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SUPPORTING INFORMATION

Title: Palladium(II)-Catalyzed Isomerization of (*Z*)-1,4-Diacetoxy-2-Butene: Solvent Effects
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Table S1. Diacetate proportions[a] obtained from the $PdCl_2(MeCN)_2$–catalyzed reaction of (*Z*)-1,4-diacetoxy-2-butene in refluxing THF.[b]

Time, h → Compound ↓	0	1	2	4	6	8	24
1	100	37.4	35.5	34.3	33.6	33.1	32.4
2	0	40.0	40.7	41.5	41.9	42.3	42.6
3	0	22.6	23.8	24.2	24.5	24.6	24.9

[a]Determined by GC.
[b]0.05 equiv. of $PdCl_2(MeCN)_2$, 15 mL of solvent

Table S2. Diacetate proportions[a] obtained from the $PdCl_2(MeCN)_2$–catalyzed reaction of (*Z*)-1,4-diacetoxy-2-butene in DMF at 70-72 °C.[b]

Time, h → Compound ↓	0	1	2	4	6	8	24	48	72[c]
1	100	84.0	76.5	64.1	56.1	47.9	28.7	23.7	23.1
2	0	13.7	19.6	28.8	35.4	41.0	50.0	53.5	53.8
3	0	2.3	3.9	7.1	8.5	11.1	21.3	22.8	23.1

[a]Determined by GC.
[b]0.05 equiv. of $PdCl_2(MeCN)_2$, 15 mL of solvent.
[c]When a new batch of $PdCl_2(MeCN)_2$ (0.05 equiv.) was added after a reaction time of 48 h, the **1**/**2**/**3** ratio at 72 h was 20.5:53.9:25.7.

Table S3. **2**/**3** ratios[a] obtained from the $PdCl_2(MeCN)_2$–catalyzed reactions of (*E*)-1,4-diacetoxy-2-butene (**2**) and 1,2-diacetoxy-3-butene (**3**) at 70-72 °C.[b]

Time, min → From ↓	0	10	20	30	40
2 in THF	100:0	69.6:30.4	66.7:33.3	66.0:34.0	65.9:34.1
3 in THF	0:100	59.7:40.3	60.9:39.1	61.6:38.4	61.9:38.1
2 in DMF	100:0	93.3:6.7	88.7:11.3	83.9:16.1	78.9:21.1
Time, min → From ↓	50	60	120	240	360
2 in THF	65.7:34.3	65.1:34.9	63.9:36.1	63.8:36.2	63.8:36.2
3 in THF	62.0:38.0	62.0:38.0	62.2:37.8	62.3:37.7	63.1:36.9
2 in DMF	74.8:25.2	73.1:26.9	72.5:27.5	72.4:27.6	72.3:27.7

[a]Determined by GC.
[b]0.05 equiv. of $PdCl_2(MeCN)_2$, 15 mL of solvent.

Table S4. Diacetate proportions[a] obtained from the $PdCl_2(MeCN)_2$–catalyzed reaction of (*Z*)-1,4-diacetoxy-2-butene in THF at room temperature.[b]

Time, min→ Compound ↓	0	1	2	3	4	5	6	7	8
1	100	89.0	84.5	81.4	78.4	76.0	73.7	71.1	67.6
2	0	7.3	10.3	12.4	14.5	16.3	18.0	19.9	22.5
3	0	3.7	5.2	6.2	7.1	7.7	8.3	9.0	10.0
Time, min→ Compound ↓	9	10	20	30	40	50	60	90	120
1	64.8	61.3	58.4	55.7	53.6	50.3	48.2	46.7	44.1
2	24.7	27.5	29.1	30.6	31.8	33.7	34.3	35.5	36.4
3	10.5	11.2	12.5	13.6	14.5	16.0	17.6	18.4	19.5

[a]Determined by GC.
[b]0.05 equiv. of $PdCl_2(MeCN)_2$, 15 mL of solvent.

Table S5. **2**/**3** ratios versus conversion of **1** in THF and DMF.[a]

Conv. % of **1**	11	15.5	16	18.6	21.6	23.5	24	26.3	28.9	32.4
2/**3** in THF	1.97	1.98		2.00	2.04		2.12	2.17	2.21	2.25
2/**3** in DMF			5.96			5.02				
Conv. % of **1**	35.2	35.9	39.1	41.6	43.9	44.3	46.4	49.7	51.8	52.1
2/**3** in THF	2.35		2.45	2.32		2.25	2.19	2.10	1.95	
2/**3** in DMF		4.06			4.16					3.69
Conv. % of **1**	53.3	55.9	62.6	64.5	65.7	66.4	66.9	67.6	71.3	76.3
2/**3** in THF	1.92	1.87	1.77	1.71	1.71	1.71	1.72	1.71		
2/**3** in DMF									2.35	2.35
Conv. % of **1**	76.9									
2/**3** in THF										
2/**3** in DMF	2.33									

[a]Established from the results gathered in Tables S1, S2 and S4.