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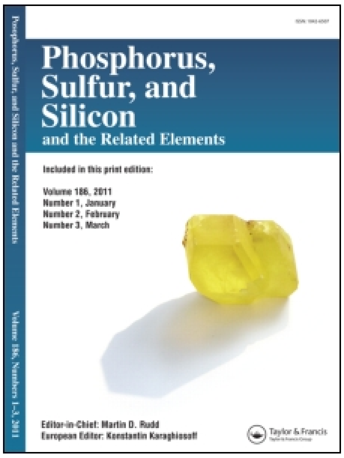

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STEREOCHEMISTRY OF THE REACTION OF α,α-DIBROMOKETONES WITH ETHYL DIPHENYLPHOSPHINITE. MOLECULAR STRUCTURE OF O-(1-PHENYL-2-BROMOVINYL)DIPHENYLPHOSPHINATE

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STEREOCHEMISTRY OF THE REACTION OF α,α-DIBROMOKETONES WITH ETHYL DIPHENYLPHOSPHINITE. MOLECULAR STRUCTURE OF O-(1-PHENYL-2-BROMOVINYL)DIPHENYLPHOSPHINATE

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This paper is dedicated to the memory of James Van der Veen.

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The reaction of α,α-dibromoacetophenone (**1**) with ethyl diphenylphosphinite (**2**) gives solid O-(1-phenyl-2-bromovinyl)diphenylphosphinate (**3**) as one stereoisomeric product. The stereochemistry of **3** is shown to be the **Z** configuration by single crystal X-ray analysis. A **Z** configuration for **3** had been predicted based on the postulated mechanism for its formation featuring nucleophilic attack on bromine by the phosphinite to give an enolate phosphonium ion-pair which then interacts further. Several lines of evidence link this demonstrated stereochemistry for **3** with a **Z** configuration for the major stereoisomeric enol phosphate formed in the Perkow reaction of several α-haloketones with trialkyl phosphites. **Z** Configurations for two different crystalline enol phosphates have been demonstrated *via* X-ray analysis by Zwierzak and by Rohrbaugh and Jacobson, respectively.

Key words: Stereochemistry; Perkow reaction; enol phosphinate; bromophilic attack.

INTRODUCTION

The reaction of trialkyl phosphites with α,α-dihaloketones often gives enol phosphates in a more stereoselective manner than do α-haloketones in the Perkow

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‡ Deceased August 4, 1986.

reaction.[1-3] In the dihaloketone reactions, one isomeric enol phosphate may be the exclusive product or nearly so. One of us has previously postulated that these reactions occur *via* abstraction of positive halogen (usually bromine rather than chlorine) by the phosphite to give the more stable enolate halophosphonium ion-pair which then interacts to give an enol phosphonium salt. The enol phosphonium salt finally proceeds to the product enol phosphate.[4]

A key point in all of the reactions involving halophilic attack is the stereochemistry of the predominant, or exclusive, enol phosphate that is formed. It is predicted to have the **Z** configuration as shown in Figure 1, which follows in the Results and Discussion section. These major isomeric enol phosphates were assigned the **Z** configuration by the application of ^{1}H NMR lanthanide induced shifts,[2] nuclear Overhauser effects,[2] and an analysis of $^4J_{PH}$ NMR coupling constants.[5] Since most enol phosphates are liquids, we set out to prepare a crystalline enol phosphorylated compound whose stereochemistry could be unambiguously determined by single crystal X-ray analysis. Such an enol phosphinate was prepared in 1972 and its stereochemistry was correlated with that of the major enol phosphate formed in Perkow reactions.[2] Its X-ray structure is presented here. The structure was determined by J. Van der Veen in 1973 but not fully analyzed before his untimely death.[6] During the ensuing years, the single crystal X-ray and molecular structures of two crystalline enol phosphates, resulting from Perkow reactions on α,α-dihaloketones, have been determined to have the **Z** configuration.[7,8]

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RESULTS AND DISCUSSION

The reaction of α,α-dibromoacetophenone (**1**) with ethyl diphenylphosphinite (**2**) gives O-(1-phenyl-2-bromovinyl)diphenylphosphinate (**3**) as one stereoisomeric, crystalline product.[4] The enolate mechanism predicts **Z** stereochemistry for **3**, as shown in Figure 1, because the more stable enolate precursor should have phenyl and bromine groups located *trans* to each other.

