An Efficient Method for the Acetalization of α,β-Unsaturated Aldehydes

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Acetals are one of the most frequently used protecting groups for aldehydes and ketones.[1] Protic acids,[2] Lewis acids,[3] ion-exchange resins,[4] and transition metal complexes[5] have been utilized as the catalyst for the acetalization of carbonyl compounds. Many efficient procedures have been developed for the acetalization of saturated aldehydes and ketones.[6] Few, however, are known for that of the α,β-unsaturated ones.[7] Moreover, available methods for the latter suffer from poor yield, tedious operation, or the use of expensive reagents. Early examples were reported by Fischer and Smith on the preparation of cyclic acrolein acetals.[8] Heywood *et al.* employed *p*-toluenesulfonic acid as the catalyst and ethylene glycol as the acetalizing reagent in refluxing benzene to give the unsaturated acetals in low to moderate yields.[9] Furfural was shown to react with ethylene glycol in the presence of aluminum chloride to generate the corresponding 1,3-dioxolane in good yield.[10,11] Noyori *et al.* reported the use of alkoxytrimethylsilane and trimethylsilyl trifluoromethanesulfonate (TMSOTf) in dichloromethane at −78 °C to afford the acetal of 2-cyclohexenone in high yield without any migration of the double bond.[12] Hwu and co-workers carried out a comprehensive study on the acetalization of α,β-unsaturated aldehydes employing Noyori's procedure.[13] Conjugated enals, dienals, and aromatic enals gave high yields of the corresponding 1,3-dioxolanes using 1,2-bis(trimethylsilyloxy)ethane and TMSOTf.

In the course of our studies on the asymmetric reduction using chirally modified lithium aluminum hydride, it was necessary to protect the carbonyl group of myrtenal.[14] Anhydrous magnesium sulfate was found to be essential in order to improve the yield of the desired 1,3-dioxolane. Due to our continuing interest in utilizing α,β-unsaturated acetals in organic synthesis,[15] we have examined this intriguing finding further, which resulted in the development of an efficient procedure for the acetalization of α,β-unsaturated aldehydes. The results are described herein.

As summarized in Table 1, the acetalization of a number of α,β-unsaturated aldehydes was carried out in refluxing benzene utilizing ethylene glycol and *p*-toluenesulfonic acid either with or without the presence of anhydrous magnesium sulfate. Among the aldehydes studied, *trans*-cinnamaldehyde, 2-butylacrolein, (*S*)-(−)-perillaldehyde, and 2-furaldehyde can be transformed smoothly into the corresponding 1,3-dioxolanes in good yield in the presence of magnesium sulfate. An examination of Table 1 reveals that both the yield of the desired product and the extent of conversion are uniformly higher for the reactions with anhydrous magnesium sulfate than for those without it. Furthermore, as indicated by the ^{1}H NMR analysis, the purity of the product resulting from the reaction with magnesium sulfate, in general, is considerably better than that produced without using magnesium sulfate.[16] These findings suggest that magnesium sulfate not only improves the acetal formation but also suppresses the generation of byproducts.

Some difficulties were also encountered. Crotonaldehyde and *trans*-2-hexenal failed to give the desired acetals **2b** and **2c** under the reaction conditions (Table 1, entries 5, 10, and 12). In the former case, the major product was identified as compound **3**, resulting from the overall addition of ethylene glycol to the double bond of the expected product (Scheme 1).[17] The acetalization of *trans,trans*-2,4-nonadienal was accompanied by isomerization of the double bonds (Table 1, entry 19).

In order to suppress the formation of **3**, 2 equiv of $MgSO_4$ was employed for the acetalization of crotonaldehyde. In the meantime, the amounts of ethylene glycol and *p*-toluenesulfonic acid were decreased to 1.07 and 0.025 equiv, respectively, and the reaction was carried

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(9) Heywood, D. L.; Phillips, B. J. Org. Chem. 1960, *25*, 1699.

