

SYNTHESIS AND CRYSTAL STRUCTURE OF 2-DICHLOROMETHYL-2-PHENYL-1,3-DIOXOLANE

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Received 18 Sept. 2012; Accepted 30 April 2013

2-Dichloromethyl-2-phenyl-1,3-dioxolane was synthesized by a sequential procedure involving microwave-assisted acetalization of benzaldehyde with glycol and carbene insertion to acetal with chloroform using TEBA as phase transfer catalyst. The X-ray structure determination confirmed the structure, and the product was further characterized by IR, ^1H NMR, ^{13}C NMR and elemental analysis. In the structure of the title compound, there were extensive hydrogen bonds between H atoms and O atoms. No significant π - π interactions were found in the crystal structure.

The 2-dichloromethyl-1,3-dioxolanes are an important heterocyclic system found in many biologically and pharmaceutically active compounds in organic synthesis¹. In particular, 2-dichloromethyl-1,3-dioxolane derivatives, such as MG-191, have been investigated for potential use as herbicide safeners which protected crops from the injury by herbicides²⁻⁴. A proposed mechanism by which MG-191 protects corn is increasing the glutathione content and glutathione-related enzyme activities, which are of great importance in thiocarbamate and chloroacetanilide herbicide detoxication^{5,6}. 2-Dichloromethyl-1,3-dioxolane derivatives are also used as protecting groups for carbohydrate derivatives⁷.

Although it has been synthesized successfully^{8,9}, there was no reports on microwave-assisted synthesis and single crystal structure of 2-dichloromethyl-2-phenyl-1,3-dioxolane. As part of our efforts to develop efficient and green synthesis procedure for bioactive molecules, here we have described the synthesis and crystal structure of 2-dichloromethyl-2-phenyl-1,3-dioxolane, which provided useful molecular information

in explaining the detoxified mechanism and relationship of structure and activity.

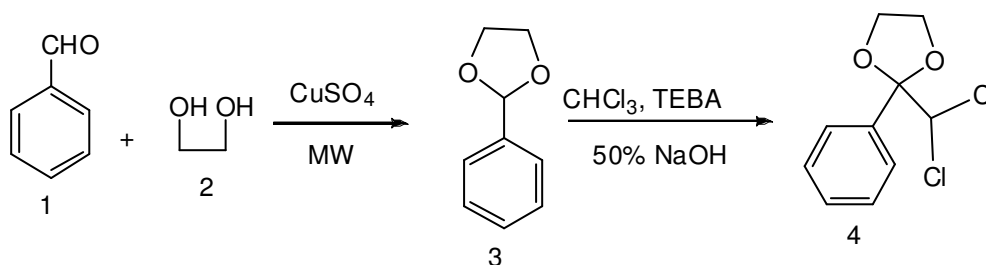
Experimental

The melting points were determined on Beijing Taike melting point apparatus (X-4) and are uncorrected. The infrared (IR) spectra were taken on a KJ-IN-27G infrared spectrophotometer (KBr). The ^1H NMR spectra and ^{13}C NMR spectra were recorded on a Bruker AVANCE 300 MHz nuclear magnetic resonance spectrometer with CDCl_3 as the solvent and TMS as the internal standard. The elemental analysis was performed on FLASH EA1112 elemental analyzer.

2-Dichloromethyl-2-phenyl-1,3-dioxolane (4)

Compound (4) was synthesized from benzaldehyde, glycol and chloroform (Scheme-1).

A mixture of 0.1 mol benzaldehyde (1), 0.15 mol glycol (2), 1.5g CuSO_4 and 40 ml cyclohexane was exposed to microwave radiation for 24 min with refluxing and removing the produced water. The



SCHEME-1

Table-1
Crystal data of the title compound

CCDC No.	892964
Molecular formula	C ₁₀ H ₁₀ Cl ₂ O ₂
Molecular weight	233.08
Temperature	293(2) K
Radiation λ	0.71073 Å
Crystal system	Orthorhombic
Space group	<i>Pnma</i>
a/Å	7.0780(14)
b/Å	11.358(2)
c/Å	13.654(3)
V/Å ³	1097.7(4)
Z	4
Crystal size/mm	0.46x0.24x0.19
Crystal color	Colorless
Absorption coefficient T_{\min} & T_{\max}	0.7841 & 0.9002
F(000)	480
Reflections collected/unique	6115/870 [$R_{\text{int}}=0.0409$]
Range/indices (h,k,l)	-8,7-12; 12,12,12
θ limit (°)	3.24-24.98
No. of observed data	870
No. of restraints	0
Goodness of fit on F^2	1.102
R_1, wR_2 [$1 > 2 \sigma [1]$]	0.0396, 0.1118
R_1, wR_2 (all data)	0.0484, 0.1150