We now report that X-ray structural studies clearly indicate that **3** indeed has the **Z** configuration and by the connectivity established using lanthanide induced shifts and nuclear Overhauser effect data,[2] so does the 2-chloroenol phosphinate major isomer (**Z-4**). Since **Z-4** was previously correlated with the corresponding 2-chloroenol phosphate major isomer,[2] the configuration of the latter is also proven

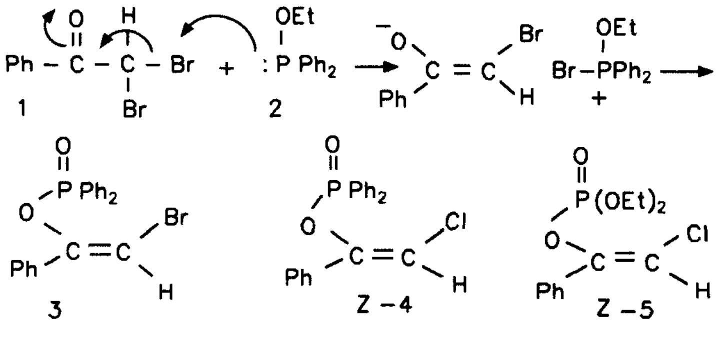

FIGURE 1 The Bromophilic attack pathway.

TABLE I

Final positional parameters ($\times 10^4$) with estimated standard deviations in the last figure in parentheses

Atom	x	y	z
Br(1)	4644(1)	6022.5(3)	2453(1)
P(1)	7078(2)	4315(1)	2621(1)
O(1)	5296(4)	4431(2)	2161(3)
O(2)	7480(4)	4320(2)	4006(3)
C(1)	3898(7)	5238(3)	3252(5)
C(2)	4283(6)	4572(3)	3053(5)
C(3)	3594(6)	3953(3)	3623(5)
C(4)	2787(8)	4030(3)	4667(6)
C(5)	2142(8)	3449(4)	5198(7)
C(6)	2290(8)	2792(4)	4689(7)
C(7)	3060(7)	2700(3)	3633(7)
C(8)	3721(7)	3274(4)	3115(6)
C(9)	7456(6)	3487(3)	1869(5)
C(10)	8760(7)	3123(4)	2368(5)
C(11)	9142(8)	2491(3)	1843(6)
C(12)	8288(8)	2220(3)	814(6)
C(13)	7005(8)	2582(4)	305(6)
C(14)	6608(7)	3209(4)	825(5)
C(15)	8010(6)	4992(3)	1802(5)
C(16)	7522(7)	5197(3)	590(6)
C(17)	8340(8)	5686(4)	-012(6)
C(18)	9652(7)	5977(3)	601(7)
C(19)	10132(7)	5778(4)	1790(7)
C(20)	9342(7)	5294(3)	2405(5)

TABLE II

Final temperature parameters ($\times 10^3$) with estimated standard deviations in the last figure in parentheses. The form of the temperature factor expression is: $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{23}klb^*c^*)]$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br(1)	61.2(5)	41.0(4)	67.6(5)	1.9(3)	15.8(4)	10.9(3)
P(1)	26.7(7)	33.6(8)	26.4(7)	2.8(7)	4.2(6)	-2.5(6)
O(1)	25(2)	46(2)	30(2)	-1(2)	5(2)	-1(2)
O(2)	39(2)	49(3)	29(2)	8(2)	5(2)	-8(2)
C(1)	38(4)	38(3)	39(3)	2(3)	10(3)	8(3)
C(2)	21(3)	43(4)	33(3)	-2(3)	-1(2)	4(3)
C(3)	24(3)	39(3)	40(3)	3(3)	-6(3)	0(3)
C(4)	48(4)	56(4)	39(4)	-12(3)	11(3)	-4(3)
C(5)	61(5)	68(6)	56(5)	-21(4)	15(4)	4(4)
C(6)	44(4)	61(5)	76(5)	-13(4)	-2(4)	12(4)
C(7)	41(4)	41(4)	76(5)	4(3)	-1(4)	-8(3)
C(8)	43(4)	43(4)	56(4)	2(3)	9(3)	1(3)
C(9)	29(3)	35(3)	32(3)	3(3)	9(3)	0(3)
C(10)	46(4)	47(4)	34(3)	6(3)	3(3)	-3(3)
C(11)	55(4)	46(4)	47(4)	17(3)	8(3)	-2(3)

