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Preliminary Communication

Synthesis of 1,3-dioxolanes by the addition of ketones to epoxides by using $[Cp^*Ir(NCMe)_3]^{2+}$ as catalyst

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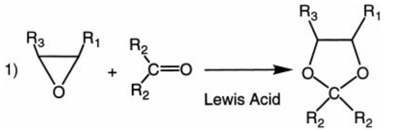
Abstract

A series of 1,3-dioxolanes have been prepared by the addition of ketones to epoxides in the presence of the catalyst $[Cp^*Ir(NCMe)_3]^{2+}$, Cp^*=C_5Me_5. The reactions proceed readily at 22°C and the yields are good. The following 1,3-dioxolanes: 2,2,4-trimethyl-1,3-dioxolane, **1**; 2,2-dimethyl-4-vinyl-1,3-dioxolane, **2**; 2,2-dimethyl-4-phenyl-1,3-dioxolane, **3**; 2,2-diethyl-4-methyl-1,3-dioxolane, **4**; 2,2-diethyl-4-vinyl-1,3-dioxolane, **5**; 2,2-diethyl-4-phenyl-1,3-dioxolane, **6** were prepared from the appropriate epoxide and carbonyl compounds. An inversion of configuration at the carbon atom at the C–O bond cleavage site of the epoxide was observed to occur in the formation of the dioxolanes: (*R*,*S*)- 2,2,4,5-tetramethyl-1,3-dioxolane, **7** and a mixture of (*R*,*R*)- and (*S*,*S*)-2,2,4,5-tetramethyl-1,3-dioxolane, **8** obtained from the reactions of acetone with (*R*,*R*)-/(*S*,*S*)-buten-2-oxide and *R*, *S*,-buten-2-oxide, respectively. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Catalyst; Epoxide; Ketone; Dioxolane; Iridium

1. Introduction

Formation of acetals is a commonly used method of protecting carbonyl functional groups during the course of organic syntheses [1]. One method for preparing the cyclic 1,3-dioxolane members of this family of compounds that has been attracting increasing interest in recent years is the Lewis acid-catalyzed addition of epoxides to carbonyl groups, Eq. (1):



(1)

BF_3 is the most active and successfully utilized Lewis acid for these reactions [2–6], however, $SnCl_4$ [6], $TiCl_4$ [7], tetracyanoethylene [8], $CuSO_4$ [9] and even bentonitic clay [10] have also been used with success. We have now found that the organometallic complex $[Cp^*Ir(NCMe)_3]^{2+}$, $Cp^* = C_5Me_5$ is also an active and effective catalyst for this reaction. Details of our studies of this catalytic reaction are reported herein.

2. Results and discussion

The 1,3-dioxolanes **1**–**8** were obtained in good yields from the reactions of the appropriate epoxide and ketone in the presence of the catalyst $[Cp^*Ir(NCMe)_3]^{2+}$. For example, the reaction of acetone and butadiene oxide yielded 2,2-dimethyl-4-vinyl-1,3-dioxolane, **2** rapidly at 22°C, see Table 1. The reaction gave 208 turnovers in less than 10 min. giving a turnover frequency TOF of 20.8 min^{-1}. The reaction of acetone with styrene oxide proceeded at an equally rapid rate to yield 2,2-dimethyl-4-phenyl-1,3-dioxolane, **3**, TOF = 26.4 min. The reactions

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Table 1
Percent yields, turnover numbers TON and turnover frequencies TOF for the products **1**–**8**

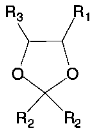
Reagents[a]	Product	% Yield[b]	TON[c]	TOF[c]
Acetone, propylene oxide	**1**	64	165	0.23
Acetone, vinyl epoxide	**2**	68	208	20.8
Acetone, styrene oxide	**3**	93	264	26.4
3-Pentanone, propylene oxide	**4**	30	79	0.078
3-Pentanone, vinyl epoxide	**5**	32	125	1.4
3-Pentanone, styrene oxide	**6**	48	139	14
Acetone, *trans*-β-butylene oxide	**7**	30	123	0.029
Acetone, *cis*-β-butylene oxide	**8**	77	338	0.078
Acetone, propylene oxide[d]	**1**	100	127	8.5

[a] Reactions were catalyzed by $[IrCp^*(CH_3CN)_3][PF_6]_2$.

[b] The percent yield was calculated using NMR spectroscopy; these are not isolated yields.

[c] The TONs and TOFs were based on a 10 min reaction time except **1**, **4**, **5**, **7** and **8**. The reaction times of these exceptions are 12, 17, 4, 72 and 72 h, respectively. All reported reactions were run at 22°C. TOF = mol product/mol catalyst-min.