Table-2
Selected bond lengths (Å) and angles (°) of the title compound

C1-C2	1.381(3)	C6-C6A	1.470(8)
C1-C2A	1.381(3)	C5-O1	1.412(2)
C1-C5	1.520(4)	C5-O1A	1.412(2)
C2-C3	1.383(4)	C6-O1	1.394(4)
C3-C4	1.370(4)	C7-Cl1	1.769(2)
C4-C3A	1.370(4)	C7-Cl1A	1.769(2)
C5-C7	1.357(5)		
C2A-C1-C2	119.4(3)	C2A-C1-C5	120.28(16)
C2-C1-C5	120.28(16)	C1-C2-C3	120.0(3)
C4-C3-C2	120.4(3)	C3-C4-C3A	119.8(4)
O1A-C5-CO1	106.9(3)	O1A-C5-C1	111.69(18)
O1-C5-C1	111.69(18)	O1A-C5-C7	105.40(19)
O1-C5-C7	105.40(19)	C1-C5-C7	115.2(3)
O1-C6-C6A	106.65(17)	C5-C7-Cl1	111.96(15)
C5-C7-Cl1A	11.96(15)	C6-O1-C5	107.2(2)

reaction mixture was washed with water until the organic phase was colorless. The organic layer was extracted with ethyl acetate and dried over anhydrous MgSO₄. Then the crude product was distilled under reduced pressure, and the acetal (**3**) was collected at 132~139° (0.096 Mpa). The yield of the intermediate was 63.7%.

To a vigorously stirred solution of 0.05 mol of acetal (**3**) in 60 ml chloroform, 30g anhydrous Na₂SO₄

Table-3
Hydrogen bond geometry (Å)

Donor---H---Acceptor	D-H	H..A	D...A	D-H..A
C(2)--H(2)....O(1)A	0.93	2.55	3.403(2)	152.3
Symmetry operation codes:A:x,y+1/2, z;B;-x,-y+1,-z				

and 2g benzyl triethyl ammonium chloride (TEBA) as the phase-transfer catalyst and 50% aq. NaOH was added at 0°. The resulting solution was stirred continuously for 24 hr. Then the organic layer was rinsed until pH=7 and dried over anhyd MgSO₄. The chloroform was removed under vacuum and 2-dichloromethyl-2-phenyl-1,3-dioxolane (**4**) was collected at 214-216° (0.096 Mpa). The yield of (**4**) was 46.2%, m.p. 62-63°; IR (KBr): 3012-2880 (C-H), 1236-1220 (C-O); ¹H NMR (CDCl₃, 300 MHz) δ: 7.56-7.60 (m, 2H, ArH), 7.37-7.41 (m, 3H, ArH), 5.85 (s, 1H, -CHCl₂-), 4.28-4.32, 3.98-4.03 (m, 4H, -O-(CH₂)₂-O); ¹³C NMR (CDCl₃, 75 MHz): 137.34, 129.19, 128.01, 127.07, 109.09, 75.48, 66.72, 66.72. [Found : C, 51.84, H, 4.30 C₁₀H₁₀Cl₂O₂ requires C, 51.72, H, 4.34%].

The X-ray data were collected on a Bruker AXS II CCD area-detector diffractometer using graphite monochromated Mo Ka radiation (γ=0.71073 Å) at

293(2) K. Selected crystallographic and experimental details are summarized in Table-1.

The structure was solved by direct methods using *SHELXS-97*⁰, and refined by full matrix least squares on F², *SHELXL-97*⁰. Minimum and maximum, final electron density was -0.198 and 0.175 eÅ⁻³. Symmetry equivalent reflections were used to optimize crystal shape and size. All non-hydrogen atoms were refined anisotropically. Aromatic H atoms were placed in calculated positions (C-H=0.93Å) and constrained to ride on their parent atoms, with U_{iso} (H)=1.2 U_{eq} (C). Crystallographic data have been deposited at the Cambridge Crystallographic data centre as supplementary publication number CCDC 892964. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK.

The single crystal of the title compound was obtained by slow diffusion of the petroleum ether to the ethanol solution. The crystal was air-stable and colorless.

The molecular structure of compound **3** with atom-numbering is shown in Figure-1.

According to X-ray analysis the structure contained 1,3-dioxolane and a benzene ring. The title compound was a symmetric molecule, located at the

plate composed of C1, C4, C5 and C7 atoms. The dihedral angle between the rings of 1,3-dioxolane and benzene is 68.6°. The bond lengths and bond angles of the 1,3-dioxolane were in their normal range (Table-2). These independent infinite chains were connected by hydrogen bonds, which stabilized the crystal structure (Figure-2). The presence of the intermolecular hydrogen bond C2-H2..... O1A led to the stability of the compound (Table-3). For benzene ring vertically aligned between two layers of molecules, no significant π - π interactions were found in the crystal structure.

Acknowledgement

This work was supported by the National Nature Science Foundation of China (No. 31101473), the Science and Technology Research Project of Heilongjiang Education Department (No. 12521015) and the Research Science Foundation in Technology Innovation of Harbin (2012RFXXN002).

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