba)$_2$ 0.2 mmol, ligand (unidentate 0.8 mmol, bidentate 0.4 mmol), butadiene 7.3 g, DMF 20 ml, $CO_2$ 50 atm; 120 °C, 20 h.

| Ligand | Product yield (%)[a] Octatrienes | **4** | Others[b] |
|---|---|---|---|
| $P(OEt)_3$[c] | 65.9 | 0 | 14.1 |
| $PPh_3$[c] | 72.5 | 0.5 | 11.3 |
| $BuPPh_2$ | 56.8 | 1.6 | 12.6 |
| $Bu_2PPh$ | 58.5 | 1.2 | 11.9 |
| $Bu_3P$ | 67.8 | 2.5 | 9.9 |
| $AsPh_3$ | trace | 0 | 4.3[d] |
| $Ph_2PCH_2CH_2OH$ | 71.6 | 0.7 | 8.0 |
| $Ph_2PCH_2CH_2NEt_2$ | 72.6 | 1.4 | 8.6 |
| $Ph_2P(CH_2)_2PPh_2$ | 74.4 | 5.4 | 9.7 |
| $Ph_2P(CH_2)_3PPh_2$ | 1.3 | 0.1 | 5.0[d] |
| $Ph_2P(CH_2)_4PPh_2$ | 58.8 | 0.8 | 11.2 |
| $Ph_2P(CH_2)_6PPh_2$ | 55.6 | 2.0 | 9.9 |
| $Me_2P(CH_2)_2PMe_2$ | 49.5 | 4.8 | 12.3 |
| $Ph_2As(CH_2)_2AsPh_2$ | trace | 0 | 3.4[d] |
| $Me_2N(CH_2)_2NMe_2$ | 56.4 | 0.7 | 3.1 |

a) Yield is based on the butadiene charged. b) "Others" mainly consists of butadiene trimers. c) Pd(ligand)$_4$ complex was used. d) Mainly 4-vinylcyclohexene.

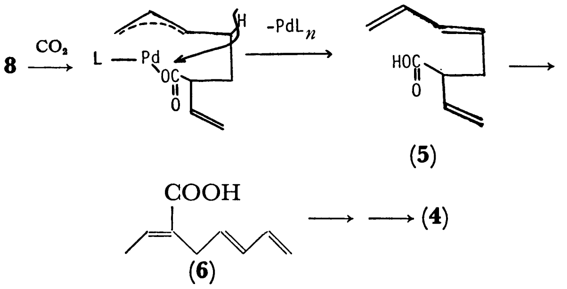
A study has been made of the effect of ligands on the yield of the lactone (**4**) using a catalyst system derived from Pd(dba)$_2$ (dba=dibenzylideneacetone) and a ligand. Results of the effects of unidentate and bidentate ligands are summarized in Table 2. Linear dimerization was also the main reaction in this catalyst system, and in some cases the activity for the dimerization was lost on addition of certain ligands, *e.g.*, arsines. The yield of the lactone (**4**) was very poor in the monodentate ligand systems in general, though basic ligand systems, *e.g.*, tributylphosphine system, brought about slightly higher yields than less basic ligand ones, *e.g.*, triphenylphosphine system. Among the bidentate ligands, $Ph_2PCH_2CH_2PPh_2$ and $Me_2PCH_2CH_2PMe_2$ appear to be suitable for the lactone formation. The $Ph_2P(CH_2)_3PPh_2$ system catalyzed the dimerization of butadiene in much less conversion. This ligand has such a high coordination ability that it may form a stable six membered chelate ring and occupies the active sites of the metal to stop the reaction.

Wilke,[6] Hagihara[7] and their co-workers have proposed π-allyl intermediates, **7** and **8**, for the palladium-catalyzed linear dimerization of butadiene. It has been assumed that the size of the palladium atom precludes the cyclization, and that a rapid hydrogen transfer occurs.



(**7**) (**8**)

We have proposed the following mechanism for this reaction, which involves the $CO_2$ insertion at the palladium-carbon bond followed by the transfer of hydrogen to give the acid (**5**).[1]



The distribution of the products is determined by the concentration and reactivity of these intermediates, **7** and **8**, which are influenced, in turn, by the reaction conditions and the steric and electronic properties of the ligands. Similar intermediates have often been proposed for the dimerization of butadiene catalyzed by nickel-phosphine complexes, and it is said that basic ligands stabilize the $\pi$-allyl, $\sigma$-allyl form, and that less basic ones stabilize the bis-$\pi$-allyl form. If this inspection is applicable to the palladium system, the experimental results for the monodentate ligands are in agreement with this hypothesis as can be seen from Table 2. This suggests that the catalyst is behaving as a nucleophile toward $CO_2$. Ditertiary phosphine-$[Ph_2P(CH_2)_nPPh_2]$ with $n=2$ may have the adequate stabilizing effect on the active intermediate (**8**) by the formation of a five membered chelate ring.

