Preparation of 1,2-Dienes by the Palladium-Catalyzed Hydrogenolysis of 3-Methoxycarbonyloxy-1-alkynes with Ammonium Formate

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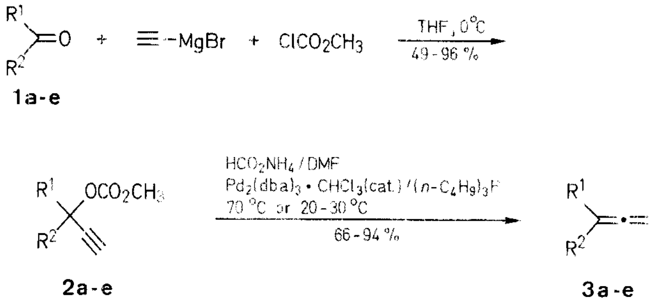
A useful preparative method for 1,2-dienes from 3-methoxycarbonyloxy-1-alkynes by the palladium-catalyzed hydrogenolysis with ammonium formate is described. 3-Methoxycarbonyloxy-1-alkynes are prepared by the addition of magnesium acetylide to ketones or aldehydes, followed by quenching with methyl chloroformate.

1,2-Dienes are useful compounds in organic synthesis and their efficient preparation without contamination by alkynes or alkenes is highly desirable.[1] Several preparative methods based on reduction of 3-chloro-1-alkynes or 1,2-dichloro-2-alkenes and elimination of 1,1-dibromocyclopropanes are known.[2] Reaction of propargylic halides, alcohols, and their derivatives with organocopper reagents is another preparative method for allenes.[3] Also, alkylation with organomagnesium reagents catalyzed by palladium[4] or nickel[5] has been reported. However, these methods still need further elaboration. Particularly, preparation of substrates used in these methods is not always easy. In the course of our studies on the palladium-catalyzed hydrogenolysis of allylic compounds with cheaply available formic acid or its ammonium salts,[6] we have found that 1,2-dienes **3** are formed in good yields with high selectivity from 3-methoxycarbonyloxy-1-alkynes **2** (Scheme A). A part of the studies has already been reported as a communication,[7] and details of the experiments are presented in this paper.

Optimum conditions for hydrogenolysis were examined with 3-methoxycarbonyloxy-1-undecyne (**2a**). In this reaction, choice of phosphine ligand is crucial and the efficiency of 1,2-undecadiene (**3a**) formation depends strongly on the phosphine ligand. As shown in Table 1, satisfactory results were obtained with tributylphosphine. With other tertiary phosphines, such as triphenylphosphine or 1,2-diphenylphosphinoethane, yields of **3a** were low (30–40%). Also we have observed before that tributylphosphine is the most suitable ligand for the selective formation of 1-alkenes by the palladium-catalyzed hydrogenolysis of terminal allylic compounds with formic acid.[6] We reasonably assume that zero-valent palladium-phosphine complexes are active species for the reaction. As an easily available and stable zero valent complex, $Pd_2(dba)_3 \cdot CHCl_3$ [tris(dibenzylideneacetone)dipalladium(chloroform)][8] is the most convenient one. It is well-known that this complex is converted to a zero-valent palladium-phosphine complex *in situ* by facile replacement of dba ligand with phosphine. Thus the reaction was carried out by adding $Pd_2(dba)_3 \cdot CHCl_3$ and tributylphosphine. The reaction proceeds smoothly in dimethylformamide at 70 °C (entry 1). At higher temperatures, yield of **3a** decreased probably due to its polymerization. As a solvent, tetrahydrofuran can be used at 20–30 °C, although it



dba = dibenzylideneacetone

Scheme A

Table 1. Preparation of 1,2-Undecadiene **3a**

Entry	Substrate	Method[a]	Yield[b] (%)	By-products (Yield)
1	**2a**	A	94	–
2	**2a**	B	89	–
3	**2a**	A[c]	32	1- and 2-undecynes (16%)
4	**2a**	A[d]	41	1- and 2-undecynes (8%)
5	**4**[e]	A	63	2-undecyne (13%)
6	**4**[e]	B	81	2-undecyne (16%)
7	**5**[f]	A	56	1-undecyne (6%) 2-undecyne (7%)
8	**5**[f]	B	–	no reaction

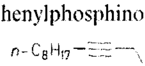
[a] See experimental.

[b] Calculated by GC analysis.

[c] $P(C_6H_5)_3$ was used instead of $P(n\text{-}C_4H_9)_3$.

