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Monoterpene Syntheses via a Palladium Catalyzed Isoprene Dimerization

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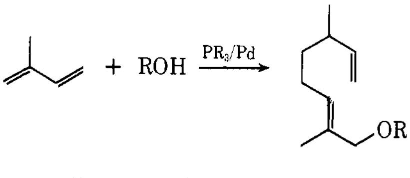
Isoprene has been reductively dimerized with formic acid and triethylamine at room temperature using 1% palladium–organophosphine catalysts, to head-to-tail dimers in up to 79% yields. The two head-to-tail dimers obtained are easily separated in high yield from the other dimers present by conversion into 7-chloro-3,7-dimethyl-1-octene with aqueous hydrochloric acid at room temperature. This chloro derivative is a convenient and practical starting material for the preparation of various terpene products. Hydroboration and pyrolysis, for example, produced a 1:3 mixture of α- and β-citronellol. *tert*-Butyl peracetate, hydrolysis, and pyrolysis gave linalool. 2,3-Dimethyl-1,3-butadiene and *cis*- and *trans*-1,3-pentadiene were also dimerized by these catalysts. Possible reaction mechanisms for the dimerization are discussed.

Several reports of transition metal catalyzed dimerizations of isoprene have appeared but yields of the dimer with the desired "head to tail" structure have generally been low and/or conversion of the dimer into useful terpene derivatives required several steps. For example, Uchida et al.[1] have reported a tetraallylzirconium–ethylaluminum sesquichloride catalyzed dimerization to 2,6-dimethyl-1,3,6-octatriene in 50% yield. The conversion of this isomer into useful terpenes probably would require several steps. Similarly, Takahashi et al.[2] have reported a dimerization catalyzed by dibromobis(diphenylphosphinoethane)palladium(II) and sodium phenoxide which produced the more desirable isomer, 2,6-dimethyl-1,3,7-octatriene, but only in 49% yield. Perhaps the most successful dimerizations were achieved in alcohol solution with triorganophosphine–palladium catalysts where ca. 75% yields of 8-alkoxy-3,7-dimethyl-1,6-octadienes were obtained.[3,4] More recently, the 8-ethoxy-3,7-dimethyl-1,6-octadiene has been converted into citronellol in three steps in 43% yield.[5] Promising dimerizations employing main group organometallics have also been reported recently.[6,7]



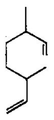
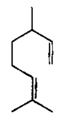
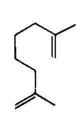
The isomeric dimers produced by palladium catalysis are clearly very dependent upon the ligands, solvent, and reaction conditions employed. Note, for example, that Josey[8] reports that in acetone solution with maleic anhydride–bis(triphenylphosphine)palladium(0) as catalyst at 105 °C isoprene gave mainly 2,7-dimethyl-1,3,7-octatriene as a product. The problem of the head to tail dimerization of isoprene with palladium catalysts seemed attractive to us because it appeared that with the proper choice of reaction conditions and ligands a practical monoterpene synthesis might be achievable.

Several of the reported palladium catalyzed dimerizations were investigated initially and eventually it was decided to concentrate on the triorganophosphine palladium salt dimerization carried out in the presence of formic acid and triethylamine which had previously been tried only with butadiene.[9,10] This reaction produced dimer dienes and carbon dioxide rather than trienes or formate esters. Preliminary experiments with isoprene indicated that good yields of head to tail dimers could be obtained under some conditions. After considerable effort, catalysts were developed which produce desirable dimers in better than 75% yields based upon the isoprene used. Experiments have determined that these dimers may be easily separated and converted into known, natural monoterpenes.

Results and Discussion

Several variables occur in the reductive diene dimerization reaction. These were investigated empirically and the results were combined in various ways to produce the most favorable yields of the desired head to tail isoprene dimers. Representative experiments of the large number carried out are shown in Table I. Very small amounts of dimers (and reduced dimers) other than those listed in Table I were observed in some experiments but these were not identified with certainty. Spectral data for the isoprene dimers and other products prepared in this investigation are listed in Table II, which will appear only in the microfilm edition of this journal. (See paragraph at end of paper regarding supplementary material.) The investigation began with the use of dichlorobis(triarylphosphine)palladium(II) complexes as catalysts. The first five entries in Table I show clear trends with changes in the para substituents in the arylphosphine ligands. The total yields of dimers decrease as the electron-donating capacity of the para substituent increases. The p-CF_3 complex gives 91% while the p-OCH_3 derivative produced only 27% dimer; the remainder of the isoprene is converted to isomeric methylbutenes. The percentage of head to tail dimers in the mixture does not vary much with these changes but, of course, the total yields based upon isoprene consumed decrease significantly, from 41 to 12% in the series. The reaction rates, on the other hand, in-

