

Concomitant Addition and Acetalization of α,β -Unsaturated Aldehydes with Diols[†]

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α,β -Unsaturated aldehydes such as acrolein and crotonaldehyde were reacted with diols in the presence of conc. sulfuric acid to give products of which concomitant addition to C-C double bond and acetalization took place. Boron trifluoride etherate and titanium tetrachloride gave only acetalization products.

Key Words : α,β -Unsaturated aldehydes, Acetalization, Addition

Introduction

During our investigation of the reduction of acrylic acid with lithium aluminum hydride, we observed several unidentified compounds.¹ One of them seemed to be 2-vinyl-1,3-dioxolane (**3a**), which is a widely known compound, but its formation under the reaction conditions was totally unexpected. In order to confirm the identity of the compound we attempted preparation of authentic compound of **3a** from acrolein (**1a**) and ethylene glycol (**2**). However, the preparation of **3a** by direct acetalization of **1a** with **2** was not straightforward. Azeotropic treatment of **1a** and **2** in benzene in the presence of H₂SO₄ as catalyst gave mostly a bis-addition product **4** in 33% yield and only a trace of the desired acetal **3** which was detected as shown in Scheme 1.

The bis-adduct is a new compound to the best of our knowledge. We now report the reactions of α,β -unsaturated aldehydes with 1,2- and 1,3-diols.

Results and Discussion

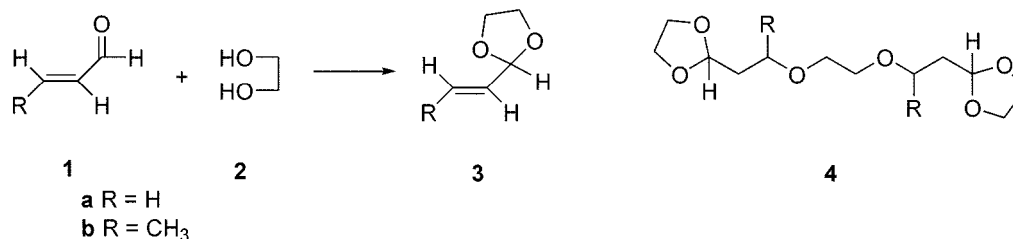
2-Vinyl derivatives of 1,3-dioxolane (**3a**) and 1,3-dioxane (**6a**) as well as the corresponding 2-(1-propenyl) analogues **3b** and **6b** are widely used in the literature. They are useful in olefin cross methathesis,^{2,3} as dienophiles,^{4,6} as dipolarophiles,^{7,8} and in C-C bond formation by umpolung addition.⁹⁻¹¹ They are also important in polymer research.^{12,14} Therefore, their preparation has also often been reported. Unlike simple aldehydes or ketones which could be converted to acetals by the reactions with an excess of

alcohols or diols in the presence of acid catalyst, the conjugated aldehydes need special conditions to prevent polymerization. For example, the diethyl acetal of acrolein (**1a**) is best prepared by employing triethyl orthoformate.¹⁵ One of the most widely cited procedures for acetalization of conjugated carbonyl compounds uses *p*-toluenesulfonic acid (*p*-TsOH) as the catalyst.¹⁶

Improved procedures for the acetalization of α,β -unsaturated aldehydes have been continually reported in literature. Natural kaolinitic clay was used for the preparation of **3b** in 92% yield.¹⁷ Cadmium iodide was employed as catalyst for the synthesis of **3b** under microwave irradiation conditions.¹⁸ Piasecki reported the formation of 2-vinyl-1,3-dioxane (**6a**) when **1a** and propylene glycol (**5**) were reacted in the presence of *p*-TsOH and various primary alcohols such as ethanol to *n*-hexanol.¹⁹ However, other compounds such as **8**, **9**, and **10** were isolated in varying yields, as shown in Scheme 2.

Lu, *et al.* used MgSO₄ in addition to *p*-TsOH to obtain the α,β -unsaturated acetals.²⁰ But 1:2 adducts such as **11** and **12** were formed in case of crotonaldehyde (**2b**), as shown in Scheme 3. However, **3b** was obtained in 88% and 86% yields by using oxalic acid (0.025 equiv)/MgSO₄ (2 equiv) and tartaric acid (0.005 equiv)/MgSO₄ (2 equiv), respectively. The yields were lowered to 68% and 76%, respectively, without MgSO₄.

