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Palladium-catalyzed Reaction of Isoprene with Water in Presence of Carbon Dioxide and Base

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Synopsis. Palladium(0)-catalyzed reaction of isoprene with water was enhanced by the presence of carbon dioxide and a base to give dimethyloctadienols. The same catalyst was found to dehydrate the dimethyloctadienols to afford the corresponding dimethyloctatrienes. The effect of acidity of water on the isoprene-water reaction was also studied.

Terpene alcohols such as geraniol and linalool are considered as made up of head-to-tail dimers of isoprene with the addition of a molecule of water. They occur in oil of rose and other flower essences and are important perfume ingredients.

It is known that the palladium-catalyzed reaction of butadiene with water to give octadienols is accelerated by the presence of carbon dioxide (CO_2).[1] The role of CO_2 is not clear. The possibility of the direct effect has been suggested. To synthesize terpene alcohols in one step from the corresponding reaction of isoprene with water is an interesting subject to be challenged. Usually the reactivity of isoprene is lower than that of butadiene and the reaction has been little studied.[2] Keim *et al.* investigated the reaction by palladium- or platinum-based system and found that the distribution of the isomeric terpenols were subtly influenced by catalyst metal, ligand, reaction temperature, and reaction time.[2a] Concerning the study on the catalytic fixation of CO_2 in 1,3-dienes,[3] we examined the isoprene-water reaction and found that the addition of a base such as $KHCO_3$ accelerated the reaction. The effect of acidity of water on the reaction was also studied.

Results and Discussion

Different from butadiene-water reaction, $Pd(PPh_3)_4$-catalyzed reaction of isoprene with water was very slow even in the presence of CO_2, and the main product was an isoprene dimer, 2,7-dimethyl-1,3,7-octatriene (**1**). But when a base such as $KHCO_3$ was added to the system, a considerable increase in the proportion of dimethyloctadienols was attained. Results are summarized in Table 1. The main alcohols formed were 2,7-dimethyl-1,7-octadien-3-ol (**2**) and 2,7-dimethyl-2,7-octadien-1-ol (**3**), tail-to-tail dimers of isoprene with addition of a molecule of water. The yield of head-to-tail type products, *i.e.*, 2,6-dimethyl-1,7-octadien-3-ol and 3,7-dimethyl-1,7-octadien-3-ol, was small (1—2%) by this catalyst system. It is reported that the addition of *p*-benzoquinone increased **3** in the yield by $Pd(PPh_3)_4$ catalyst.[2a] The reaction occurred from the reaction temperature 80 °C and the conversion of isoprene increased as the temperature was raised. Bases such as trimethylamine, tetramethylammonium hydroxide, and K_2CO_3 can be used as the co-catalyst. Interestingly $KHCO_3$ was effective by itself as co-catalyst without CO_2, whereas trimethylamine and K_2CO_3 were not effective. $Pd(diphos)_2[diphos=Ph_2PCH_2CH_2PPh_2]$ scarecely showed the catalytic activity. Dioxane and diethylene glycol dimethyl ether were the best solvent tested. Tetrahydrofuran, 1,2-dimethoxyethane, and *t*-butyl alcohol, which were used for the butadiene-water reaction, were not so effective for the isoprene-water reaction. The same catalyst system accelerated also the butadiene-water reaction. For instance butadiene (180 mmol) and $KHCO_3$ (1 mmol) in 5 ml water gave 1,7-octadien-3-ol (13 mmol), 2,7-octadien-1-ol (49 mmol), and 1,3,7-octatriene (3 mmol) for 4 h reacton at 80 °C in dioxane by $Pd(PPh_3)_4$ (0.18 mmol) and CO_2 (40 atm), while 1,7-octadien-3-ol (7 mmol), 2,7-octadien-1-ol (44 mmol), and 1,3,7-octatriene (4 mmol) were produced under CO_2 pressure without $KHCO_3$.

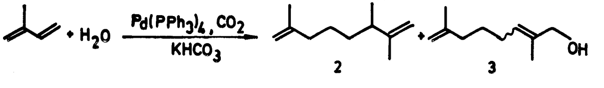

Table 1. Reaction of isoprene with water[a)]

Base (mmol)	Isoprene conversion %	Isoprene dimer[b)] (%)	C_{10}-Alcohol (%)	Yield/%[c)] 2	3
—[d)]	20	≈100	≈0	Trace	0
—	45	86	14	4	Trace
$Me_3N(33)$	74	67	33	12	4
$Me_3N(30)$[e)]	64	52	48	17	4
$KHCO_3(26)$	76	54	46	19	6
$KHCO_3(26)$[d)]	59	50	50	16	10
$K_2CO_3(27)$	79	71	29	12	6
$Me_4NOH(5)$	59	59	41	16	9

a) Isoprene, 45 mmol; $Pd(PPh_3)_4$, 0.2—0.3 mmol; water, 200—300 mmol; dioxane, 20 ml; CO_2, 40 atm(initial); 110—120 °C; 20 h. b) The main dimer was **1**. c) The yield is based on the isoprene charged (by gas chromatography). d) Without CO_2(under N_2 1 atm). e) Reaction temperature was 90 °C.