Table I. Isoprene Reductive Dimerizations

						Composition of dimer mixture				
Expt no.	Catalyst	Registry no.	Solvent (22 mmol added)	Reaction time, h	% dimers					Total % head to tail dimer
1	$Cl_2[P(p\text{-}C_6H_4CF)_3]_2Pd^a$	59840-39-0		24	91	25	38	7	25	41
2	$Cl_2[P(p\text{-}C_6H_4F)_3]_2Pd^a$	31173-69-0		10	59	45	35	6	11	24
3	$Cl_2[P(p\text{-}C_6H_4Cl)_3]_2Pd^a$	57457-62-2		10	73	37	35	7	17	31
4	$Cl_2[P(C_6H_5)_3]_2Pd^a$	13965-03-2		24	24[b]	39	38	7	11	11
5	$Cl_2[P(p\text{-}C_6H_4OCH_3)_3]_2Pd^a$	56781-20-5		24	27	57	43			12
6	$Cl_2[P(OCH_2)_3CCH_2CH_3]_2Pd^a$	59840-37-8		24	55	28	26	22	5	31
7	$Cl_2[P(OCH_3)_3]_2Pd^a$	30153-54-9		24	33	44	25	14	3	13
8	$Cl_2[P(O\text{-}o\text{-}C_6H_4CH_3)_3]_2Pd^a$	41871-92-5		24	28[b]	19	34	10	21	12
9	$Cl_2[P(o\text{-}C_6H_4OCH_3)(C_6H_5)_2]Pd^a$	59840-40-3		24	16	51	42	4	4	7
10	$Cl_2[P(o\text{-}C_6H_4CH_3)_3]_2Pd^a$	40691-33-6		24	23[b]	40	29	17	9	11
11	$Cl_2[P(C_6H_{11})_3]_2Pd^a$	29934-17-6		24	60	57	38	1	4	23
12	$(AcO)_2[P(C_6H_{11})_3]_2Pd^a$	59840-38-9		7	96	38	37	3	6	38
13	$(AcO)_2[P(C_6H_5)_3]_2Pd^a$	14588-08-0		4	56	49	33	6	8	22
14	$Cl_2[P(OCH_2)_3CCH_2CH_3]_2Pd^a$		THF	24	89	12	40	18	13	52
15	$Cl_2[P(p\text{-}C_6H_4Cl)_3]_2Pd^a$		THF	24	83	15	58	8	16	55
16	$(AcO)_2[P(C_6H_5)_3]_2Pd^a$		THF	1	77	33	41	13	13	42
17	$(AcO)_2[P(C_6H_5)_3]_2Pd^d$		THF	3	98	8	61	5	18	65
18	$(AcO)_2[P(C_6H_5)_3]_2Pd$ + $2\ P(C_6H_5)_3$		THF	24	10	25	62	4	9	7
19	$[P(C_6H_5)_3]_4Pd$	14221-01-3	THF	24	5	22	68	3	8	4
20	$\frac{1}{2}(\eta^3\text{-}C_3H_5PdOAc)_2$ + $P(C_6H_5)_3{}^{c,e}$	12084-71-8	THF	12	93	18	64	5	14	64
21	$\frac{1}{2}(\eta^3\text{-}C_3H_5PdOAc)_2$ + $P(p\text{-}C_6H_4CH_3)_3{}^{c,e}$		THF	12	97	22	61	6	11	64
22	$\frac{1}{2}(\eta^3\text{-}C_3H_5PdOAc)_2$ + $P(C_6F_5)_3{}^{c,e}$		THF	12	0					0
23	$\frac{1}{2}(\eta^3\text{-}C_3H_5PdOAc)_2$ + $P(OCH_2)_3CCH_2CH_3{}^{c,d,e}$		THF	12	88	3	41	21	16	54
24	$\frac{1}{2}(\eta^3\text{-}C_3H_5PdOAc)_2$ + $P(p\text{-}C_6H_4CF_3)_3{}^{c,d}$		THF	2	80	35	53	13		53
25	$\frac{1}{2}(\eta^3\text{-}C_3H_5PdOAc)_2$ + $P(o\text{-}C_6H_4CF_3)_3{}^{c,d}$		THF	2	68	50	22	10	11	22
26	$\frac{1}{2}(\eta^3\text{-}C_3H_5PdOAc)_2$ + $P(1\text{-}C_{10}H_7)_3{}^{c,e}$		THF	12	93	30	65		5	60
27	$\frac{1}{2}(\eta^3\text{-}C_3H_5PdOAc)_2$ + $P(o\text{-}C_6H_5C_6H_4)_3{}^{c,e}$		THF	12	8	68	32			3
28	$\frac{1}{2}(\eta^3\text{-}C_3H_5PdOAc)_2$ + $P[2,3,4,5\text{-}C_6H(CH_3)_4]_3{}^{c,e}$		THF	16	95	13	31	20	5	47
29	$\frac{1}{2}(\eta^3\text{-}C_3H_5PdOAc)_2$ + $P(o\text{-}C_6H_4CH_3)_3{}^{c,d,e}$		THF	5	98	6	55	26	12	79
30	$\frac{1}{2}(\eta^3\text{-}C_3H_5PdOAc)_2$ + $P(o\text{-}C_6H_4C_2H_5)^{c,e}$		THF	12	95	4	42	34	6	72
31	$\frac{1}{2}(\eta^3\text{-}C_3H_5PdOAc)_2$ + $P\{2,5\text{-}C_6H_3[CH(CH_3)_2]_2\}_3{}^{c,e}$		THF	12	71	11	45	36	1	58
32	$\frac{1}{2}(\eta^3\text{-}C_3H_5PdOAc)_2$ + $P\{2,5\text{-}C_6H_3[CH(CH_3)_2]_2\}_3{}^{c,d,e}$		THF	12	98	18	37	33	1	68
33	$\frac{1}{2}(\eta^3\text{-}C_3H_5PdOAc)_2$ + $\frac{1}{2}P(o\text{-}C_6H_4CH_3)_3{}^{c,d,e}$		THF	12	59		21	40	10	36
34	$\frac{1}{2}(\eta^3\text{-}C_3H_5PdOAc)_2$ + $P(CH_2CH_2CN)_3{}^{c,d,e}$		THF	1.5	90	48	44	4	5	43
35	$Pd(OAc)_2$ + $P(o\text{-}C_6H_4CH_3)_3{}^{e,f}$	127-08-2	THF	5	85	18	42	31	7	62
36	$\frac{1}{2}(\eta^3\text{-}C_3H_5PdOAc)_2$ + $P(2\text{-}CH_3,\ 5\text{-}CF_3C_6H_3)_3{}^{c,d,e}$		THF	12	84	1	33	32	23	55