(10) Chan, T. H.; Rook, A.; Chaly, T. Synthesis 1983, 203.

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(15) We have been studying the [2 + 3] cycloaddition of nitrile oxides to α,β-unsaturated acetals. See: (a) Lee, J.-I. M.S. Thesis, National Chung-Hsing University, Taichung, Taiwan, 1992. (b) Yang, J.-F. M.S. Thesis, National Chung-Hsing University, Taichung, Taiwan, 1993. (c) Hsü, H.-H. M.S. Thesis, National Chung-Hsing University, Taichung, Taiwan, 1994.

(16) The ^{1}H NMR spectrum of the reaction mixture of *trans*-2-hexenal in the absence of magnesium sulfate clearly showed that byproducts similar to those found in the protection of crotonaldehyde were the major components in the reaction. The extent of double bond isomerization can be minimized with the presence of magnesium sulfate.

(17) Similar results were published by Piasecki. See: Piasecki, A. *Tetrahedron* **1984**, *40*, 4893. He found that acetal **2b** was an intermediate in the reaction of crotonaldehyde with ethylene glycol and *p*-toluenesulfonic acid. Acetal **2b** was converted gradually to 2-[2-(2-hydroxyethoxy)propyl]-1,3-dioxolane (**3**) as well as *cis*- and *trans*-5-(2-hydroxyethoxy)-7-methyl-1,4-dioxepane (**4**) under the reaction conditions until **2b** was totally consumed.

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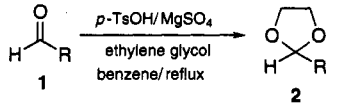
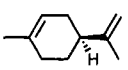
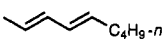
Table 1. Preparation of α,β-Unsaturated Acetals Using *p*-TsOH

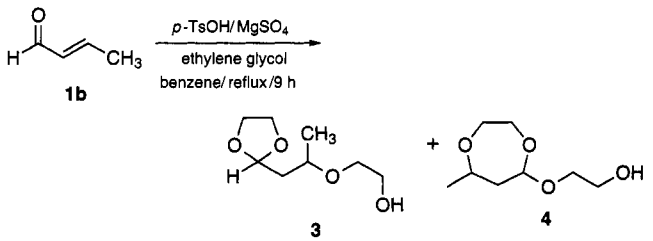


1a: *trans*-cinnamaldehyde
1b: crotonaldehyde
1c; *trans*-2-hexenal
1d: 2-butylacrolein
1e: (*S*)-(−)-perillaldehyde
1f: 2-furaldehyde
1g: *trans,trans*-2,4-nonadienal

entry	enal no.	enal R	acid (equiv)	$MgSO_4$ (equiv)	time (h)	acetal	ratio[a]	yield[b] (%)
1	**1a**	$-CH{=}CHC_6H_5$	0.025	–	6	**2a**	0:1[c]	97
2	**1a**	$-CH{=}CHC_6H_5$	0.005	–	6	**2a**	1:17	97
3	**1a**	$-CH{=}CHC_6H_5$	0.005	–	4.5	**2a**	1:12	87
4	**1a**	$-CH{=}CHC_6H_5$	0.005	2.0	4.5	**2a**	0:1[c]	97 (92)
5	**1b**	$-CH{=}CHCH_3$	0.1	–	1	**2b**	0:1[c]	–[d]
6	**1b**	$-CH{=}CHCH_3$	0.025	–	1	**2b**	0:1[c]	–[d]
7	**1b**	$-CH{=}CHCH_3$	0.005	–	1	**2b**	0:1[c]	–[d]
8[e]	**1b**	$-CH{=}CHCH_3$	0.025	2.0	1	**2b**	1:13	~80
9	**1c**	$-CH{=}CH(n\text{-}C_3H_7)$	0.025	2.0	7	**2c**	0:1[c]	97
10	**1c**	$-CH{=}CH(n\text{-}C_3H_7)$	0.025	–	7	**2c**	0:1[c]	–[f]
11	**1c**	$-CH{=}CH(n\text{-}C_3H_7)$	0.005	2.0	7	**2c**	0:1[c]	98 (87)
12	**1c**	$-CH{=}CH(n\text{-}C_3H_7)$	0.005	–	7	**2c**	0:1[c]	–[f]
13	**1d**	$-CH(n\text{-}C_4H_9){=}CH_2$	0.025	2.0	26	**2d**	0:1[c]	96 (88)
14	**1d**	$-CH(n\text{-}C_4H_9){=}CH_2$	0.025	–	26	**2d**	1:12	93
15	**1e**		0.025	2.0	16	**2e**	0:1[c]	96 (84)
16			0.025	–	16	**2e**	1:16	77
17	**1f**		0.025	2.0	14	**2f**	0:1[c]	87
18			0.025	–	14	**2f**	1:21	76
19	**1g**		0.025	2.0	18	**2g**	0:1[c]	86[g]