The suitability of polar, aprotic solvents for the lactone synthesis may be ascribable partly to the higher solubility of $CO_2$ in these media, and partly to their solvation effects; the nucleophilic nature of the intermediate (**8**) is supposed to be enhanced by the solvation of these solvents.

As an extention of the study we investigated the reaction of isoprene with $CO_2$. In the absence of $CO_2$, $Pd(dpe)_2$ complex catalyzed the dimerization of isoprene only in low conversions. In the presence of $CO_2$, the catalytic activity of the palladium complex was enhanced to yield considerable amounts of isoprene dimers. The major dimer was 2,7-dimethyl-1,3,7-octatriene, a tail-to-tail dimer. Several $CO_2$-incorporated products of five membered lactone structures were also formed in very low yields (about 1%). The detailed results may be published elsewhere.

## Experimental

GLC analyses were performed on a Shimadzu GC-3AH instrument [20% Silicone DC 550 (2 m) on Diasolid M (60—80 mesh) and 10% FFAP (2 m) on Chromosorb W (60—80 mesh) (He as the carrier gas)]. The measuring conditions were as follows: for the lactone (**4**); at 205 °C on the FFAP column with benzophenone as an internal standard: for the butadiene dimers; at 145 °C on the Silicone DC 550 column with *t*-butylbenzene as an internal standard. Preparative GLC for the $CO_2$-incorporated products was performed on a Shimadzu GC-2H instrument at 180 °C using $H_2$ as the carrier gas [10% FFAP (2.5 m) on Chromosorb W (60—80 mesh)]. The PMR spectra were recorded on a Hitachi R-24 apparatus (60 MHz), using the proton decouple method at the same time. IR and UV spectra were recorded on a Shimadzu IR 430 and a Shimadzu UV 200 apparatus, respectively.

*Reagents.* Solvents were dried by appropriate drying agents and distilled under nitrogen atmosphere. Butadiene (purity 99.99%) and $CO_2$ (purity 99.50%) were used without further purification. $BuPPh_2$,[8] $Bu_2PPh$,[9] $Ph_2PCH_2CH_2OH$,[10] $Ph_2PCH_2CH_2NEt_2$,[11] and $Me_2PCH_2CH_2PMe_2$[12] were prepared according to the published methods. The ditertiary phosphines $[Ph_2P(CH_2)_nPPh_2$ ($n=2$, 3, 4, and 6)] were prepared according to the method described by Hewertson and Watson.[8] The other ligands were commercially obtained. $Pd(dpe)_2$,[13] $Pt(dpe)_2$,[13] $Ni(dpe)_2$,[13] $HCo(dpe)_2$,[14] $H_2Fe(dpe)_2$,[15] $Pd(PPh_3)_4$,[16] $Pt(PPh_3)_4$,[17] $RhCl(PPh_3)_3$,[18] $H_2Ru(PPh_3)_4$,[19] $H_3Ir(PPh_3)_3$,[19] $Pd[P(OEt)_3]_4$,[20] and $Pd(dba)_2$,[21] were synthesized by the reported methods.

*Procedure.* A typical procedure was as follows. Into a 100 ml stainless steel autoclave equipped with an inductive rotary agitator, $Pd(dpe)_2$ (0.2 mmol), DMF (10 ml), and butadiene (7.3 g) were added under nitrogen atmosphere, then $CO_2$ was introduced to the pressure of 50 atm. The autoclave was heated to 120 °C and stirred for 20 h. The products were analyzed by GLC.

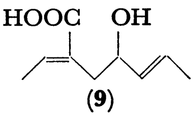
*Identification.* The octatrienes (bp ≈90 °C/100 mmHg) and the lactone (**4**) (bp ≈138 °C/5—6 mmHg) were distilled from the reaction mixture and purified by preparative GLC. The acids (**5**) and (**6**) were isolated from the reaction mixture by extraction with aqueous NaOH and after acidification were purified by preparative GLC.

*1,3,7-Octatriene (1).* PMR ($CCl_4$): $\delta$ 2.0—2.3 (m, 4H, $-CH_2-$), 4.7—5.2 (m, 4H, $CH_2=$), and 5.3—6.8 (m, 4H, $CH=$).