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TABLE II (*Continued*)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(12)	64(5)	44(4)	52(4)	6(4)	20(4)	-11(3)
C(13)	46(4)	78(5)	47(4)	-1(4)	0(3)	-23(4)
C(14)	38(4)	61(4)	39(3)	9(3)	-1(3)	-10(3)
C(15)	27(3)	36(3)	32(3)	2(3)	6(3)	2(3)
C(16)	44(4)	47(4)	43(4)	-3(3)	2(3)	5(3)
C(17)	63(5)	51(4)	51(4)	8(4)	17(4)	22(4)
C(18)	41(4)	46(4)	88(5)	0(3)	28(4)	6(3)
C(19)	32(4)	59(4)	87(5)	-9(3)	0(4)	1(4)
C(20)	38(4)	49(4)	46(4)	-2(3)	-1(3)	3(3)

TABLE III

Positional coordinates ($\times 10^3$) and isotropic temperature factors ($\times 10^2$) for hydrogen atoms, together with C-H distances in Å. Hydrogen atoms are bonded to a carbon atom with the same number.

Atom	x	y	z	U	Bond Length
H(1)	331(7)	539(3)	375(6)	6(2)	0.83
H(4)	254(8)	438(3)	498(6)	2(2)	0.78
H(5)	155(7)	360(3)	604(5)	6(2)	1.12
H(6)	179(7)	241(3)	507(5)	6(2)	0.96
H(7)	299(8)	229(4)	312(7)	9(2)	0.94
H(8)	406(7)	325(3)	241(5)	5(2)	0.83
H(10)	923(8)	316(4)	314(6)	7(2)	0.88
H(11)	1007(8)	209(4)	229(6)	8(2)	1.17
H(12)	859(7)	183(3)	53(5)	4(2)	0.85
H(13)	639(6)	240(3)	-55(5)	5(1)	1.06
H(14)	582(6)	343(3)	44(5)	5(3)	0.88
H(16)	666(6)	498(3)	14(5)	5(2)	0.94
H(17)	812(5)	578(3)	-84(4)	4(2)	0.89
H(18)	1036(7)	631(3)	49(6)	9(3)	0.91
H(19)	1110(7)	602(3)	230(5)	6(2)	1.07
H(20)	965(7)	529(3)	313(5)	2(1)	0.78

TABLE IV

Bond lengths and valency angles for non-hydrogen atoms, with estimated standard deviations in parentheses

(a) Bond lengths

Br(1)-C(1)	1.856(11)	C(9)-C(10)	1.39(2)
		C(10)-C(11)	1.37(1)
P(1)-O(1)	1.61(2)	C(11)-C(12)	1.35(2)
P(1)-O(2)	1.47(1)	C(12)-C(13)	1.38(2)
P(1)-C(9)	1.80(1)	C(13)-C(14)	1.36(1)
P(1)-C(15)	1.79(1)	C(14)-C(9)	1.37(2)

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TABLE IV (*Continued*)

(a) Bond lengths

C(1)-C(2)	1.32(1)	C(15)-C(16)	1.36(1)
C(2)-O(1)	1.40(2)	C(16)-C(17)	1.37(1)
C(2)-C(3)	1.47(1)	C(17)-C(18)	1.38(2)
		C(18)-C(19)	1.33(2)
C(3)-C(4)	1.39(2)	C(19)-C(20)	1.36(1)
C(4)-C(5)	1.38(1)	C(20)-C(15)	1.40(2)
C(5)-C(6)	1.36(1)		
C(6)-C(7)	1.38(2)		
C(7)-C(8)	1.37(1)		
C(8)-C(3)	1.39(1)		