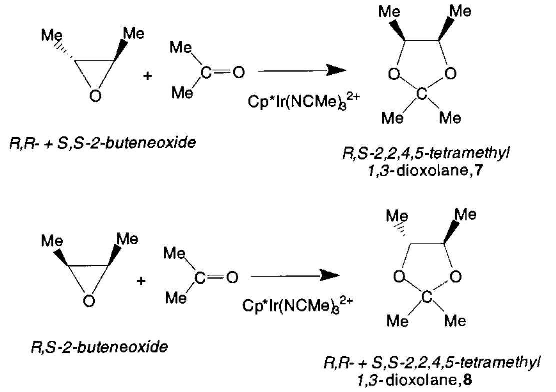
[d] Using $BF_3 \cdot OEt_2$ as catalyst. This reaction is complete within 15 min.



1 R1 = R2 = CH_3, R3 = H (2,2,4-trimethyl-1,3-dioxolane)
2 R1 = $CHCH_2$, R2 = CH_3, R3 = H (2,2-dimethyl-4-ethenyl-1,3-dioxolane)
3 R1 = C_6H_5, R2 = CH_3, R3 = H (2,2-dimethyl-4-phenyl-1,3-dioxolane)
4 R1 = CH_3, R2 = CH_2CH_3, R3 = H (2,2-diethyl-4-methyl-1,3-dioxolane)
5 R1 = $CHCH_2$, R2 = CH_2CH_3, R3 = H (2,2-diethyl-4-ethenyl-1,3-dioxolane)
6 R1 = C_6H_5, R2 = CH_2CH_3, R3 = H (2,2-diethyl-4-phenyl-1,3-dioxolane)
7 R1 = R2 = R3 = CH_3(R1, R3) (*R,S*-2,2,4,5-tetramethyl-1,3-dioxolane)
8 R1 = R2 = R3 = CH_3(R1, R3) (*R,R*+ *S,S* -2,2,4,5-tetramethyl-1,3-dioxolane)

slowed considerably when alkyl substituents were introduced to the epoxide ring. For example, the reaction of propylene oxide with acetone required 12 h for completion, while the reactions with 2-butene oxide with acetone required 72 h. No reactions occurred in the absence of the catalyst.

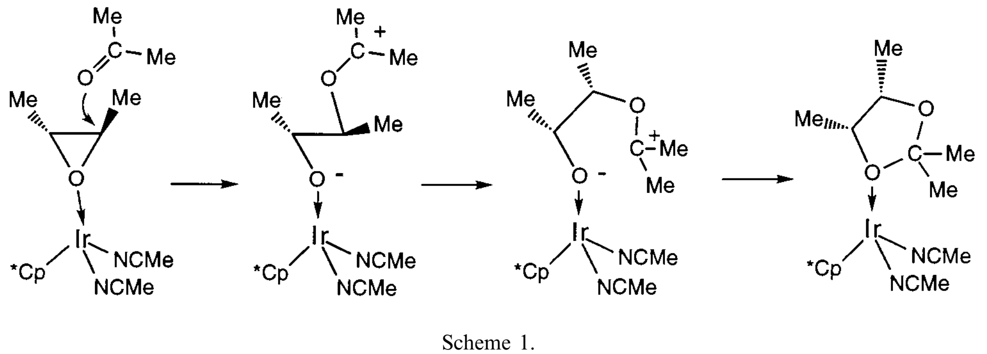
The reactions of the stereochemically defined epoxides, (*R*,*R*)-/(*S*,*S*)-buten-2-oxide and (*R*,*S*)-buten-2-oxide, with acetone yielded the dioxolanes: (*R*,*S*)-2,2,4,5-tetramethyl-1,3-dioxolane, **7** and a mixture of (*R*,*R*)- and (*S*,*S*)-2,2,4,5-tetramethyl-1,3-dioxolane, **8**, respectively. These results confirm the occurrence of stereochemical inversion at the carbon atom at the C–O bond cleavage site in the epoxide, Eqs. (2a) and (2b).



(2a and 2b)

Similar inversions of configuration have been found to occur for other Lewis acid catalyzed additions of epoxides to carbonyls [4,5]. These observations are in accord with previously proposed mechanisms in which the epoxide is activated by coordination of the oxygen atom to the Lewis acid (in this case the iridium atom) followed by a backside addition of the acetone to one of the carbon atoms, see Scheme 1. In recent studies, we have shown that thiiranes also undergo activation toward ring opening upon coordination of their sulfur atom to transition metal atoms [11,12].

For comparative purposes we have performed the synthesis of **1** from acetone and propylene oxide using BF_3OEt_2 as the catalyst. BF_3OEt_2 was reported to be the most active of the known catalysts for producing these catalytic dioxolane syntheses. Using our conditions we found that **1** was formed with a TOF of 8.5, which is ca. 40 times faster than that of $[Cp^*Ir(NCMe)_3]^{2+}$ [2].



