Palladium-catalysed Preparation of 1,2-Dienes by Selective Hydrogenolysis of Alk-2-ynyl Carbonates with Ammonium Formate

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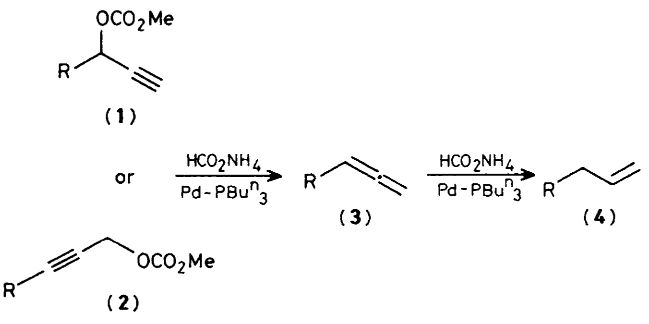
1,2-Dienes were prepared by the selective hydrogenolysis of alk-2-ynyl carbonates with HCO_2NH_4 catalysed by $Pd_2(dba)_3{\cdot}CHCl_3$–$PBu^n{}_3$ (dba = dibenzylideneacetone).

Palladium-catalysed selective hydrogenolysis of some functional groups such as vinyl and aryl halides (avoiding attack on other functional groups) with cheaply available formic acid or its derivatives is useful in organic synthesis.[1] We have shown that terminal allylic esters can be converted into alk-1-enes selectively by using palladium–phosphine complexes as a catalyst.[2] We now report facile hydrogenolysis of alk-2-ynyl carbonates (**1**) or (**2**) to give 1,2-dienes (Scheme 1). The reaction is stepwise, and 1,2-dienes (**3**) are converted into alk-1-enes (**4**) by treatment with an excess of HCO_2NH_4 at 65—100 °C. The reaction offers a convenient synthetic method for 1,2-dienes.

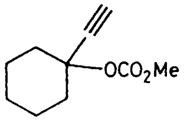
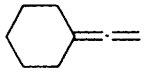
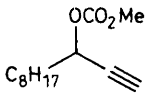
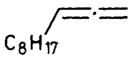
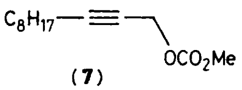
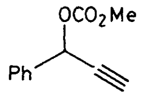
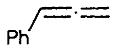
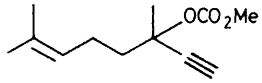
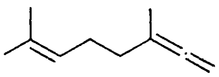
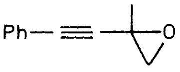
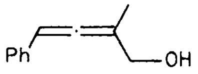
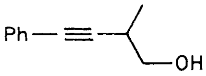
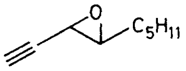
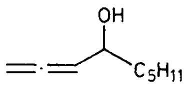
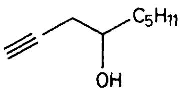
As shown in Table 1, alk-2-ynyl carbonates were converted into 1,2-dienes (**3**) at 20—30 °C in tetrahydrofuran (THF). At this temperature, reduction of (**3**) (the second step in Scheme 1) is extremely slow and (**3**) was obtained with high selectivity. When the reaction was carried out at 65 °C, alk-1-ene (**4**) was also obtained even when one equivalent of HCO_2NH_4 was used. For this reaction, alk-2-ynyl carbonates are the best substrates. Alk-2-ynyl acetates are not suitable. At room temperature, almost no reaction took place with acetates, and a mixture of 1,2-diene (**3**) and alk-1-ene (**4**) was obtained at an elevated temperature. These results show the high reactivity of the carbonates.[3] As for the ligand, $PBu^n{}_3$ gave the best results. With PPh_3 or bis(1,2-diphenylphosphino)ethane (dppe), (**3**) was not obtained cleanly. The best selectivity to 1,2-dienes (**3**) was obtained in THF. Dimethylformamide (DMF) also gave satisfactory results at 80 °C. In other solvents, (**3**) was the major product but a considerable amount of (**4**) was obtained. For the effective 1,2-diene formation, secondary or tertiary alk-2-ynyl carbonates (**1**) are better than primary carbonates (**2**). For example, reaction of (**5**) gave (**6**) without forming by-products. However reaction of its isomer (**7**) gave a small amount of the acetylenic compound (**8**) in addition to the diene (**6**). Contrary to the expected 1,2-diene-4-ols, reaction of α-alkynyl epoxides gave alk-1-yn-4-ols as by-products.

The alk-1-ene (**12**) was obtained from (**9**) directly by the reaction with five equivalents of HCO_2NH_4 at 100 °C in dioxane (Table 2); (**12**) was also obtained by the reaction of



Scheme 1

Table 1. Preparation of 1,2-dienes.[a]