[a] Reaction carried out in a 30-ml capped, heavy-walled Pyrex tube with 0.069 mmol of catalyst, 11 mmol of triethylamine, 10 mmol of isoprene, and 0.5 ml of 98% formic acid under an argon atmosphere at 40–45 °C except where noted. [b] Yield of isolated dimer mixture. [c] Reaction carried out in a 30-ml capped, heavy-walled Pyrex tube with 0.065 mmol of $(\pi\text{-}C_3H_5PdOAc)_2$ and 0.128 mmol of triorganophosphine, 11 mmol of triethylamine, 10 ml of isoprene, and 0.5 ml of 98% formic acid under an argon atmosphere at 40–45 °C unless otherwise noted. [d] Formic acid added last in 50-μl amounts every 15 min. [e] Carried out at 20–25 °C. [f] The amount of catalyst employed was 0.128 mmol. The reaction was otherwise the same as *a*.

crease with increasing electron-donating ability of the substituents.

Steric effects upon the isoprene dimerization were investigated in experiments 6–11. These effects are apparently not separable from electronic effects and no clear trends can be observed. Similar total yields of dimers are obtained from the smallest ligand investigated, $P(OCH_2)_3CCH_2CH_3$, and the largest one looked at, $P(C_6H_{11})_3$. Much more head to head dimer is produced with the larger ligand, however.

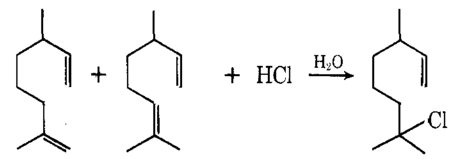
The anion present in the catalyst proved to be an important variable. Both reaction rates and product composition are significantly affected. changing the anions from chloride to acetate increases reaction rates by a factor of about 10 in the two cases studied as can be seen by comparing the results of experiments 4 and 13, and 11 and 12. In both cases, the change to the acetate complex also significantly increases the yields of head to tail dimers obtained.

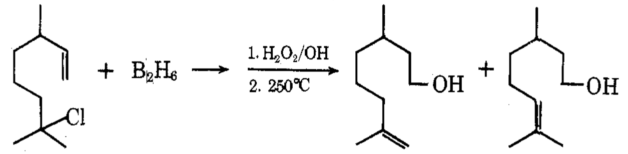
The use of THF as a solvent also has been shown to be beneficial, particularly when acetate complexes are used as catalysts. Total yields of dimers and relative yields of head to tail dimers improve upon addition of THF. The effect of THF can be seen by comparing experiments 14 with 6, 15 with 3, and 16 with 13. At this point the remarkable improvement produced by adding the formic acid slowly rather than all initially was discovered. Experiment 16 with diacetatobis(triphenylphosphine)palladium(II) as catalyst, with an initial 2.6 equiv of formic acid added, gave a 77% yield of dimers with a total yield of head to tail dimers of 42%. Slow addition of the same amount of formic acid, experiment 17, improves the total yield to 98% and the head to tail dimer yield to 65%. This effect was subsequently found to be more the result of the amount of acid added initially rather than the rate of addition. The use of 1 equiv of formic acid initially substantially improves the yield of diene dimer over the reaction with 2.6 equiv. The slow addition of the 1 equiv of acid improves the yields somewhat more but this procedure significantly increases the tme required to complete the reaction. The major influence of reducing the formic acid concentration is to decrease the amount of methylbutenes formed.

The triorganophosphine to palladium ratio was found to be another, very important, variable. Addition of 2 equiv of triphenylphosphine to reaction 16, in which 77% dimers were obtained, lowers the yield of dimers to only 10% (experiment 18). There is a corresponding increase in the yield of methylbutenes obtained. Similarly, the use of tetrakis(triphenylphosphine)palladium(0) as catalyst produces only 5% dimers and 95% methylbutenes (experiment 19). Lowering the phosphine to palladium ratio below 2:1 improves yields further. A ratio of 1:1 proved to be optimum. For these experiments, "π-allylpalladium acetate dimer"[11] has been employed with the organophosphine being added separately to the reaction mixtures. Experiments 20–34 illustrate the improvements brought about with lower PR_3:Pd ratios sometimes combined with slow addition of the formic acid. Changes in the para substituent of the phosphine now show smaller effects than in the 2:1 catalysts, but distinct trends are not seen. Steric effects appear to be more significant with the 1:1 than with the 2:1 catalysts, with the tri-*o*-tolylphosphine ligand being about the best (experiment 29). With slow addition of the formic acid this catalyst produces head to tail dimers in 79% yield based upon the isoprene added.