Interestingly the base-added system catalyzed the dehydration of dimethyloctadienols to give the corresponding dimethyloctatrienes. For example dimethyloctadienols which were composed of **2** (2.8 mmol), **3** (0.7 mmol), and the other octadienols (0.6 mmol) afforded **1** (1.2 mmol) and the other dimers (1.2 mmol) on treatment with $Pd(PPh_3)_4$ (0.2 mmol), trimethylamine (19 mmol), and CO_2 (40 mmol) in dioxane (20 ml) and water (2.6 ml) at 120 °C for 20 h. Control experiments showed that both CO_2 and a base were necessary to the dehydration. This can partly explain the relatively low yield of dimethyloctadienols.

Co-existence of CO_2 and a base is a sort of buffer. The change of acidity of water may accelerate the reac-

Table 2. Effect of the acidity of water[a)]

Buffer solution (pH)	Ionic strength	Isoprene conversion %	Isoprene dimer (%)	C_{10}-Alcohol[b)] (%)
6.8[c)]	0.11	69	80	20
7.2[c)]	0.08	82	72	28
8.1[c)]	0.10	68	77	23
11.0[d)]	0.10	66	72	28
12.3[d)]	0.13	64	76	24

a) Isoprene, 45 mmol; $Pd(PPh_3)_4$, 0.2 mmol; buffer solution, 5 ml; dioxane, 20 ml; 110—120 °C; 20 h. b) The main alcohols were **2** and **3**. c) KH_2PO_4–Na_2HPO_4. d) KH_2PO_4–NaOH.

tion. So the effect of water acidity on the reaction was examined using several buffer solutions of various pH. Results are shown in Table 2. The reaction did not occur under pH 6 and almost no effect of ionic strength (μ) was observed between μ 0.11 and μ 2.7 at pH 6.8. A slight increase in the proportion of dimethyloctadienols was observed compared to the base-free system, and the proportion was almost constant (about 25%) between pH 6.8 and 12.3. When CO_2 was introduced to 40 atm at pH 6.8, it was improved to 43%. CO_2 in water exists mainly as the form of HCO_3^- in the pH range 7 to 10.[4)] Taking the novel effect of $KHCO_3$ on the isoprene-water reaction, the anion HCO_3^- is possibly playing an important part.[1)]

Experimental

The diene-water reaction was done in a 100 ml stainless-steel autoclave. Typically, isoprene (2.9 g, 43 mmol), $Pd(PPh_3)_4$ (0.36 g, 0.3 mmol), trimethylamine 30% solution (5.4 g), and dioxane (20 ml) were charged in it under an inert atmosphere. Then CO_2 was introduced up to 40 atm and the autoclave was heated at 112 °C for 20 h. After the reaction the organic layer was quantitatively analyzed by gas chromatography (FFAP, 2 m, 150 °C, helium as a carrier gas), showing the formation of 3,7-dimethyl-1,7-octadien-3-ol (0.2 mmol), 2,6-dimethyl-1,7-octadien-3-ol (0.4 mmol), **2** (2.4 mmol), and **3** (0.8 mmol) in addition to isoprene dimers (8.0 mmol). Separation of the octadienols formed from the reaction mixture was done by column chromatography (silica gel/benzene, then methanol). Individual alcohol was isolated by preparative gas chromatography (FFAP, 2 m, 185 °C, hydrogen as a carrier gas).

*2,7-Dimethyl-1,7-octadien-3-ol (**2**)*: IR(neat); 3400, 1650, 890 cm^{-1}. NMR (CCl_4); δ 1.1 (1H, s), 1.4 (4H, m), 1.6 (6H, s), 1.8—2.1 (2H, m), 3.9 (1H, br), 4.55 (2H, s), 4.7 (2H, m). MS (*m/e*); 68, 71, 98, 111, 137, 139, 154 (M^+).

*2,7-Dimethyl-2,7-octadien-1-ol (**3**)*: IR(neat); 3400, 1650, 890 cm^{-1}. NMR (CCl_4); δ 1.2 (1H, s), 1.55 (3H, s), 1.6 (3H, s), 1.9 (6H, m), 3.8 (2H, s), 4.5 (2H, s), 5.25 (1H, t).

3,7-Dimethyl-1,7-octadien-3-ol: IR(neat); 3400, 1650, 1000, 910, 890 cm^{-1}. NMR (CCl_4); δ 1.0 (1H, s), 1.1 (3H, s), 1.4 (4H, m), 1.6 (3H, s), 1.9 (2H, m), 4.55 (2H, s), 4.75—5.15 (2H, m), 5.45 (1H, m).

2,6-Dimethyl-1,7-octadien-3-ol: IR(neat); 3400, 1000, 900, 890 cm^{-1}. NMR (CCl_4); δ 0.96 (3H, d), 1.1 (1H, s), 1.3 (4H, m), 1.65 (3H, s), 2.0 (1H, br), 3.9 (1H, br), 4.7 (2H, s), 4.9 (2H, m), 5.3—5.6 (1H, m).

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