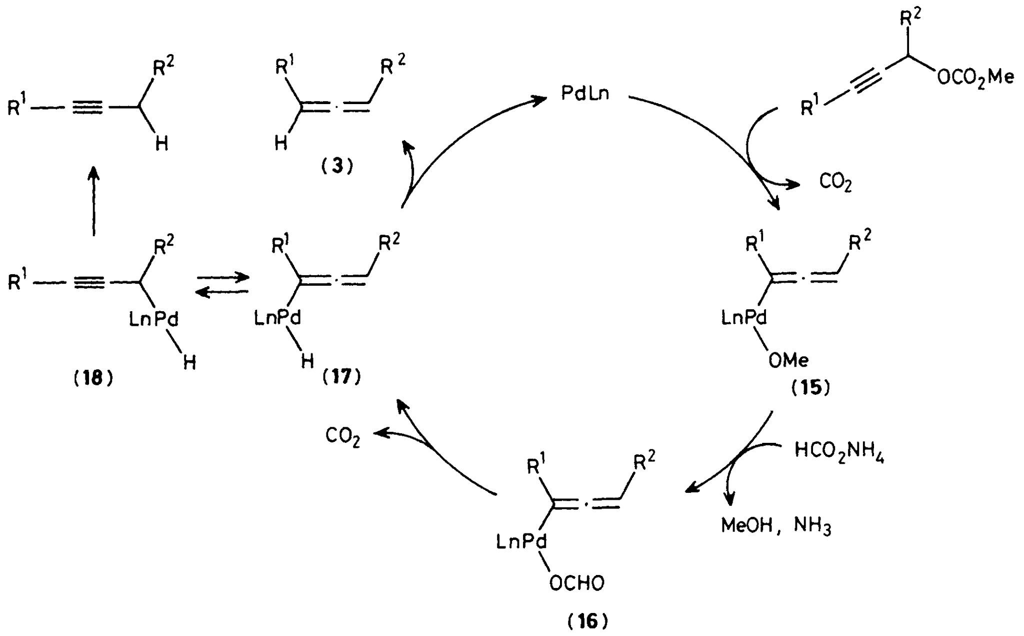
Run	Alk-2-ynyl carbonate	Time (h)	Product	Yield (%)[b]
1[c]		10		66
2	 (**5**)	5	 (**6**)	87
3	 (**7**)	5	(**6**), $C_8H_{17}-\equiv-$ (**8**) (**6**):(**8**) = 5:1[d]	81
4[c]		3		79
5	 (**9**)	8	 (**10**)	76
6[e]		3	 (26)  (74)	
7[e,f]	 (**11**)	1	 (43)  (57)	

[a] General procedure; A mixture of $Pd_2(dba)_3{\cdot}CHCl_3$ (0.05 mmol) (dba = dibenzylideneacetone), $PBu^n{}_3$ (0.2 mmol), alk-2-ynyl carbonate (1 mmol), and NCO_2NH_4 (2 mmol) in tetrahydrofuran (5 ml) was stirred at 20—30 °C under argon. Then the reaction mixture was filtered through Florisil and purified by column chromatography on silica gel. [b] G.l.c. yield in parenthesis. [c] 10 mol% of the palladium catalyst was used. [d] Calculated by g.l.c. analysis. [e] HCO_2H (1 mmol) and Et_3N (1 mmol) were used instead of HCO_2NH_4. [f] Reaction at 65 °C.

Table 2. Formation of alk-1-enes from 1,2-dienes or alk-2-ynyl carbonates.[a]

Run	Substrate	Solvent	Temp. (°C)	Time (h)	Product	Yield (%)[b]
1	**(9)**	dioxane	100	6	$Me_2C{=}CHCH_2CH_2CH(Me)CH{=}CH_2$ **(12)**	93
2	**(10)**	dioxane	100	1	**(12)**	77
3	**(6)**	DMF	80	4	$C_8H_{17}CH_2CH{=}CH_2$ **(13)**	90[c]
4[d]	**(11)**	THF	65	3	$C_5H_{11}CH(OH)CH_2CH{=}CH_2$ **(14)**	100

[a] General procedure; a mixture of $Pd_2(dba)_3{\cdot}CHCl_3$ (0.05 mmol), $PBu^n{}_3$ (0.2 mmol), substrate (1 mmol), and HCO_2NH_4 (5 mmol) in a solvent was heated under argon. [b] Calculated by g.l.c. analysis. [c] Formation of undec-2-ene was observed (10%). [d] HCO_2H (2 mmol) and Et_3N (2 mmol) were used instead of HCO_2NH_4.



Scheme 2

1,2-diene **(10)** with HCO_2NH_4. The results indicate that the palladium-catalysed reaction of alk-2-ynyl carbonates with HCO_2NH_4 is stepwise. However in the reaction of 1,2-diene **(6)**, the selectivity for alk-1-ene was not complete. Although the selectivity for 1,2-diene-4-ols from α-alkynyl epoxides was poor, non-1-en-4-ol **(14)** was formed with high selectivity by the reaction with an excess of HCO_2H–Et_3N.

The reaction can be explained by the following mechanism. Oxidative addition (S_N2' type reaction) of alk-2-ynyl carbonate with Pd(0) species and subsequent decarboxylation gives (1,2-dienyl)palladium alkoxide complex **(15)**, which reacts with HCO_2NH_4 to afford (1,2-dienyl)palladium formate complex **(16)** (Scheme 2). Then decarboxylation of **(16)** gives (1,2-dienyl)palladium hydride complex **(17)**. Finally, reductive elimination of **(17)** gives 1,2-dienes **(3)**, and the Pd(0) species is regenerated. The by-product acetylenes are obtained from the (α-acetylenic)palladium hydride complex **(18)** which is considered to be in equilibrium with **(17)**.

A number of preparative methods for 1,2-dienes are known,[4] but these methods still need further elaboration. The present method offers a new and efficient preparative method for 1,2-dienes from alk-2-ynyl carbonates.† As a related reaction, palladium catalysed reduction of propargyl halides with $LiAlH_4$ or $LiHBEt_3$ has been reported.[5]

This research was financially supported by Grants-in-Aid for Developmental Scientific Research and for Encourage-

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† Alky-2-nyl carbonates were prepared by nucleophilic addition of magnesium or lithium acetylides to ketones or aldehydes followed by quenching with methyl chloroformate.

ment of Young Scientists, from the Ministry of Education, Science and Culture.

Received, 24th January 1986; Com. 240

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