Notes

The crystal structure of dimethyl 4-methoxy-2,3,5,6tetrachlorophenyl phosphate

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The crystal structure of dimethyl 4-methoxy-2,3,5,6-tetrachlorophenyl phosphate was determined by X-ray analysis. It crystallized in the space group $P2_1/c$ (#14) with a = 9.446(2), b = 11.977(2), c = 12.306(2) Å, $\beta = 96.55(1)^\circ$, V = 1383.1(4) Å³, $D_{calc} = 1,665$ 5/cm³, and Z = 4.

KEY WORDS: Chloranil; phosphite; phosphate; hydroquinone.

Introduction

It is well known that the reaction of triisopropyl phosphite with chloranil afforded the corresponding benzoquinone (1), while the reaction of trimethyl phospite or triethyl phospite with chloranil gave hydroquinone monoalkyl ether (2) or (3) (Scheme 1).¹ The reaction difference between the two phosphites has been explained by the fact that the attack of the bulky tetrachlorophenoxide ion on a secondary carbon would be more difficult than on a primary carbon.^{1c} However, the real structure of 2 has not



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Fig. 1. Molecular structure of **2.**2

been previously disclosed. Herein, we wish to report the X-ray crystal structure of **2**.

 Table 1. Crystal data and summary of intensity data collection and structure refinement

Empirical formula	$C_9H_9Cl_4O_5P$
CCDC deposit no.	CCDC-1003/5550
Formular weight	369.95
Crystal color, habit	colorless, prismatic
Crystal Dimensions	$0.20 \times 0.20 \times 0.30 \text{ mm}$
Crystal system	monoclinic
Lattice type	Primitive
Lattice parameters	
a, Å	9.446(2)
b, Å	11.977(2)
<i>c</i> , Å	12.306(2)
β , °	96.55(1)
$V, Å^3$	1383.1(4)
Space group	P2 ₁ /c (#14)
Z value	4
$D_{ m calc}$	1.776 g/cm ³
$F_{(000)}$	744.00
μ (MoK α)	9.80 cm ⁻¹
Diffractometer/scan	Rigaku AFC7R
Radiation, graphite monochromator	$MoK\alpha \ (\lambda = 0.71069 \text{ Å})$
Temperature	20.0°C
$2\theta_{\rm max}$	50.0°
Scan width	$(1.78 + 0.30 \tan \theta)^{\circ}$
ρ-factor	0.03
Residuals: R ; R_w	0.032; 0.045

Atom	x	у	z	$B_{ m eq}{}^a$	
C1(1)	0.51115(7)	0.45844(6)	0.23921(6)	3.91(2)	
C1(2)	0.56216(8)	0.22029(6)	0.14516(6)	3.88(2)	
C1(3)	0.85745(8)	0.40335(6)	-0.15730(5)	3.54(2)	
C1(4)	0.82154(8)	0.64000(6)	-0.05384(6)	3.91(2)	
P(1)	0.86705(7)	0.14174(5)	-0.00129(5)	2.84(1)	
O(1)	0.6412(2)	0.6399(1)	0.1265(2)	3.57(4)	
O(2)	0.7306(2)	0.2194(1)	-0.0413(1)	2.81(4)	
O(3)	0.9324(2)	0.1687(2)	0.1072(1)	3.99(4)	
O(4)	0.8063(2)	0.0235(2)	-0.0255(2)	4.15(5)	
O(5)	0.9724(2)	0.1547(2)	-0.0894(1)	3.46(4)	
C(1)	0.6683(2)	0.5363(2)	0.0872(2)	2.75(5)	
C(2)	0.6101(2)	0.4421(2)	0.1311(2)	2.66(5)	
C(3)	0.6326(2)	0.3366(2)	0.0891(2)	2.53(5)	
C(4)	0.7129(2)	0.3245(2)	0.0026(2)	2.50(5)	
C(5)	0.7688(3)	0.4178(2)	-0.0438(2)	2.53(5)	
C(6)	0.7484(3)	0.5235(2)	-0.0002(2)	2.72(5)	
C(7)	0.7476(4)	0.6797(3)	0.2111(3)	4.30(8)	
C(8)	0.7157(4)	-0.0340(3)	0.0432(4)	4.85(9)	
C(9)	0.9335(4)	0.1223(3)	-0.2013(3)	4.29(8)	
H(1)	0.751(4)	0.629(3)	0.273(3)	5.4(8)	
H(2)	0.834(4)	0.683(3)	0.179(3)	6.9(10)	