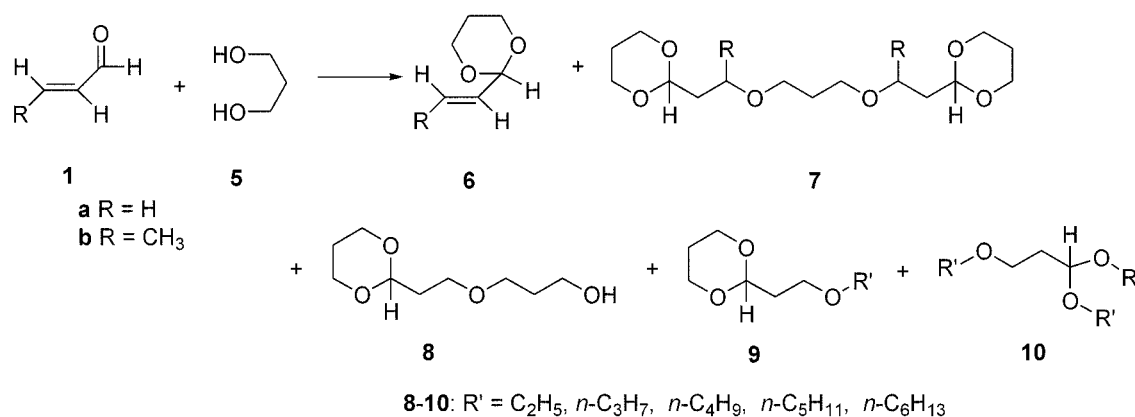
We extensively examined the effect of catalysts. When a mixture of **1a** and **2** (1 : 1 by mole) in benzene in the presence of a few drops of conc. H₂SO₄ was heated at reflux for 12 h using a Dean-Stark trap, about two equivalents of



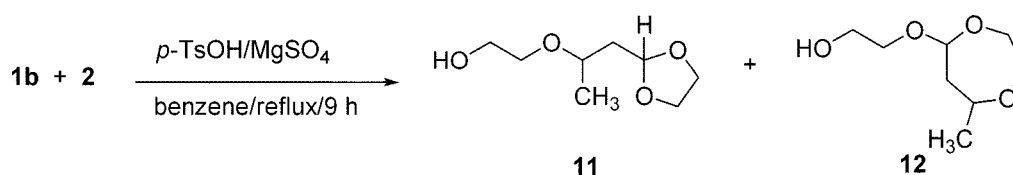
Scheme 1

[†]Dedicated to Professor Yong Hae Kim for his distinguished achievements in organic chemistry.

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Scheme 2



Scheme 3

water was collected. After a typical work-up, the final product only **4a** was obtained in 33% yield based on **1a**. The yield could be improved to about 80% by using three molar equivalents of **2**. Apparently, the low-boiling acrolein (bp 53 °C) was evaporated off when the solvent (benzene) was removed under aspirator pressure.

The structure of **4a** was readily confirmed by its ¹H and ¹³C

NMR as well as IR spectra. There is no signal corresponding to the presence of vinyl and hydroxyl groups. The peak at 102.75 ppm in ¹³C correlates to δ 4.98 in ¹H in the HETCOR spectra (not shown) of **4a**, which indicates the presence of a cyclic acetal functionality. The ¹³C signal of 2-C appearing at significantly down field compared to that of unsubstituted 1,3-dioxane (94.29 ppm), which indicates that the vinyl group is at equatorial position.²¹ A similar type of reaction took place between **1a** and **5** to give **7a**. Figures 1 and 2 are the COSY and HETCOR spectra of **7a**, respectively. Both **4a** and **7a** are C₂ symmetric molecules and the spectral assignments are unambiguous. The presence of seven peaks and, especially, the peak at 29.89 ppm in Figure 2 clearly confirm the structure of the bis-adduct **7a**. Mass spectra of **4** and **7** also confirm the bis-adduct composition.