Scheme 1.

Table 2
^{1}H- and ^{13}C-NMR data for compounds **4**–**6**

Compound	^{1}H	^{13}C
4	0.85 (t, 6H, $J = 7.5$); 0.86 (t, 6H, $J = 7.5$); 1.22 (d, 3 H, $J = 5.9$); 1.59 (q, 4H, $J = 7.5$);); 1.57 (q, 4H, $J = 7.5$); 3.35 (dd, 1H, $J = 7.9$); 4.01 (dd, 1H, $J = 7.6$); 4.16 (m, 1H)	112.64 (C2); 72.20 (C5); 71.49 (C4); 30.00, 29.95 (CH_2CH$_3$); 18.19 (CHCH_3); 8.23, 7.88 (CH$_2$$CH_3$)
5	0.89 (t, 6H, $J = 7.4$, 7.5); 0.90 (t, 6H, $J = 7.4$, 7.5); 1.62 (q, 4 H, $J = 7.5$, 7.4); 1.64 (q, 4 H, $J = 7.5$, 7.4); 3.53 (dd, 1H, $J = 8.1$); 4.08 (dd, 1H, $J = 6.2$, 8.0); 4.46 (m, 1H); 5.25 (m, 2H); 5.79 (m, 1H)	135.70, 113.19 (vinyl); 117.91 (C2); 77.70 (C4); 69.77 (C5); 29.88, 29.67 (CH_2CH$_3$); 8.02, 7.92 (CH$_2$$CH_3$)
6	0.95 (t, 6H, $J = 7.5$); 0.99 (t, 6H, $J = 7.5$); 1.75 (m, 4 H); 3.62 (dd, 1H, $J = 8.1$); 4.72 (dd, 1H, $J = 6.1$, 8.0); 5.03 dd, 1H, $J = 6.1$, 8.9); 7.30 (m, C_6H_5)	138.80, 128.47, 128.25, 127.98, 126.22, 126.15 (C_6H_5); 113.39 (C2); 78.22 (C4); 72.07 (C5); 29.94, 29.62 (CH_2CH$_3$); 8.17, 7.83 (CH$_2$$CH_3$)

3. Experimental

3.1. General data

Unless specified otherwise, all reactions were carried out under an atmosphere of nitrogen. The carbonyl compounds were purchased from Aldrich. Butadiene oxide was received from Eastman and was vacuum distilled before use. All other epoxides were obtained from Aldrich and were used without further purification. $[Cp^*Ir(NCMe)_3]^{2+}$ was synthesized by the reported procedure [13]. TLC separations were performed in air by using silica gel (60 Å, F_{254}) on plates (Analtech, 0.25 mm). Mass spectra were collected using a VG SE-70 in the direct inlet mode using electron impact ionization. NMR spectra were run on a Bruker AM-300 spectrometer operating at 300 MHz. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY.

3.2. Synthesis of 1,3-dioxolanes from epoxides and ketones

A typical procedure for the synthesis of 2,2-dimethyl-4-phenyl-1,3-dioxolane is given here. 2 ml of the ketone (acetone), 500 µl of the epoxide (6.2:1 ratio of ketone to epoxide) and 20 mg C_6Me_6 (to serve as a quantitative internal standard) were placed in a small vial with a stir bar and a rubber septum cap. The vial was placed in a water bath at 22°C. With stirring 10 mg of the catalyst $[IrCp^*(CH_3CN)_3][PF_6]_2$, was added to the vial (ketone/catalyst ratio was 1600/1). Periodically, 20 µl samples were removed and analyzed by ^{1}H-NMR spectroscopy. The endpoint of the reaction was determined when product formation ceased. Most reactions were complete within 10 min (see Table 1 for the exceptions). The other compounds were synthesized similarly. Note: We observed that if the dioxolanes are left in contact with the catalyst beyond the endpoint, they will decompose slowly. Compounds **1** [14], **2** [15], **3** [9], **7** [4,16], and **8** [4,16] were reported previously.

The products **4**, **5** and **6** were isolated by vacuum distillation to give viscous oils. ^{1}H-NMR and ^{13}C-NMR spectra for **4**–**6** are listed in Table 2. The mass spectra of compounds **4**–**6** did not show parent ions, but all did show a peak for the parent minus an ethyl group. The mass spectrum of **4** shows a peak at 115 m/e, as well as additional ions at 100, 86, 71 and 57. The mass spectrum of **5** shows a peak at 127 m/e, with additional ions at 100, 71 and 57. The mass spectrum of **6** shows a peak at 177 m/e, with additional ions at 103, 91, 77, 65 and 57. This is consistent with the fragmentation patterns reported by Hanzlik et al. [17].

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