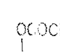
[d] Diphenylphosphinoethane was used instead of $P(n\text{-}C_4H_9)_3$.

[e] **4** =



$n\text{-}C_8H_{17}-C\equiv C-CH_2OCO_2CH_3$

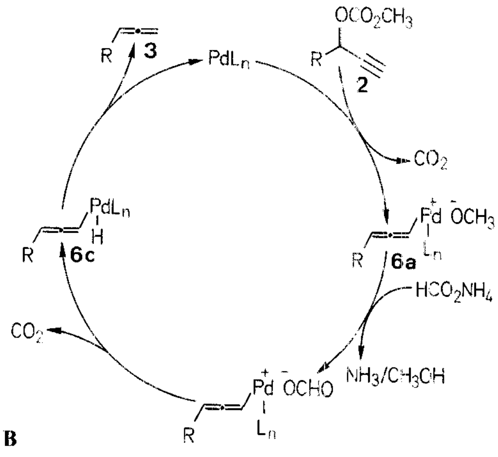
[f] **5** =



$n\text{-}C_8H_{17}CH(OCOCH_3)C\equiv CH$

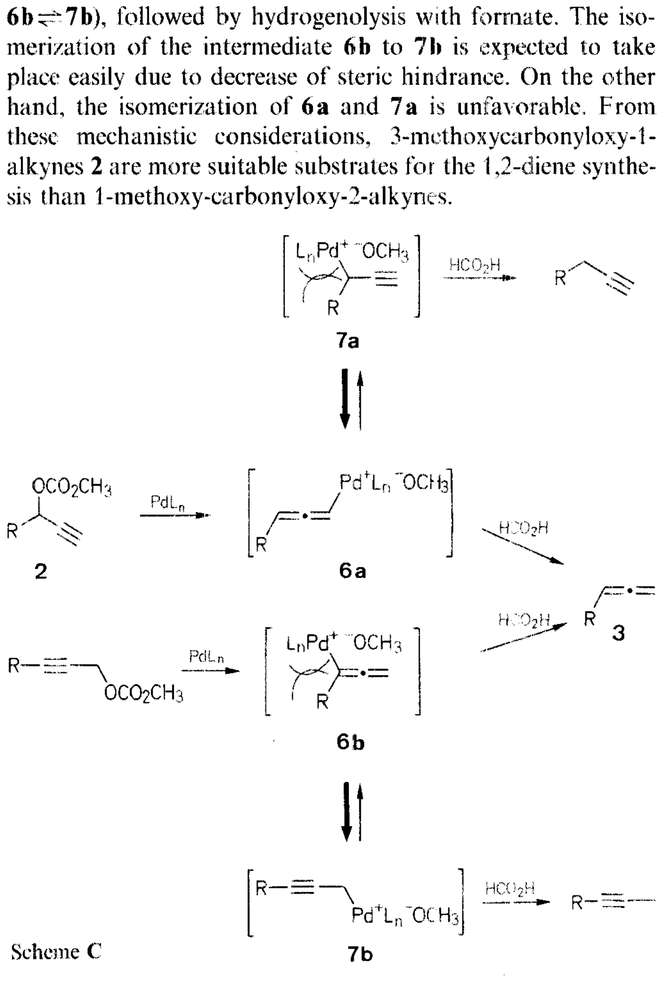
requires somewhat longer reaction times. Dioxane and benzene are not suitable solvents giving 1- and 2-undecenes and 1-undecyne as by products (15–50%). At room temperature, the reaction proceeds slowly with one equivalent of ammonium formate. Addition of two equivalents of the reductant accelerates the reaction. In this case, tetrahydrofuran ist the best solvent without giving any by-product (entry 2). As for the reductant, ammonium formate gives the best results. Combination of formic acid with tertiary amines such as triethylamine, 1,8-diazabicyclo[5.4.0]-7-undecene or dicyclohexylmethylamine gave unsatisfactory results giving undecenes as by-products (10–50%). 1-Methoxycarbonyloxy-2-undecyne (**4**), regioisomer of **2a**, is inferior to **2a** for selective 1,2-diene synthesis, giving 2-undecyne in a considerable extent. In general, acetates are less reactive than corresponding carbonates in the palladium-catalyzed reactions.[9] The same tendency was observed in the present reaction. When 3-acetoxy-1-undecyne (**5**) was used as the substrate, **3a** was obtained in a low yield at 70 °C in dimethylformamide (run 7). At room temperature, no reaction took place (entry 8).