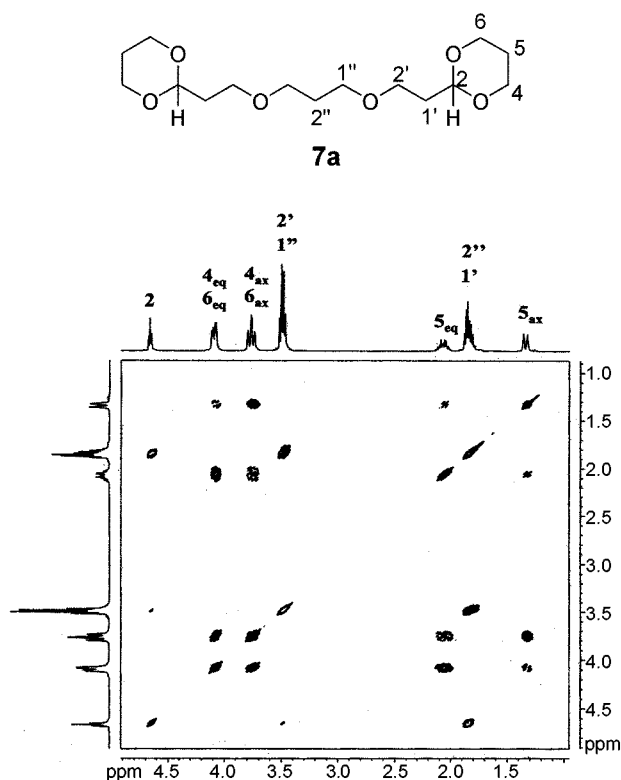
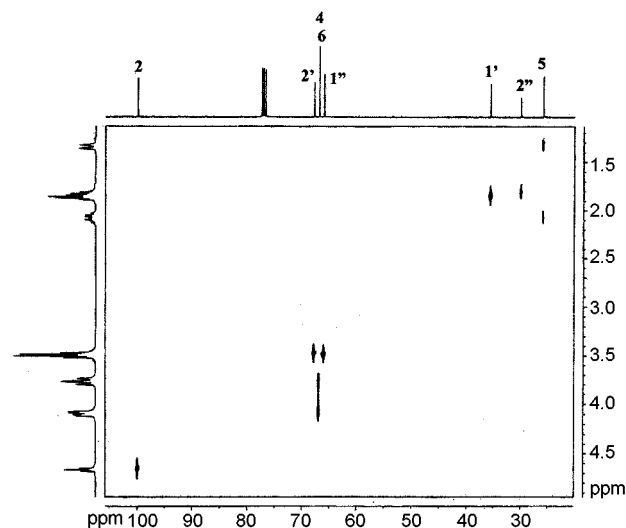
Figure 1. ¹H-¹H COSY spectra of **7a**.Figure 2. ¹H-¹³C HETCOR spectra of **7a**.

Table 1. ^1H and ^{13}C Chemical shift values of the acetals

	4a		4b		7a		7b	
	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C
2	4.98	102.75	4.98	102.33	4.67	99.87	4.67	101.12
4,6 _{ax}	3.85	67.29	3.84	67.96	3.77	66.82	3.75	66.92
4,6 _{eq}	3.96	–	3.96	–	4.09	–	4.09	–
5 _{ax}	–	–	–	–	1.34	25.77	1.34	25.72
5 _{eq}	–	–	–	–	2.07	–	2.03	–
1	1.96	34.60	1.97	41.18	1.84	35.46	1.80	42.59
2	3.62	65.20	3.65	64.82	3.50	65.92	3.41	65.86
1''	3.60	65.33	3.50	64.61	3.50	67.72	3.59	66.96
2''	–	–	–	–	1.84	29.89	1.80	30.74
CH ₃	–	–	1.20	20.15	–	–	1.16	15.28

Table 2. Yields and products composition after reflux of the 1 : 1 mixture of α,β -unsaturated aldehydes and diols for 12 h

Catalyst	Aldehyde	Diol	Yield, %	3 : 4	Aldehyde	Diol	Yield	6 : 7
H ₂ SO ₄	1a	2	33	0:100	1a	5	27	0:100
	1b	2	62	0:100	1b	5	76	0:100
<i>p</i> -TsOH	1a	2	44	66:34	1a	5	84	70:30
	1b	2	53	50:50	1b	5	67	50:50
TiCl ₄	1a	2	10	100:0	1a	5	43	100:0
	1b	2	38	100:0	1b	5	44	100:0
BF ₃ ·OEt ₂	1a	2	47	100:0	1a	5	12	100:0
	1b	2	87	100:0	1b	5	83	100:0

Concomitant addition and acetalization of the diols **2** and **5** to crotonaldehyde (**1b**) were the major reaction when H₂SO₄ was used, and compounds **4b** and **7b** were isolated in 62% and 76% yields, respectively. Table 1 lists the chemical shift values of the bis adducts.

In contrast to the report,¹⁶ *p*-TsOH-catalyzed reactions of **1** with **2** under azeotropic conditions gave a mixture of **3** and **4** in about 2 : 1 ratio. Similar results were obtained from the reactions of **1** and **5**, giving **6** and **7** in about 1 : 1 ratio. The combined yields based on **1** were about 40-50% in the case of the 1,3-dioxolanes **3** and **4** and 70-80% in the case of the 1,3-dioxanes **6** and **7**. The mixture was separated by flash column chromatography using silica gel and eluting with ethyl acetate-hexane.