*1,3,6-Octatriene (2).* PMR ($CCl_4$): $\delta$ 1.6 (d, 3H, $CH_3$), 2.5—2.9 (m, 2H, $-CH_2-$), 4.6—5.1 (m, 2H, $CH_2=$), and 5.2—6.7 (m, 5H, $CH=$).

*2,4,6-Octatriene (3).* PMR($CCl_4$): $\delta$ 1.7 (d, 6H, $CH_3$) and 5.2—6.2 (m, 6H, $CH=$).

*2-Ethylidene-5-hepten-4-olide(4).* Found: C, 71.20; H, 8.12%. Calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95%. IR (neat): 1755 (C=O), 1675, and 970 $cm^{-1}$ (*trans* CH=CH). PMR ($CCl_4$): $\delta$ 1.6—1.9 (m, 6H, $CH_3C=$), 2.1—3.3 (m, 2H, $CH_2$), 4.5—4.9 (m, 1H, HC), 5.1—6.0 (m, 2H, CH=CH), and 6.3—6.7 (m, 1H, $CH_3C\underline{H}=$). UV (EtOH): $\lambda_{max}$ 217 nm ($\varepsilon$16,300). The methyl proton peaks separated into two parts, centered at $\delta$ 1.70 and at $\delta$1.80, which were assigned by PMR spin decoupling method to the methyl group at position 7 and to the one in the ethylidine moiety, respectvely. The ordinal chemical shift value of the methyl group in ethylidine moiety ($\delta$ 1.80) indicates that the methyl group is *trans* position to the carbonyl group, becauce if it is *cis* position, the peak might appear in the lower field due to the anisotropy from the carbonyl group. The geminal protons in position 3 are non-equivalent due to the ring formation and give a typical AB pattern signal. In order to confirm this structure, the lactone (**4**) was hydrolyzed by aqueous NaOH. White solid (mp 101—103 °C) was obtained after acidification, which was identified to be a hydroxyl acid, 2-ethylidene-4-hydroxy-5-heptenoic acid (**9**), by the following data. Found:



(**9**)

C, 63.18; H, 8.54%. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29%. IR(KBr): 3400—3200 (OH), 3000—2500 (COOH), 1680 (C=C–COOH), and 960 $cm^{-1}$ (*trans* $CH=C\underline{H}$). UV (EtOH): $\lambda_{max}$ 213 nm ($\varepsilon$10480). PMR ($CD_3COCD_3$): $\delta$ 1.61 (m, 3H, $CH_3$-position 7), 1.82 (d, 3H, $CH_3$ in ethylidine moiety), 2.51 (d, 2H, $CH_2$), 4.16 (m, 1H, CH), 5.3—5.6 (m, 2H, CH=CH), 6.93 (q, 1H, $CH_3C\underline{H}=$), and 7.00 (b, 2H, COOH and OH). The methyl group in the ethylidene moiety confirmed to be *trans* position to the carbonyl group on the basis of the value of its PMR chemical shift.

*2-Vinyl-4,6-heptadienoic Acid (5).* IR (neat): 3200—2400 (COOH), 1705 (C=O), 1418 (COOH), 1005 and 905 cm$^{-1}$ ($CH_2$=CH). PMR ($CCl_4$): $\delta$ 2.2 (q, 2H, $-CH_2-$), 2.8 (t, 1H, CH), 4.7—5.2 (m, 2H, $CH_2$=), 5.3—6.4 (m, 4H, CH=), and 11.2 (s, 1H, COOH).

*2-Ethylidiene-4,6-hept-dienoic Acid (6).* Found: C, 71.06, H; 7.88%. Calcd for $C_9H_{12}O_2$: C, 71.03, H; 7.95%. IR (neat): 3200—2400 (COOH), 1680 (C=C–COOH), 1635 (C=$CH_2$), 1420 and 1280 (COOH), and 1005 and 900 cm$^{-1}$ ($CH_2$=CH). PMR($CCl_4$): $\delta$ 1.80 (d, 3H, $CH_3$), 3.00 (d, 2H, $-CH_2-$), 4.94 (m, 2H, $CH_2$=), 5.4—6.2 (m, 3H, CH=), 6.94 (q, 1H, $CH_3C\underline{H}$=), and 11.65 (s, 1H, COOH). UV (EtOH): $\lambda_{max}$ 209 nm ($\varepsilon$ 4900).

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