The reaction can be explained by the following mechanism (Scheme **B**). Oxidative addition (S_N2' type reaction) of Pd(0) species to **2** followed by decarboxylation affords (σ-allenyl)palladium methoxide complex **6a**.[10] Then the formate complex is formed by the displacement of methoxide in **6a** with ammonium formate. The facile decarboxylation of the formate complex gives the hydride palladium complex **6c**. Finally, reductive elimination of **6c** gives 1,2-diene **3** and regenerates Pd(0) species.



Scheme **B**

In the present reaction, formation of alkynes is sometimes observed. For example, 1-undecyne (5%) was formed as a by-product by the reaction of **2a** in benzene. On the contrary, 2-undecyne was formed in a considerable amount from **4**. No other undecynes were detected in these cases. These results are explained by 1,3-shift of palladium atom[11] (**6a**$\rightleftharpoons$**7a** and **6b**$\rightleftharpoons$**7b**), followed by hydrogenolysis with formate. The isomerization of the intermediate **6b** to **7b** is expected to take place easily due to decrease of steric hindrance. On the other hand, the isomerization of **6a** and **7a** is unfavorable. From these mechanistic considerations, 3-methoxycarbonyloxy-1-alkynes **2** are more suitable substrates for the 1,2-diene synthesis than 1-methoxy-carbonyloxy-2-alkynes.



Scheme **C**

Other detectable by-products are alkenes formed by over-reduction of the product, 1,2-dienes.[7] In other words, the reaction is stepwise, and the over-reduction proceeds at 70–100 °C, but does not take place at room temperature. Thus exactly one equivalent of ammonium formate must be used for the reaction in dimethylformamide at 70 °C (Method A). The over-reduction takes place in less extent with ammonium formate, which is not completely soluble in tetrahydrofuran at room temperature, and gives better results than formic acid-trialkylamine system which is soluble in tetrahydrofuran.

Table 2. Preparation of 1,2-Dienes **3a**–**e**

Entry	Sub-strate	Method, Time(h)	Product			Yield[a] (%)	b.p. (°C)/mbar	Molecular Formula or Lit. b.p.(°C)/mbar	IR (Neat) ν(cm^{-1})	^{1}H-NMR (CDCl$_3$/TMS) δ(ppm)	^{13}C-NMR (CDCl$_3$/TMS) δ(ppm)
				R^1	R^2						
1 2	**2a**	B,5 C,1.5	**3a**	n-C_8H_{19}	H	87 (79)	102–103/44	77–81/12[16]	2980, 2850, 1955, 1470, 840	0.88 (t, 3H, J = 5 Hz); 1.06–1.66 (m, 12H); 1.76–2.12 (m, 2H); 4.64 (dt, 2H, J = 6.5, 3.1 Hz); 5.10 (tt, 1H, J = 6.5, 6.5 Hz)	14.2, 22.8, 28.5, 29.3, 29.4, 29.6, 32.1, 74.5, 90.2, 208.7
3	**2b**	B,3	**3b**	C_6H_5	H	79	oil	C_9H_8 (116.2)	3020, 1940, 1580, 1470, 1455, 850, 760, 690, 625	5.12 (d, 2H, J = 6.8 Hz); 6.15 (t, 1H, J = 6.8 Hz); 6.96–7.54 (m, 5H)	78.7, 94.1, 126.8, 126.9, 128.7, 134.0, 209.9
4	**2c**	B,8	**3c**	$(CH_3)_2C{=}CH(CH_2)_2$	CH_3	76	oil	$C_{10}H_{16}$ (136.2)	2970, 2910, 2850, 1960, 1440, 1380, 845	1.64–2.32 (m, 13H); 4.59 (tq, 2H, J = 3.1, 3.1 Hz); 4.96–5.24 (m, 1H)	17.8, 18.9, 25.8, 26.3, 33.7, 74.1, 98.4, 124.2, 131.7, 206.3
5 6	**2d**	B,10 C,1	**3d**	$-(CH_2)_5-$		66 (71)	50–52/43	56.5–58.5/60	2920, 2850, 1960, 1690, 1445	1.30–1.88 (m, 6H); 1.88–2.44 (m, 4H); 4.52 (tt, 2H, J = 2.4, 2.4 Hz)	26.2, 27.2, 31.2, 72.5, 101.2, 203.5
7	**2e**	A,0.2	**3e**	$-(CH_2)_2CH(t\text{-}C_4H_9)(CH_2)_2-$		85	oil	$C_{12}H_{20}$[b] (164.3)	1960, 1390, 1360, 840	0.86 (s, 9H); 0.8–2.48 (m, 9H); 4.50 (d, 1H, J = 4.5 Hz); 4.55 (d, 1H, 4.5 Hz); 4.54 (t, 2H, J – 4.1 Hz)	27.6, 28.0, 31.3, 32.5, 47.8, 72.6, 101.1, 203.1

[a] Isolated yield by column chromatography. Yield obtained by distillation is given in parenthesis. Purity of isolated product is higher than 95% (GC analysis).