[a] The ratio between the starting material and the product(s). [b] Yields of the crude products based on ^1H NMR analysis. Those in parentheses are isolated yields after distillation. [c] Within the detection limit, the GC–MS chromatogram of the crude reaction mixture shows the absence of the starting aldehyde. [d] The major product was compound **3**. [e] The reaction was performed in refluxing dichloromethane. [f] Although the ^1H NMR spectrum of the crude reaction mixture indicated the presence of the desired 1,3-dioxolane, the major compound was the undesired Michael addition product (see ref 16). [g] As determined by the GC–MS chromatogram, there was 12% of double bond-isomerized acetal in the crude reaction mixture.

Scheme 1



out in refluxing dichloromethane (Table 1, entry 8). Under these conditions, the ratio of the starting material **1b** and the desired acetal **2b** was improved to 1:13 after 14.5 h, but the formation of a small amount of compound **3** was evident from the ^1H NMR spectrum of the crude product. A complex mixture containing mainly compound **3** resulted when the reaction was performed in the absence of magnesium sulfate even with a reduced amount of acid (Table 1, entries 6 and 7). In addition, a dramatic improvement of the yield of the desired 1,3-dioxolane of *trans*-2-hexenal was observed in the presence of magnesium sulfate (Table 1, entries 9 and 11).

We reasoned that the difficulties encountered in the acetalization of crotonaldehyde, *trans*-2-hexenal, and *trans,trans*-2,4-nonadienal might have been due to the high acidity of *p*-toluenesulfonic acid. Thus, in the ensuing studies, oxalic acid was used to replace *p*-toluenesulfonic acid in the acetalization of these conjugated aldehydes. As shown in Table 2, the yields of the desired acetals were greatly improved as a result of this modification. It is noteworthy that the magnitude of double bond isomerization of the acetal product derived from *trans,trans*-2,4-nonadienal was significantly reduced (Table 1, entry 19: Table 2, entry 12) by using oxalic acid. However, 2-butylacrolein required 0.3 equiv of oxalic acid

Table 2. Preparation of α,β-Unsaturated Acetals Using Oxalic Acid

entry	enal	acid (equiv)	$MgSO_4$ (equiv)	time (h)	acetal	ratio[a]	yield[b] (%)
1	**1a**	0.025	2.0	6	**2a**	0:1[c]	96
2	**1a**	0.005	2.0	12	**2a**	0:1[c]	98
3	**1a**	0.005	–	12	**2a**	1:32	93
4	**1b**	0.025	2.0	1.5	**2b**	0:1[c]	88
5	**1b**	0.025	–	20	**2b**	1:18	68
6	**1b**	0.005	2.0	1.5	**2b**	0:1[c]	86
7	**1c**	0.025	2.0	8	**2c**	0:1[c]	94
8	**1c**	0.005	2.0	8	**2c**	0:1[c]	97
9	**1c**	0.005	–	8	**2c**	0:1[c]	94[d]
10	**1d**	0.3	2.0	20	**2d**	0:1[c]	96
11	**1d**	0.3	–	20	**2d**	1:19	88
12	**1g**	0.005	2.0	20	**2g**	0:1[c]	94[e]

[a] The ratio between the starting material and the product(s). [b] Yields of the crude products based on ^1H NMR analysis. [c] Within the detection limit, the GC–MS chromatogram of the crude reaction mixture shows the absence of the starting aldehyde. [d] Five percent of double bond-isomerized acetal was observed. [e] Four percent of double bond-isomerized acetal was observed.

