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Reaction of Allene with Water Catalyzed by Palladium(0) in the Presence of Carbon Dioxide

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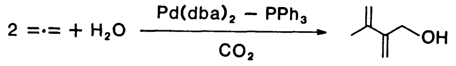
Synopsis. A novel reaction involving allene and water took place using palladium(0)–triphenylphosphine as a catalyst in the presence of carbon dioxide to yield 3-methyl-2-methylene-3-buten-1-ol, selectively. A related reaction of allene with methanol or ethanol was found to occur without carbon dioxide.

It has been reported that the dimerization of allene by palladium catalysts involves the incorporation of nucleophiles. The reaction produces functionalized 2,3-dialkyl-1,3-butadiene derivatives. The nucleophiles used so far has been carboxylic acids,[1] amines,[2] and active methylene compounds.[2] Triethylsilane also adds to allene to form triethylallylsilane.[2] In connection with the reaction of 1,3-diene with water,[3] we have studied the reaction of allene with water in the presence of palladium(0) catalysts and have found that a novel reaction took place under a carbon dioxide (CO_2) atmosphere to yield 3-methyl-2-methylene-3-buten-1-ol (**1**). The effect of CO_2 on the reaction of 1,3-butadiene with water has also been reported.[4] The related reaction of allene with alcohols, such as methanol and ethanol, was found to occur in the absence of CO_2. In this paper we describe the scope of the reaction.

Results and Discussion

It is possible to react allene with water in the presence of Pd(dba)$_2$–triphenylphosphine [dba=dibenzylideneacetone] (the catalyst) under a certain pressure of CO_2 to give 3-methyl-2-methylene-3-buten-1-ol (**1**). Allene oligomers were also formed in small amounts as byproducts. Without CO_2 the reaction was very sluggish and gave only a trace amount of **1**.



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Results are shown in Table 1. Generally ethers, such as tetrahydrofuran (THF) and 1,4-dioxane, were suitable as the solvent for the formation of **1**, except diethyl ether. Among them, THF was the best with respect to yield and selectivity toward **1**. Employment of a large excess of water (water/allene=10) did not give rise to **1**.

A reaction temperature of 80—90 °C and a reaction time of 1 h were the most suitable conditions. Longer reaction times caused a decrease in the yield, indicating that the product underwent further reaction.

The effect of the molar ratio PPh_3/Pd(dba)$_2$ on the reaction was investigated. The best result was obtained at a P/Pd ratio of 3 with 63% yield and 93% selectivity toward **1** at 80 °C in THF. A further addition of phosphine (P/Pd=4) led to a pronounced reduction of **1** (yield only 5%). When a molar ratio P/Pd=1 was used, a solvent-insoluble allene-polymer was formed at the expense of **1** (yield of **1**, 25%). The IR spectrum of the allene-polymer showed peaks at 1630, 1420, and 890 cm^{-1} indicating its structure as $[-CH_2C(=CH_2)-]_n$.[5]

The effect of diphosphines of the structure $Ph_2P(CH_2)_nPPh_2$ (n=1, 2, 3, 4, 6, 10, 12) was also examined under standard reaction conditions (diphosphine/Pd=1, THF, 80 °C, 1 h). Generally, these diphosphines retarded the formation rate of **1** (yield< 23%), especially with n=2 and 3, the reaction stopped. These observations may be explained by the chelating

Table 1. Reaction of allene with water[a)]

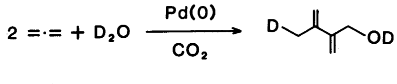
Solvent	PPh_3/Pd	Reaction Temp/°C	Reaction Time/h	Yield of $1^{b)}$/%	Selectivity$^{c)}$ %
Acetone	2	80	0.5	10	71
		80	1	26	74
		80	2	21	62
		80	4	16	71
THF	2	60	1	13	71
		80	1	58	93
		100	1	57	87
		120	1	42	90
	3	60	1	12	98
		80	1	63	93
		90	1	61	93
		100	1	35	97
1,4-Dioxane	2	80	1	40	67
Diethyl ether	2	80	1	6	75
Diglyme$^{d)}$	2	80	1	44	59
Acetonitrile	2	80	1	10	50
t-Butyl alcohol	2	80	1	10	50

a) Allene (1.0 g, 24.9 mmol) in most cases. Pd(dba)$_2$(0.5 mmol), H_2O(50 mmol), solvent(10 cm^3), CO_2(10 atm). b) Based on allene charged. c) Apparent selectivity based on the area ratio in the glc chart. d) $(CH_3OCH_2CH_2)_2O$.

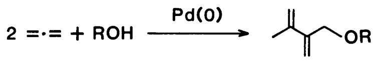
effect of the diphosphine ligands. They occupy coordination sites of the metal and prevent allene from occupying sufficient coordination sites for the reaction.

The introduction of CO_2 changes the acidity of the medium. Thus, further studies examined the effects of acids and bases. The addition of an acid such as $BF_3 \cdot OEt_2$ (10 equiv with respect to Pd) or trifluoroacetic acid (1.5 equiv) inhibited the formation of alcohol **1**. The formation of **1** was also inhibited by $NaHCO_3$ (2 equiv with respect to Pd) or NaOH (10 equiv). Interestingly, the catalytic activity was restored by the introduction of CO_2 in the case of $NaHCO_3$. The effect of CO_2 was characteristic.