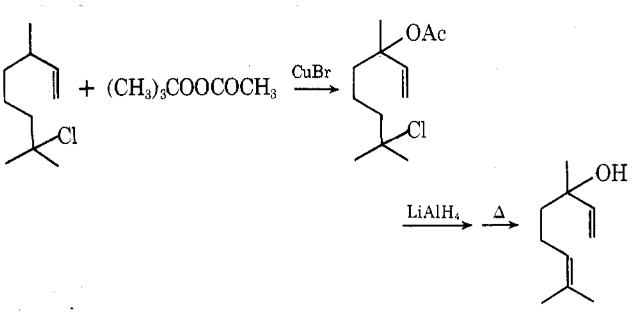
The selectivity of the dimerization to head to tail products is also improved slightly by lowering reaction temperatures from 40–45 °C to 20–25 °C.

The dimerization shown in experiment 29 has been scaled up and carried out with 0.50 mol of isoprene. There was obtained an 87% isolated yield of dimer which contained 71% head to tail isomers. While the isomeric dienes could be separated by careful fractional distillation, for the purpose of preparing terpene derivatives this was not necessary. The mixture was found to be converted into easily separable products if it was reacted with concentrated aqueous hydrochloric acid at room temperature. Only the di- and trisubstituted double bonds reacted to form tertiary chlorides while the terminal, monosubstituted double bonds were unaffected. Thus, the head to head dimer remained unchanged after HCl treatment, the tail to tail isomer formed a dichloride, and the desired head to tail dimers both gave the same monochloride. These reaction products were very easily separated by distillation under reduced pressure. The monochloro product, 7-chloro-3,7-dimethyl-1-octene, was isolated in 84% yield based upon the head to tail dimers present. This monochloride is a convenient starting material for terpene syntheses. Reaction with diborane, for example, followed by oxidation and pyrolytic dehydrohalogenation at 250 °C produced an approximately 1:3 mixture of α- and β-citronellols in 70% yield.

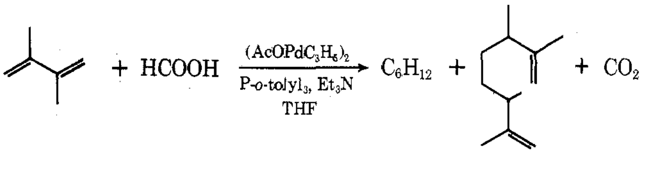




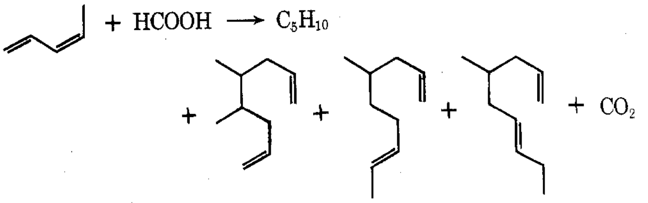
About 5–10% of secondary alcohol also appeared to be formed in the hydroboration, as expected. The monochloro compound was also oxidized with *tert*-butyl peracetate and a cuprous bromide catalyst to the chloro acetate which was reduced with $LiAlH_4$ and pyrolyzed to linalool in 64% overall yield.



The utility of the reductive dimerization reaction for dimerization of dienes other than butadiene and isoprene has also been explored briefly. Both 2,3-dimethyl-1,3-butadiene and *cis*- and *trans*-1,3-pentadiene were found to dimerize slowly with the π-allylpalladium acetate dimer–tri-*o*-tolylphosphine catalyst in yields of 42, 67, and 68%, respectively. The dimethylbutadiene, as might have been expected, gave largely 2,3,6,7-tetramethyl-1,7-octadiene while the pentadienes gave mixtures of at least three compounds.

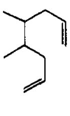
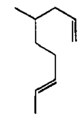


The major product from *cis*-1,3-pentadiene (65% of dimers) proved to be 4,5-dimethyl-1,7-octadiene. The other dimers appeared to be *trans*-4-methyl-1,7-nonadiene (24%) and *trans*-4-methyl-1,6-nonadiene (8%). The assignment of stereochemistry is based only upon the absence of the cis-alkene band at ca. 700 cm^{-1} and could be incorrect. No isomerization of unreacted *cis*-pentadiene was observed at 25 °C during the dimerization.