Table 3. Preparation of α,β-Unsaturated Acetals Using Tartaric Acid

entry	enal	acid (equiv)	$MgSO_4$ (equiv)	time (h)	acetal	ratio[a]	yield[b] (%)
1	**1a**	0.025	–	6	**2a**	0:1[c]	98
2	**1a**	0.005	2.0	10	**2a**	0:1[c]	98 (92)
3	**1a**	0.005	–	10	**2a**	1:11	90
4	**1b**	0.025	–	1	**2b**	0:1[c]	76
5	**1b**	0.005	2.0	1.5	**2b**	0:1[c]	86 (78)
6	**1b**	0.005	–	1.5	**2b**	0:1[c]	76
7	**1c**	0.025	–	7	**2c**	0:1[c]	94[d]
8	**1c**	0.025	2.0	5.5	**2c**	0:1[c]	98 (83)
9	**1c**	0.025	–	5.5	**2c**	1:12	84[e]
10	**1c**	0.005	2.0	10	**2c**	0:1[c]	98
11	**1c**	0.005	–	10	**2c**	1:16	90
12	**1d**	0.3	2.0	17	**2d**	0:1[c]	96 (81)
13	**1d**	0.3	–	17	**2d**	1:16	89
14	**1e**	0.025	2.0	24	**2e**	0:1[c]	95 (87)
15	**1e**	0.025	–	24	**2e**	1:35	90
16	**1f**	0.005	2.0	12	**2f**	0:1[c]	98 (80)
17	**1f**	0.005	–	12	**2f**	1:38	84
18	**1g**	0.005	2.0	20	**2g**	0:1[c]	97[f] (78)
19	**1g**	0.005	–	20	**2g**	1:38	92[g]

[a] The ratio between the starting material and the product(s). [b] Yields of the crude products based on ^1H NMR analysis. Those in parentheses are isolated yields after distillation. [c] Within the detection limit, the GC–MS chromatogram of the crude reaction mixture shows the absence of the starting aldehyde. [d] As determined by the GC–MS chromatogram, there was 5% of double bond-isomerized acetal. [e] Three percent of double bond-isomerized acetal was detected. [f] Less than 2% of double bond-isomerized acetal was observed. [g] Seven percent of double bond-isomerized acetal was present.

to drive the reaction to completion. Again, the importance of anhydrous magnesium sulfate in achieving high efficiency and in suppressing byproduct formation was noted.

Since oxalic acid proved to be superior to *p*-toluenesulfonic acid as a catalyst in the acetalization reaction, we envisaged that an acid of even lower acidity might further enhance the efficiency of the desired transformation. A survey of the acidities of several readily available acids revealed that the pK_a values of *p*-toluenesulfonic acid, oxalic acid, and tartaric acid are −6.5, 1.23, and 2.93, respectively. Under the conditions specified in Table 3, the acetalization of a number of α,β-unsaturated aldehydes was carried out using tartaric acid, resulting in the formation of the corresponding unsaturated acetals in excellent yields.[18] Compared with that using oxalic acid, the extent of double bond isomerization is further reduced when tartaric acid is utilized (Table 2, entries 9 and 12; Table 3, entries 11 and 18). Once again, anhydrous magnesium sulfate proved to be crucial in obtaining a high yield of the desired product.