[b] calc. C 87.73 H 12.27
found 87.36 12.50.

Table 3. Compounds **2a**–**e** Prepared

Product	Yield (%)	b.p. (°C)/mbar	Molecular Formula or Lit. b.p. (°C)/mbar	IR (Neat) ν(cm^{-1})	^{1}H-NMR (CDCl$_3$/TMS) δ(ppm)
2a	70	79–82/3	$C_{13}H_{22}O_3$[a] (226.3)	3300, 2110, 1750, 1260	0.55–2.10 (m, 17H); 2.30 (d, 1H, J = 2 Hz); 3.60 (s, 3H); 5.09 (dt, 1H, J = 6.2 Hz)
2b	96	92/3	$C_{11}H_{10}O_3$ (190.2)	3280, 2950, 2850, 1750, 1495, 1260, 930, 765	2.58 (d, 1H, J = 2.5 Hz); 3.75 (s, 3H); 6.24 (d, 1H, J = 2.5 Hz); 7.20–7.70 (m, 5H)
2c	49	116/5	$C_{12}H_{18}O_3$[b] (210.3)	3260, 2100, 1750, 1440, 1270, 1085, 895, 800	1.45–1.80 (m, 9H); 1.45–2.38 (m, 4H); 2.40 (s, 1H); 3.65 (s, 3H); 5.05 (t, 1H, J = 7 Hz)
2d	89	69–71/7	$C_{10}H_{14}O_3$[c] (182.2)	3280, 2940, 2110, 1760, 1270, 1240, 940, 790	0.90–2.60 (m, 10H); 2.51 (s, 1H); 3.70 (s, 3H)
2e[d]	77	m.p. 64.5–65.5	$C_{14}H_{22}O_3$[c] (238.3)	3270, 2850, 2100, 1750, 1020, 780	0.87 (s, 9H); 0.96–1.91 (m, 7H); 2.34–2.60 (m, 2H); 2.66 (s, 1H); 3.77 (s, 1H)

[a] calc. C 68.99 H 9.80
found 68.82 10.03.

[b] HRMS: calc. m/e = 210.2730; found 210.1222.

[c] HRMS: calc. m/e = 182.2194; found 123.0820 ($C_8H_{11}^+$).

[d] ^{13}C-NMR(CDCl$_3$/TMS): δ = 24.2, 27.6, 32.2, 37.2, 47.1, 54.3, 78.5, 82.4, 153.4.

[e] HRMS: calc. m/e = 238.3266; found 162.1377 ($C_{12}H_{18}^+$).

As the substrates of the present reaction, 3-methoxycarbonyloxy-1-alkynes **2** can be prepared by the reaction of 3-hydroxy-1-alkynes with methyl chloroformate. However, reactivity of tertiary and certain secondary alcohols with chloroformate is not high enough to yield corresponding carbonates in a quantitative yield. For these unreactive alcohols, metal alkoxides should be used for smooth esterification.[12] More conveniently, we developed a one-pot synthesis of 3-methoxy-carbonyloxy-1-alkynes from ketones, magnesium acetylides, and methyl chloroformate as shown in Scheme **A**.

Based on these results, various 1,2-dienes were prepared from 3-methoxycarbonyloxy-1-alkynes. In a small scale experiment, both the method A (dimethylformamide, 70 °C) and the method B (tetrahydrofuran, 20–30 °C) are acceptable and the latter is more convenient. In a preparative scale, with a smaller amount of the catalyst, the method C (dimethylformamide, 70 °C) is the best choice for efficient 1,2-diene synthesis.

In conclusion, the present reaction offers a facile and efficient synthetic method for 1,2-diene from ketones or aldehydes based on the two-carbon homologation and palladium-catalyzed hydrogenolysis with ammonium formate. As a related reaction, the palladium-catalyzed reduction of propargylic halides with lithium aluminium hydride or lithium triethylborohydride,[13] and palladium-catalyzed reaction of 3-acetoxy alkynes with samarium(II) iodide[14] have been reported.