Under the same conditions *trans*-1,3-pentadiene gave the same three major dimers but in different amounts. The major isomer was *trans*-4-methyl-1,7-nonadiene (72%). The 1,6-diene was formed in 20% yield while the 4,5-dimethyl isomer was obtained in only 8% yield. No isomerization of the *trans*-pentadiene was observed at 25 °C. At 40 °C, however,

Table III. 1,3-Pentadiene Reductive Dimerizations[a]

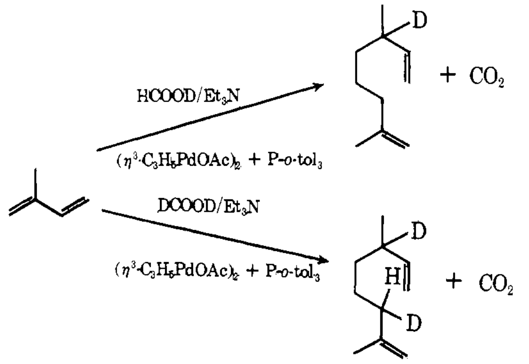
					Composition of dimer mixture		
Isomer	Catalyst	Temp, °C	Reaction time, h	% dimers			
Cis	½$(\eta^3\text{-}C_3H_5PdOAc)_2 + P(p\text{-}FC_6H_4)_3$	25	70	52	38	41	19
Trans	½$(\eta^3\text{-}C_3H_5PdOAc)_2 + P(p\text{-}FC_6H_4)_3$	25	70	59	6	67	27
Cis	½$(\eta^3\text{-}C_3H_5PdOAc)_2 + P(o\text{-}CF_3C_6H_4)_3$	25	70	4	100		
Trans	½$(\eta^3\text{-}C_3H_5PdOAc)_2 + P(o\text{-}CF_3C_6H_4)_3$	25	70	0			
Cis	½$(\eta^3\text{-}C_3H_5PdOAc)_2 + P(o\text{-}CH_3C_6H_4)_3$	25	69	67	65	24	8
Trans	½$(\eta^3\text{-}C_3H_5PdOAc)_2 + P(o\text{-}CH_3C_6H_4)_3$	25	69	68	8	72	20
Cis	½$(\eta^3\text{-}C_3H_5PdOAc)_2 + P(o\text{-}CH_3C_6H_4)_3$	40[b]	20	42	49	34	15
Trans	½$(\eta^3\text{-}C_3H_5PdOAc)_2 + P(o\text{-}CH_3C_6H_4)_3$	40	20	49	2	71	27

[a] Reaction conditions: 0.069 mmol of catalyst, 11 mmol of triethylamine, 10 mmol of diene, and 0.5 ml of 98% formic acid carried out under argon. [b] *cis*-1,3-Pentadiene isomerized to the trans isomer during the reaction as determined by VPC.

cis-1,3-pentadiene was isomerized to the trans isomer during the dimerization. Even at 40 °C, however, there was still a substantial difference in the composition of the product mixtures obtained from the two isomeric pentadienes. The results obtained in the above experiments and with a few other catalysts are listed in Table III.

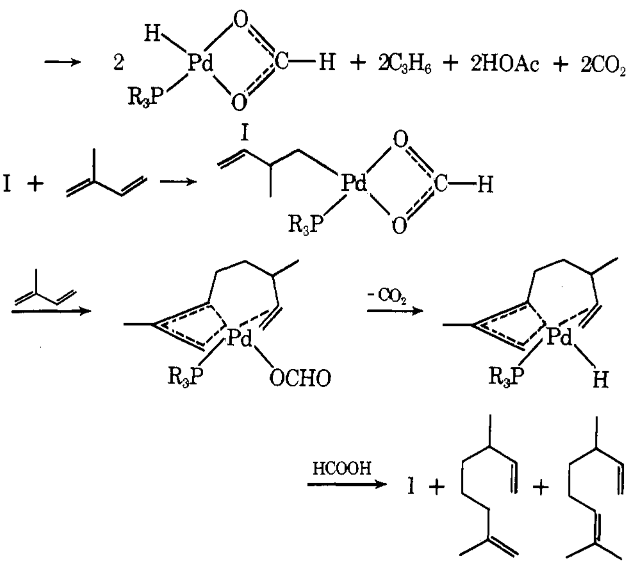
Dimerization did not occur under the above conditions with 1,3-cyclohexadiene, *trans,trans*-2,4-hexadiene, or myrcene. In all cases, CO_2 was evolved suggesting that reduction took place.

Mechanism of Reductive Dimerization. Various attempts to isolate pure organometallic intermediates from the dimerization of isoprene were unsuccessful. Only amorphous, unstable materials could be obtained. Some useful information was gained by carrying out the dimerization in the presence of deuterated formic acid, however, Reactions similar to experiment 29 were carried out with both dideuterated and carboxyl deuterated formic acid. The carboxyl deuterium was found on carbon 6 and the other deuterium on carbon 3 of the 2,6-dimethyl-1,7-octadiene chain.



Two mechanisms appear reasonable to consider for this dimerization. In both, palladium(0) is a necessary starting material. Palladium metal was shown to be formed within 5 min when formic acid was added to the usual reaction mixtures at 25 °C without the diene being present. In one mechanism formic acid may add oxidatively to the Pd(0) phosphine complex to form a hydridoformatopalladium(II) complex which reacts with isoprene to produce a formato(methylbutenyl)palladium complex. This complex could then add to a second isoprene, perhaps forming a chelated complex, which ultimately decomposes by losing CO_2 and reductively eliminating the diene dimer. The deuterium experiments are consistent only with metal hydride addition to the disubstituted isoprene double bond initially. A possible formulation is the following.