In conclusion, an economical and practical method for the acetalization of a wide range of α,β-unsaturated aldehydes has been developed using inexpensive and readily available reagents under mild conditions. Tartaric acid has been shown to be the catalyst of choice, especially for acid sensitive enals, and anhydrous magnesium sulfate has been shown to be essential[19] in order to achieve a high yield of the desired product and to minimize the formation of side products. In light of its operational simplicity and high efficiency, the procedure is expected to have broad synthetic utility.

Experimental Section

Melting points are uncorrected. ^1H NMR spectra ($CDCl_3$ solutions) were measured at 200 MHz. Solvents and reagents were dried prior to use as required. The ratio of the starting material and the product(s) was determined by the GC–MS chromatogram of the crude reaction mixture as performed with a Hewlett-Packard 5989B MS engine using a 50 m × 0.22 mm i.d. BP5 capillary column (SGE; 1.0 μm film thickness) and He as the carrier gas.

The following procedure, illustrated with tartaric acid, is representitive for the acetalization of α,β-unsaturated aldehydes. Specific conditions for individual reactions are to be found in the tables.

To a 100 mL two-necked, round-bottomed flask, equipped with a Dean-Stark adapter and a condenser, containing the aldehyde (50 mmol), L-tartaric acid (0.25 mmol), and anhydrous $MgSO_4$ (50 mmol) in benzene (50 mL) was added a solution of ethylene glycol (100 mmol) in benzene (10 mL) over 20 min.[20] The reaction mixture was heated to reflux and was monitored by GC–MS until no starting aldehyde was detected. After the mixture was cooled, solid $NaHCO_3$ (0.5 mmol) was added to neutralize the acid, and the mixture was stirred for 30 min. The reaction mixture was then filtered through a pad of anhydrous $NaHCO_3$, and the filter cake was washed with CH_2Cl_2 (10 mL × 3). Concentration of the filtrate gave the acetal in high purity. This material was further purified by vacuum distillation to give the desired 1,3-dioxolane.

1,3-Dioxolane of *trans*-Cinnamaldehyde (2a). With *trans*-cinnamaldehyde (7.096 g, 53.69 mmol) as the starting material, practically pure acetal **1b** (9.273 g, 98%) was obtained after workup. Vacuum distillation (84 °C/0.1 mm; lit.[13] 114 °C/0.3 mm; lit.[21] 84 °C/0.1 mm) afforded 8.705 g (92%) of the title compound as a colorless liquid. ^1H NMR: δ 7.45–7.29 (m, 5H), 6.79 (d, J = 16.0 Hz, 1H), 6.62 (dd, J = 16.0, 6.0 Hz, 1H), 5.44 (d, J = 6.0 Hz, 1H), 4.11–3.92 (m, 4H).

1,3-Dioxolane of Crotonaldehyde (2b). After crotonaldehyde (4.226 g, 58.61 mmol) was subjected to the above reaction conditions, virtually pure acetal **2b** (5.753 g, 86%) was obtained. Purification by vacuum distillation (70 °C/49 mm; lit.[9] 71 °C/50 mm) yielded 5.218 g (78%) of the pure acetal as a colorless liquid. ^1H NMR: δ 5.96 (dq, J = 15.6, 6.4 Hz, 1H), 5.51 (ddq, J = 15.6, 6.6, 1.6 Hz, 1H), 5.18 (d, J = 6.6 Hz, 1H), 4.07–3.82 (m, 4H), 1.75 (dd, J = 6.6, 1.6 Hz, 3H).

1,3-Dioxolane of *trans*-2-Hexenal (2c). Treatment of *trans*-2-hexenal (2.581 g, 26.30 mmol) with the reagents specified in the general procedure generated the crude acetal (3.664 g, 98%), the ^1H NMR spectrum of which indicated the presence of only the desired product. Vacuum distillation (35 °C/0.6 mm; lit.[22] 86–87 °C/22 mm) furnished 3.104 g (83%) of acetal **2c** as a colorless liquid. ^1H NMR: δ 5.94 (dt, J = 15.4, 6.6 Hz, 1H), 5.49 (ddt, J = 15.4, 6.6, 1.4 Hz, 1H), 5.19 (d, J = 6.6 Hz, 1H), 4.05–3.85 (m, 4H), 2.07 (dq, J = 7.1, 1.4 Hz, 2H), 1.44 (sextet, J = 7.4 Hz, 2H), 0.91 (t, J = 7.3 Hz, 3H).