In order to minimize the addition and maximize the acetalization, other catalysts were also examined. We found that the procedure employing *p*-TsOH/MgSO₄²⁰ was not suitable with **1a** which is low-boiling and readily polymerizes. Table 2 shows the products and yields after reflux for 12 h with azeotropic removal of water by benzene.

As shown in Table 2, it is apparent that using H₂SO₄ is the catalyst of choice for the preparation of **4** and **7**, but that TiCl₄ and BF₃·OEt₂ are preferable for the preparation of **3** and **6**. The Table is only for the purpose of comparison. We found that the yields of **4** and **7** could be improved to about 80% by employing an excess of the diols and refluxing for 24 h. On the other hand, the yields of **3** and **6** could be increased to about 90% by using BF₃·OEt₂.

It is conceivable that a strong protic acid like H₂SO₄ readily protonates the carbonyl oxygen atom leading to

preferable addition of the diol to the β -carbon, which results in the formation of the bis-adduct **4** and **7**. On the other hand, this kind of activation may not be feasible with TiCl₄ or BF₃·OEt₂. These catalysts may form weak complexes with the carbonyl oxygen atom, which prevents the addition but facilitates the acetalization.

In conclusion, TiCl₄ or BF₃·OEt₂ seems to be the choice of catalyst for the acetalization of conjugated aldehydes with diols. Sulfuric acid causes concomitant addition and acetalization.

Experimental Section

General. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DPX-400 FT NMR spectrometer in the Central Lab of Kangwon National University at 400 MHz for ^1H and 100 MHz for ^{13}C and were referenced to tetramethylsilane. Infrared spectra were recorded on a JASCO FT/IR-460 Plus spectrophotometer. Low resolution mass spectra were obtained using Micromass Autospec M363 at 25 °C and 70 eV.

Materials. Acrolein (**1a**), crotonaldehyde (**1b**), ethylene glycol (**2**), and propylene glycol (**5**) were used as received as the commercial products. Benzene was distilled from over sodium metal prior to use.

Reaction of α,β -unsaturated aldehydes with diols. An illustrative procedure. A mixture of the aldehyde (24 mmol) and the diol (24 mmol) in benzene (80 mL) was placed in a flask equipped a Dean-Stark trap. Catalyst (< 1%) was added and the mixture was heated at reflux for 12 h. The solution was evaporated under aspirator pressure,

and the residual liquid was mixed with water (70 mL). The aqueous solution was neutralized with saturated NaHCO₃ solution, and then extracted with diethyl ether (25 mL, 4 times). The ethereal extract was dried over MgSO₄ and evaporated to give a colorless liquid.

1,2-Bis-[2-(1,3-dioxolan-2-yl)ethoxy]ethane (4a): IR (neat) 2880, 1477, 1116, 1015, 733 cm⁻¹; MS (%) 261 (2, M⁺-H), 217 (62, M⁺-C₂H₅O), 161 (19), 131 (22), 117 (21), 101 (78), 100 (78), 99 (88), 73 (100), 57 (64).

1,2-Bis-[1-(1,3-dioxolan-2-yl)-2-propoxy]ethane (4b): IR (neat) 2885, 1470, 1118, 1051 cm⁻¹; MS (%) 245 (5, M⁺-C₂H₅O), 217 (62), 115 (28), 114 (31), 99 (34), 73 (100).

1,3-Bis-[2-(1,3-dioxan-2-yl)ethoxy]propane (7a): IR (neat) 2962, 2857, 1479, 1142, 1100, 1011 cm⁻¹; MS (%) 304 (3, M⁺), 303 (13, M⁺-H), 246 (35), 245 (72, M⁺-C₃H₇O), 228 (14), 189 (54), 187 (36), 172 (24), 131 (60), 114 (83), 113 (77), 100 (43), 96 (64), 87 (94), 73 (100), 56 (72).

1,2-Bis-[1-(1,3-dioxan-2-yl)-2-propoxy]propane (7b): IR (neat) 2965, 2856, 1470, 1404, 1378, 1141, 1100, 1050 cm⁻¹; MS (%) 331 (3, M⁺-H), 273 (26, M⁺-C₃H₇O), 201 (19), 171 (25), 145 (29), 130 (57), 129 (99), 128 (93), 113 (94), 87 (100), 71 (76), 59 (93).

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