Apparently hydrogen in the water was incorporated into the C_6 moiety of dienol **1**. ^1H NMR analysis clearly showed that a deuterium migrated into the methyl group of product **1** obtained from the experiment employing D_2O. However the reaction mechanism cannot be easily delineated by this observation alone, because such an incorporation of hydrogen may occur *via* a variety of mechanisms including the bis(σ-allyl)palladium intermediate.[2] At present we hesitate to propose a conclusive mechanism.



Unlike the allene–water reaction, the related reaction of allene with alcohol took place in the absence of CO_2. The product was 4-alkoxy-2-methyl-3-methylene-1-butene (**2**). The results are summarized in Table 2. The introduction of CO_2 led to a decreased formation of **2**, contrary to the case of water. The reaction was markedly effected by the molecular weight of the alcohol employed. Thus, methanol gave rise to a higher yield of **2a**, whereas 1-butanol gave this product only in trace amounts. Since there is only a little difference in the acidity constant among the alcohols used, steric factors may be responsible for such an effect.



2a R=Me
b R=Et

TABLE 2. REACTION OF ALLENE WITH ALCOHOL[a]

Alcohol		Solvent	Yield[b]	Selectivity[c]
cm³		cm³	%	%
MeOH	10	—	**2a** 9	100
	5	THF 5	40	96
	5	C_6H_6 5	29	100
	5	THF 5	11[d]	100
	5	THF 5	1[e]	26
	5	THF 5	25[f]	94
EtOH	5	THF 5	**2b** 16	84
n-BuOH	5	THF 5	trace	—

a) Allene(1.0 g, 24.9 mmol) in most cases. $Pd(dba)_2$ (0.5 mmol), PPh_3(1.0 mmol); 100 °C, 2 h. b) Based on allene charged. c) Apparent selectivity based on the area ratio in the glc chart. d) Under CO_2 pressure (10 atm). e) CH_3ONa(5.0 mmol) was added. f) Under CO_2 pressure(10 atm) in the presence of CH_3ONa(5.0 mmol).

Experimental

Reaction of Allene with Water. Typically, allene (1.0 g, 24.9 mol) was allowed to react with H_2O (50 mmol) in THF (10 cm³) in the presence of $Pd(dba)_2$ (0.5 mmol) and PPh_3 (1.0 mmol) at 80 °C for 1 h under CO_2 pressure (10 atm) in an autoclave. After the reaction, the mixture was filtered to remove allene polymers, if any. The filtrate was analyzed by glc; Silicone GE SE-52, 90 °C.

Isolation of 3-Methyl-2-methylene-3-buten-1-ol (1). The products of several experiments were combined. The solvent (THF) was removed by distillation under a reduced pressure at room temperature. The residue was subjected to flash-distillation under reduced pressure. The distillate consisted of organic and water layers. Glc analysis showed that the organic layer contained dienol **1** with a purity of ≈93% (area ratio). This organic sample yielded the following data: IR (neat) 3300, 1600, 1440, 1380, 1040, and 890 cm^{-1}. ^1H NMR ($CDCl_3$) δ=1.62 (s, 1H), 1.94 (s, 3H), 4.36 (s, 2H), 5.08 (m, 2H), and 5.23 (m, 2H). ^{13}C NMR ($CDCl_3$) δ=21.05 (q), 63.88 (t), 112.52 (t), 112.66 (t), 140.78 (s), and 145.60 (s). MS (20 V) *m/z* 98 (M^+), 79, 69, and 55.

Reaction of Allene with Deuterium Oxide. This reaction was carried out in a manner similar to that described for the reaction of water with allene (1.0 g, 24.9 mmol), $Pd(dba)_2$ (0.5 mmol), PPh_3 (1.0 mmol), and D_2O (0.9 cm³) in THF (10 cm³) under CO_2 pressure (10 atm) at 80 °C for 1 h. Isolation by flash-distillation gave 0.27 g (22%) of the deuterated dienol in 95% purity. ^1H NMR analysis revealed that the incorporation of deuterium was exclusively on the methyl carbon, δ=1.95 (br. s, ≈2H).

Reaction of Allene with Methanol and Ethanol. The reaction was performed in a manner similar to that described above for the corresponding reaction of water employing allene (1.0 g, 24.9 mmol), $Pd(dba)_2$ (0.5 mmol), PPh_3 (1.0 mmol), and methanol (or ethanol) (5 cm³) in THF (5 cm³) at 100 °C for 2 h. The product analysis was carried out by glc.

Isolation of 4-Methoxy-2-methyl-3-methylene-1-butene (2a) and 4-Ethoxy-2-methyl-3-methylene-1-butene (2b). Most of the THF was removed by distillation under reduced pressure. The flash-distillation of the residue gave a mixture of **2a** and methanol (or **2b** and ethanol). A pure product was obtained by preparative glc. **2a**: IR (CCl_4) 1595, 1085, and 890 cm^{-1}. ^1H NMR ($CDCl_3$) δ=1.90 (s, 3H), 3.31 (s, 3H), 4.10 (s, 2H), 5.00 and 5.10 (m, 2H), and 5.20 (s, 2H). MS (20 V) *m/z* 112 (M^+), 97, 82, 79, and 67. **2b**: IR (CCl_4) 1590, 1090, and 890 cm^{-1}. ^1H NMR ($CDCl_3$) δ=1.21 (t, 3H), 1.92 (s, 3H), 3.50 (q, 2H), 4.16 (s, 2H), 5.00 and 5.10 (m, 2H), and 5.22 (s, 2H).

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