1,3-Dioxolane of 2-Butylacrolein (2d). With 2-butylacrolein (2.207 g, 19.68 mmol) as the starting material, the reaction furnished practically pure acetal **2d** (2.951 g, 96%). Vacuum distillation (34 °C/1.7 mm) gave 2.490 g (81%) of the acetal **2d** as a colorless liquid. ^1H NMR: δ 5.25 (s, 1H), 5.22 (s, 1H), 5.04 (unresolved dd, 1H), 4.06–3.87 (m, 4H), 2.09 (t, J = 8.5 Hz, 2H), 1.52–1.30 (m, 4H), 0.92 (t, J = 7.0 Hz, 3H).

1,3-Dioxolane of (*S*)-(−)-Perillaldehyde (2e). Acetal **2e** (1.783 g, 95%) was prepared from (*S*)-(−)-perillaldehyde (1.451 g, 9.66 mmol). Vacuum distillation (56 °C/0.1 mm; lit.[13] 60 °C/

(18) Unfortunately, *trans,trans*-2,4-nonadienal underwent some double bond isomerization using either oxalic acid or L-tartaric acid, although to a less extent (<2%) in the latter case as estimated by the ^1H NMR spectrum and the GC–MS chromatogram of the product mixture. In order to solve the problem, adipic acid (pK_a = 4.42, 0.005 equiv) was used as the catalyst. There was no isomerization detected under the conditions; however, the ratio of the starting material and the acetal was only 2.5:1 after refluxing in benzene for 44 h. When the amount of adipic acid was increased to 0.1 equiv, the ratio of the starting material and the product was improved to 1:6 but some isomerization was also detected.

(19) The efficiencies of other dehydrating agents such as sodium sulfate, silica gel, and molecular sieves have been studied in the acetalization of 2-hexenal under similar conditions, but all were found to be inferior to magnesium sulfate.

(20) It is crucial to maintain good stirring during the addition of ethylene glycol solution to the reaction mixture to achieve high yields.

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0.4 mm) furnished 1.633 g (87%) of the desired product as a colorless liquid. ^{1}H NMR: δ 5.95 (br, s, 1H), 5.14 (s, 1H), 4.73–4.72 (br, 2H), 4.04–3.87 (m, 4H), 2.24–1.23 (m, 7H), 1.74 (br, s, 3H).

1,3-Dioxolane of 2-Furaldehyde (2f). From 2-furaldehyde (1.590 g, 16.55 mmol) was obtained acetal **2f** (2.273 g, 98%). Vacuum distillation (42 °C/1.7 mm; lit.[13] 60 °C/0.35 mm; lit.[23] 93 °C/13 mm) afforded 1.855 g (80%) of the title compound as a colorless liquid. ^{1}H NMR: δ 7.43 (dd, J = 1.5, 0.9 Hz, 1H), 6.45 (d, J = 3.0 Hz, 1H), 6.36 (dd, J = 3.3, 1.5 Hz, 1H), 5.93 (s, 1H), 4.17–3.99 (m, 4H).

1,3-Dioxolane of *trans,trans*-2,4-Nonadienal (2g). *trans,trans*-Nonadienal (1.781 g, 12.89 mmol) was subjected to acetalization to produce virtually pure acetal **2g** (2.278 g, 97%). Vacuum distillation (53 °C/0.1 mm; lit.[13] 104–105 °C/6 mm) afforded 1.820 g (78%) of the title compound as a colorless liquid. ^{1}H NMR: δ 6.77–5.24 (m, 5H), 4.06–3.83 (m, 4H), 2.12 (unresolved q, 2H), 1.41–1.24 (m, 4H), 0.88 (unresolved t, 3H).

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