Table 2. Atomic coordinates and B_{iso}/B_{eq}

$^{a}B_{\mathrm{eq}}$	=	$\frac{8}{3}$	$\pi^2(U_{11})$	$(aa^*)^2 +$	$U_{22}(l)$	$(bb^*)^2 +$	$U_{33}(cc^*)^2$	+	$2U_{12}aa*bb*$
cos	γ.	+	$2U_{13}aa^*$	$cc^* \cos$	$\beta + 2$	$U_{23}bb*c$	$c^* \cos \alpha$).		

0.755(3)

0.008(3)

0.005(4)

0.156(4)

0.043(3)

0.146(3)

-0.100(4)

0.227(3)

0.111(3)

0.023(4)

0.031(4)

-0.232(4)

-0.207(3)

-0.237(3)

6.1(8)

6.9(9)

7(1)

9(1)

6.8(10)

6.4(10)

11(1)

Experimental

Compound **2** was obtained from the reaction of trimethyl phosphite (1.0 g, 8.2 mmol) with chloranil (2.0 g, 8.2 mmol) in benzene under reflux for 4 h. After the benzene was removed under reduced pressure, **2** was obtained as a colorless solid m.p. 92–94°C; UV (MeCN) $\lambda_{\text{max}} = 276 \text{ nm}$ ($\epsilon = 1120 \text{ dm}^3 \text{ mol}^{-1}$ cm⁻¹); IR (KBr) ν 1290 cm⁻¹ (P=O); δ_{H} (CDCl₃) 3.90 (3H, *s*, Me), 3.98 (6H, d, *J* 11.7 Hz, OMe); δ_{c} (CDCl₃) 55.60, 55.66, 60.82, 126.36, 126.40, 128.04, 142.05, 142.12, 151.322; δ_{P} (CDCl₃, 85% H₃PO₄)—4.46; MS (FAB) *m*/*z* 371 (M⁺ + 1); (Found: C, 29.24; H, 2.40. Calc. for C₉H₉Cl₄O₅P requires C, 29.22; H, 2.45%).

The melting point was obtained with a Yanagimoto micro melting point apparatus and is uncorrected. ¹H and ¹³C nmr spectra were determined for a solution in CDCl₃ with tetramethylsilane as an internal standard on a JNM-GX 270 spectrometer. The ³¹P nmr spectrum was recorded on the same spectrometer using 85% H₃PO₄ as an external standard. The mass spectrum was recorded with a JMS D-300 instrument. CHN microanalysis was carried out with a Perkin-Elmer Model 240 analyzer.

A single crystal of this compound could be obtained by recrystallization from ethyl acetate and hexane (1:1). The X-ray crystal structure of **2** is shown in Fig. 1 and the X-ray data are summarized in Table 1. Atomic coordinates are given in Table 2.

Results

H(3)

H(4)

H(5)

H(6)

H(7)

H(8)

H(9)

0.717(4)

0.765(4)

0.640(5)

0.722(5)

0.852(6)

0.935(4)

0.997(4)

Compound **2** was readily synthesized by the reaction of chloranil with trimethyl phosphite in benzene under reflux and was readily characterized by ¹H nmr, ¹³C nmr, ³¹P nmr, mass spectroscopy, and microanalysis.

The C-C bond lengths of the six-membered ring are essentially equivalent (1.383-1.390 Å) and the benzene ring is completely planar. The bond lengths of C1-O1 and C4-O2 are 1.367 and 1.388 Å, respectively. They are the C-O single bonds.

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The four Cl atoms are located at the 2,3,5,6-position of the benzene ring and the methoxy group and phosphate group are on the 1,4-positions, respectively. All of the bond lengths and bond angles are normal. Thus, the structure of $\mathbf{2}$ was clearly elucidated by X-ray analysis.

References

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