^{1}H-NMR spectra were recorded on a JEOL Model FX-90Q Fourier transform spectrometer in $CDCl_3$ solution at 90 MHz or Hitachi Model R-24A at 60 MHz using tetramethylsilane as an internal standard. Infrared spectra were obtained on a JASCO Model IRA-2 spectrometer. Gas chromatography (GC) analyses were performed on a Shimadzu Model GC-4C(PT) gas chromatograph. The column was 3 m × 3 ∅, 10% silicone SE-30 on 80/100 Celite 545. The carrier gas was helium.

Commercial tri(*n*-butyl)phosphine was distilled and stored under argon. Tetrahydrofuran was dried over lithium aluminium hydride, distilled, and stored under argon. Dimethylformamide was dried over calcium hydride, distilled, and stored under argon. Ketones and aldehydes were distilled prior to use. Methyl chloroformate was distilled and stored over calcium carbonate. Commercially available ammonium formate was used without purification. Tris(dibenzylideneacetone)dipalladium(chloroform) was prepared by the published procedure.[8] It should be pointed out that the use of freshly distilled tri(*n*-butyl)phosphine and carbonate gives satisfactory results with good reproducibility. Addition of solvent, carbonate, and tri(*n*-butyl)phosphine to the reaction flask was carried out with syringes.

3-Methoxycarbonyloxy-1-alkynes; General Procedure:

To a solution of ethynylmagnesium bromide [0.31 mol, prepared from ethylmagnesium bromide (0.31 mol) and acetylene[15]] in tetrahydrofuran (450 ml), a solution of ketone or aldehyde (0.30 mol) in dry tetrahydrofuran (30 ml) is added at 0 °C over 20 min. After the addition is complete, the mixture is stirred for an additional 10 min. Then a solution of methyl chloroformate (31 ml, 0.4 mol) in dry tetrahydrofuran (30 ml) is added at 0 °C over 10 min and the resultant mixture is vigorously stirred at 20–30 °C for 5 h. After the reaction is complete (TLC and GC analyses), the mixture is poured into a cold water (100 ml). The aqueous layer is extracted with ether (2 × 200 ml, 1 × 100 ml). The combined organic extract is washed with saturated brine (50 ml) and dried with magnesium sulfate. The solvent is evaporated and the residue is distilled to give pure carbonate (Table 3).

Palladium-Catalyzed Hydrogenolysis of 2; General Procedure:

Method A: In a 30 ml two-necked flask, fitted with a reflux condenser and a rubber cap, $Pd_2(dba)_3 \cdot CHCl_3$ (13 mg, 0.025 mmol) and ammonium formate (63 mg, 1 mmol) are placed and the apparatus is flushed with argon. Then, dimethylformamid (3 ml) and tri(*n*-butyl)phosphine (25 µl, 0.1 mmol) are added and the resultant suspension is stirred at 20–30 °C for 5 min under argon. To this yellow solution, a solution of carbonate **2** (1 mmol) in dry dimethylformamide (2 ml) is added and the mixture is stirred at 70 °C under argon. After the reaction is complete (TLC and GC analyses), the mixture is diluted with ether (50 ml), washed with water (3 × 10 ml) and dried with magnesium sulfate. The mixture is concentrated *in vacuo* and purified by column chromatography on silica-gel using pentane-ether as eluent.

Method B: A mixture of $Pd_2(dba)_3 \cdot CHCl_3$ (52 mg, 0.1 mmol), tri(*n*-butyl)phosphine (100 µl, 0.4 mmol), and ammonium formate (126 mg, 2 mmol) in tetrahydrofuran (3 ml) is stirred at 20–30 °C for 5 min under argon. To this yellow solution, a solution of carbonate **2** (1 mmol) in tetrahydrofuran (2 ml) is added and the mixture is stirred at 20–30 °C under argon. After the reaction is complete (TLC and GC analyses), the mixture is filtered through a short florisil column and the filtrate is concentrated *in vacuo*. The residue was purified by column chromatography on silica gel as mentioned above.

Method C: A mixture of $Pd_2(dba)_3 \cdot CHCl_3$ (78 mg, 0.15 mmol), tri(*n*-butyl)phosphine (150 µl, 0.6 mmol), and ammonium formate (1.89 g, 30 mmol) in dimethylformamide (5 ml) is stirred at 20–30 °C for 5 min under argon. To this yellow solution, a solution of carbonate **2** (30 mmol) in dimethylformamide (5 ml) is added and the mixture is stirred at 70 °C under argon. After the reaction is complete (TLC and GC analyses), the mixture is diluted with ether (100 ml), washed with water (3 × 10 ml), and dried with magnesium sulfate, and the solvent removed (Table 2).

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