$(\eta^3\text{-}C_3H_5PdOAc)_2 + 4HCOOH + 2PR_3$

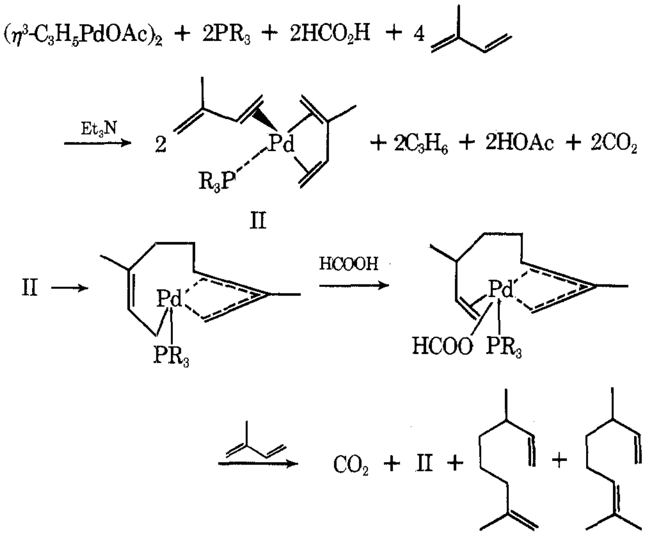


The function of the tertiary amine would be to allow the formation of a small equilibrium concentration of formic acid necessary to produce I but not have enough present to react rapidly with the methylbutenylpalladium intermediate and form methylbutenes. The preference for addition of the metal hydride to the disubstituted double bond of isoprene is difficult to explain. Results from presumed hydridohalopalladium catalyzed carbonylations of dienes do not appear consistent with the above proposed mechanism. Carbonylation of butadiene in methanol at 70 °C gives entirely methyl 3-pentenoate[12] rather than the 4-pentenoate required to be consistent with the above mechanism. Isoprene under similar conditions gave three isomeric esters. The formation of the

$$CH_2{=}CHCH{=}CH_2 + CO + CH_3OH \xrightarrow[1000\text{ psi},\ 70\,°C]{[Bu_3PPdI_2]_2} CH_3CH{=}CHCH_2COOCH_3$$

major product, methyl 4-methyl-3-pentenoate,[12] is also not consistent. The carbonylation of *trans*-1,3-pentadiene in ethanol likewise produced only ethyl 2-methyl-3-pentenoate,[13] a product not expected if the pentadiene dimerization proceeds by an initial 1,2-hydridopalladium addition to the more substituted double bond. While these results do not necessarily rule out the above mechanism, the second mechanism below appears to better explain the facts.

The other mechanism we consider possible involves coupling of two isoprene units on Pd)0) to form a dimethyloctadienediylpalladium(II) complex which is then reduced by formic acid with CO_2 elimination. The intermediate bisallylic complex would be analogous to the isolated nickel complex obtained in the reaction of isoprene with triphenylphosphine-1,5,9-cyclododecadienenickel(0)[14] with a similar mechanism of formation as suggested by Wilke et al.[15] A possible formulation for the palladium catalyzed reaction is the following.



The tertiary amine would be necessary to reduce the formic acid concentration, so that II undergoes coupling rather than reduction by reacting with formic acid.

In either mechanism, formation of the minor, second isomeric head to tail dimer could occur by hydrogen transfer to the primary end of the π-allylic group rather than the secondary end.

The details as to why the head to tail isoprene dimers are preferentially formed with some catalysts and not with others remain to be explained. It is clear that both chloride ligands and more than one organophosphine ligand per palladium favor formation of methylbutenes rather than dimers. A competition appears to exist between dimerization and reduction. If the dimerization is prevented or inhibited by the presence of an excess of "good ligands" (such as phosphine or chloride ion) which take up coordination positions required by the second diene unit, then reduction appears to occur. The coupling of the diene units would seem to be best explained by formation of a tetrahedral intermediate such as II where an η^4 diene reacts with an η^2 diene ligand. If both dienes were only η^2 and coupling occurred through the uncoordinated double bonds, it would be difficult to explain why one diene would be attached at the monosubstituted double bond and the other at the disubstituted one, particularly when increasing the steric bulk of the phosphine group would require an increase in coordination to the disubstituted double bond. Electronic and steric effects in the phosphine would be felt by both the η^4 and η^2 dienes and their orientations with respect to each other would be influenced by these factors. Coupling will presumably occur between the ends of the diene units closest together.

The dimeric products obtained from 2,3-dimethylbutadiene and the 1,3-pentadienes are explicable in terms of the mechanism proposed above for the isoprene dimerization. The formation of some of the same three isomeric products from both *cis*- and *trans*-1,3-pentadienes simply may be the result of a partial isomerization of the cis to the trans isomer on the catalyst before dimerization occurs. Alternatively, the expected intermediates for the formation of the two methylnonadienes may be isomerized through π to σ allylic transformations with bond rotations. If equilibration were rapid compared to reduction the same ratio of the 4-methyl-1,6-nonadiene to the 1,7-diene would be expected from both the *cis*- and *trans*-1,3-pentadiene and this is approximately correct as shown in Table II.

Experimental Section

Reagents. Isoprene, formic acid (98%), and 2,3-dimethylbutadiene were obtained from the Aldrich Chemical Co. and used without further purification. The triethylamine was obtained from the Eastman Organic Chemicals Co. and dried over molecular sieves (4 Å). The THF was obtained from the Fisher Scientific Co. and used without further purification except when used in the deuteration experiments, when it was dried over the sodium benzophenone ketyl. Formic acid-d_2 was obtained from Stohler Isotope Chemicals. Formic acid-*O*-d_1 was obtained by treating excess sodium formate with trifluoroacetic acid-d_1 and distilling the volatile material at 25 mm. *cis*- and *trans*-1,3-pentadiene were obtained from the Chemical Samples Co. Catalysts of formula L_2PdCl_2 were obtained by treating $(PhCN)_2PdCl_2$ with 2 equiv of the phosphine in benzene and filtering the resulting precipitates. The catalysts were routinely recrystallized from CH_2Cl_2/hexane. Complexes of the form $L_2Pd(OAc)_2$ were prepared by treating $Pd(OAc)_2$ in benzene with 2 equiv of the phosphine and recovering the resulting solid by concentrating the solution. The $[(\eta^3\text{-allyl})PdOAc]_2$ dimer was prepared according to the method of Robinson and Shaw.[9] The tri-*o*-ethylphenylphosphine, tri-2,3,4,5-tetramethylphenylphosphine, tri-*o*-phenylphenylphosphine, and the tri-2,5-diisopropylphenylphosphine were prepared by the Grignard reaction of the bromides with phosphorus trichloride in THF. Other phosphines and phosphites were commercially available from the Alfa Chemical Corp.

General Procedure for Small-Scale Reductive Dimerization. Reactions were carried out in 30-ml heavy-walled Pyrex tubes which had a lip around the opening so that the tubes could be sealed with rubber-lined bottle caps. The catalysts, 0.069 mmol, and a magnetic stirring bar were placed in the tube and the system purged with argon. The tube was then quickly capped and 1.6 ml (11 mmol) of triethylamine, 1 ml (10 mmol) of isoprene, and ca. 0.13 g of 1,3,3,4-tetramethylpentane as internal standard were injected by means of syringes through a small hole in the metal cap on the tube, through the rubber liner. The formic acid could now be introduced all at once, 0.5 ml (13 mmol) usually or in 50-μl portions at 15-min intervals while the reaction mixture was stirred at the required temperature. If solvent was used it was added before the formic acid. Two liquid phases were usually noted when the formic acid was all added initially. The rate of the reactions could be conveniently measured by noting the rate of pressure increase in the tubes due to formation of carbon dioxide. In our reaction vessels 30–50 psig developed depending upon the reaction temperature. Pressure gauges attached to syringe needles were inserted in the reaction tubes to measure the pressure changes. Reaction mixtures were analyzed by VPC directly with reference to the internal standard present. Analyses were carried out on a 10-ft DC 550 column at 120 °C. The major isoprene products eluted in the following order: 3,6-dimethyl-1,7-octadiene, 3,7-dimethyl-1,7-octadiene, 3,7-dimethyl-1,6-octadiene, and 2,7-dimethyl-1,7-octadiene.

7-Chloro-3,7-dimethyl-1-octene. In a 500-ml three-necked round-bottomed flask equipped with a mechanical stirrer, dry ice condenser attached to an argon cylinder, and a gas bubbler outlet were placed 0.95 g (2.3 mmol) of acetato-η^3-allylpalladium(II) dimer,[11] 1.41 g (4.6 mmol) of tri-*o*-tolylphosphine, 90 ml of tetrahydrofuran, 80 ml of triethylamine, and finally 50 ml (0.3 mol) of 98% formic acid was added dropwise over a period of 2–3 h. After stirring for a total of 5 h VPC analyses showed that all of the isoprene had reacted. The total reaction mixture was then subjected to distillation under reduced pressure. The tetrahydrofuran and amine were removed at 25–30 °c at 40 mm. The higher boiling fraction, bp up to 60 °C at 20 mm, was the isoprene dimer mixture. There was obtained 30.1 g (87.5% based upon the isoprene used). VPC analyses showed the product to contain 72% of the two isomeric head to tail dimers.

The entire dimer product was then added to 120 ml of concentrated hydrochloric acid and the two-phase mixture was stirred at room temperature for 24 h. The reaction mixture was next diluted with 200 ml of water and extracted three times with ether and the combined extracts were washed with saturated aqueous sodium bicarbonate. After drying over anhydrous magnesium sulfate, the ether was removed on a rotary evaporator at room temperature and the residue was distilled under reduced pressure through a short Vigreux column. There was obtained 1.83 g of 3,6-dimethyl-1,7-octadiene, bp 30–35 °C (9 mm), 22.7 g (84%) of 7-chloro-3,7-dimethyl-1-octene, bp 55–60 °C (9 mm), and 11 g of 2,7-dichloro-2,7-dimethyloctane, bp 90–102

°C (9 mm). The latter compound crystallized on cooling in the freezer.

Anal. Calcd for $C_{10}H_{20}Cl_2$: C, 56.87; H, 9.47. Found: C, 57.13; H, 9.65.

Preparation of Citronellol. A solution of 5.0 g (28.6 mmol) of 7-chloro-3,7-dimethyl-1-octene and 4.65 g (123 mmol) of sodium borohydride in 150 ml of THF was stirred while 16.5 ml (105 mmol) of boron trifluoride etherate was added dropwise. After the addition, stirring was continued for 1 h. Then a solution of 4 g of sodium hydroxide in 50 ml of water was added slowly (foaming). After the addition, 33 ml of 30% hydrogen peroxide was added. Stirring was continued at room temperature for 1 h and then at reflux temperature for 3 h. Addition of water and extraction with ether gave 6.05 g of crude chloro alcohol after evaporation of the solvent. Attempts to dehydrohalogenate with alcoholic potassium hydroxide gave only low yields of the desired products. Better results were obtained by pyrolysis in a gas chromatograph. With an inlet temperature of 250 °C on a 10-ft 20% Carbowax 20M column at 200 °C, a 70% yield of a mixture of α- and β-citronellol was obtained. The β isomer predominated in about a 3:1 ratio over the α. The NMR spectra of the products confirmed their identities. About 10% of another isomeric product was also present. It was probably secondary alcohol from addition of boron to the secondary position of the chloro olefin.

Preparation of Linalool. A mixture of 1.90 g (10.9 mmol) of 7-chloro-3,7-dimethyl-1-octene and 0.111 g of cuprous bromide was stirred and heated on a steam bath while 0.586 g (4.44 mmol) of *tert*-butyl peracetate was added dropwise over a period of 10 min. Heating was continued for 3 h. After cooling to room temperature a solution of 0.10 g of sodium iodide in 3 ml of acetic acid containing a trace of ferric chloride was added to decompose the excess perester. The resulting mixture was diluted with aqueous sodium carbonate and the products were extracted with ether. After drying over anhydrous magnesium sulfate, the solvent was evaporated and the red-brown oil remaining was rediissolved in ether and added to 0.57 g (15 mmol) of lithium aluminum hydride in 10 ml of ether. After stirring at room temperature for 2 h, water was added. The ether phase was separated and the aqueous residue was extracted again with ether. The combined extracts were dried and concentrated. The chloro alcohol so obtained was readily pyrolyzed in the gas chromatograph to linalool. Analyses by gas chromatograph on a 9-ft 20% SE-30 on Chromosorb W column at 175 °C (inlet 175 °C) indicated that a 64% yield of linalool had been obtained. Isolation of a sample of the product by preparative GLC and comparison of the NMR spectrum with that of authentic linalool showed the materials to be identical. Two other minor products were also present which were not identified.

Isoprene Reductive Dimerization with Deuterated Formic Acids. Reaction with both mono- and dideuterated formic acid were carried out as in experiment 20 in Table I. Products were isolated by diluting the reaction mixture with 50 ml of water, extracting with 100 ml of ether, washing the extracts with 2 N hydrochloric acid, and drying over anhydrous magnesium sulfate. The ether was evaporated and the deuterated 2,6-dimethyl-1,7-octadiene was isolated from the product mixture by preparative VPC on a 10-ft DC-550 column at 120 °C. Comparison of the NMR spectra of the deuterated products with the undeuterated ones indicated the position of the deuteriums. The 2,6-dimethyl-1,7-octadiene product was 72% monodeuterated, 27% undeuterated, and 4% dideuterated when HCOOD was used and 87% dideuterated, 3% mono- and 10% tetradeuterated when DCOOD was used as determined by mass spectroscopy.

Reductive Dimerization of 2,3-Dimethyl-1,3-butadiene. To a 30-ml Pyrex tube containing a magnetic stirring bar, as described in the general procedure for isoprene dimerization above, was added 0.057 g (0.13 mmol) of acetato-η^3-allylpalladium dimer,[11] 0.078 g (0.26 mmol) of tri-*o*-tolylphosphine, 3.6 ml of tetrahydrofuran, 3.2 ml of triethylamine, 2.3 ml (20 mmol) of 2,3-dimethyl-1,3-butadiene, and 0.025 g (1.93 mmol) of 2,3,3,4-tetramethylpentane as internal standard. The mixture was stirred in the capped tube under argon at room temperature and 0.5 ml (0.13 mmol) of 98% formic acid was added. Three days were required for complete reaction. VPC analysis then showed a 42% yield of one dimer and <5% of another formed.

The products were isolated as in the experiments described above with deuterated formic acid. Only the major product could be isolated in sufficient quantity to be identified by NMR. (See Table II for spectrum.) The molecular weight determined by high-resolution mass spectroscopy was 166.172 (calcd, 166.172).

Reductive Dimerization of *cis*- and *trans*-1,3-Pentadiene. These reactions were carried out exactly as in the preceding experiment using 2 ml (20 mmol) of the diene in place of the dimethylbutadiene. Three days were required for complete reaction. The major products were isolated by preparative VPC. Identification was made from ir and NMR spectra (See Table II) and molecular weights.

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Supplementary Material Available. Table II, a listing of NMR, ir, and mass spectroscopy data for the products prepared in this study (3 pages). Ordering information is given on any current masthead page.

Registry No.—Respective compounds in Table II, 59840-09-4, 6874-35-7, 2436-90-0, 59840-10-7, 59840-11-8, 59840-12-9, 106-22-9, 141-25-3, 59840-13-0, 59840-14-1, 59840-15-2, 59840-16-3; isoprene, 78-79-5; *cis*-1,3-pentadiene, 1574-41-0; *trans*-1,3-pentadiene, 2004-70-8.

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