(b) Valency angles

Br(1)-C(1)-C(2)	124.7(5)	P(1)-C(9)-C(10)	116.4(4)
C(2)-O(1)-P(1)	120.2(3)	P(1)-C(9)-C(14)	125.1(4)
O(1)-P(1)-O(2)	114.9(2)	P(1)-C(15)-C(16)	122.6(4)
O(1)-P(1)-C(9)	102.0(2)	P(1)-C(15)-C(20)	118.7(4)
O(1)-P(1)-C(15)	104.2(2)		
O(2)-P(1)-C(9)	114.2(2)	C(14)-C(9)-C(10)	118.4(5)
O(2)-P(1)-C(15)	113.7(2)	C(9)-C(10)-C(11)	120.3(5)
C(9)-P(1)-C(15)	106.6(3)	C(10)-C(11)-C(12)	120.7(6)
C(1)-C(2)-O(1)	119.0(5)	C(11)-C(12)-C(13)	119.3(6)
C(3)-C(2)-O(1)	116.8(5)	C(12)-C(13)-C(14)	120.5(6)
C(1)-C(2)-C(3)	123.9(5)	C(13)-C(14)-C(9)	120.8(6)
C(2)-C(3)-C(4)	121.0(5)	C(20)-C(15)-C(16)	118.6(5)
C(2)-C(3)-C(8)	120.8(5)	C(15)-C(16)-C(17)	119.8(6)
C(8)-C(3)-C(4)	118.1(6)	C(16)-C(17)-C(18)	120.6(6)
C(3)-C(4)-C(5)	120.9(6)	C(17)-C(18)-C(19)	119.7(6)
C(4)-C(5)-C(6)	119.8(7)	C(18)-C(19)-C(20)	120.7(6)
C(5)-C(6)-C(7)	120.7(7)	C(19)-C(20)-C(15)	120.6(5)
C(6)-C(7)-C(8)	119.6(6)		
C(7)-C(8)-C(3)	120.9(6)		

to be **Z** and the major isomer is labeled **Z-5**. Similar correlations confirm the **Z** configuration for enol phosphate major isomers produced by the Perkow reaction.[2]

X-ray structural data for compound **3** are listed in Tables I–III. These data include final positional parameters for nonhydrogen atoms with estimated standard deviations (Table I), final temperature parameters for these atoms (Table II), and positional coordinates for hydrogen atoms and C-H distances in Å (Table III). Bond lengths and angles are given in Table IV. The ORTEP drawing of the molecule is presented in Figure 2. The geometry found is unexceptional. Double bond character for P-O(2) is indicated by the reduced bond length compared with the P(1)-O(1) distance and by increased angles at P(1). The geometry of the phenyl groups is that of a regular hexagon except for a slight reduction in the ring angle at the point of attachment to the rest of the molecule. None of the ring atoms deviate from their mean plane by more than 0.01 Å. The shortest intermolecular

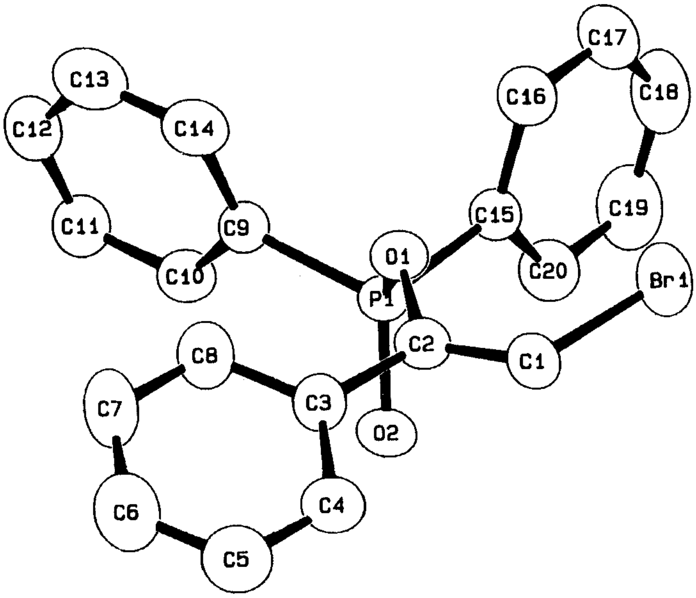

FIGURE 2 ORTEP drawing of O-(1-phenyl-2-bromovinyl)diphenylphosphinate, (**3**).

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contacts are 3.37 Å and 3.42 Å between O(2) and atoms C(1) and C(4) in a molecule related by an inversion center. The dihedral angle for P-O-C(2) = C(1) in **3** is found to be 97.3° in the solid phase. This is in agreement with the gauche angles of 80–120° calculated for a series of enol phosphates in the liquid phase from the $^4J_{PH}$ proton NMR values[5] and CNDO/2 calculations[9] by Gaydou.

EXPERIMENTAL

Preparation and X-Ray Structure Analysis: O-(1-Phenyl-2-Bromovinyl)diphenylphosphinate (**3**). The preparation of **3** from α,α-dibromoacetophenone (**1**) and ethyl diphenylphosphinite (**2**) has been described previously.[4] Product **3** was recrystallized twice from diethyl ether-petroleum ether (30–60° bp range) to give monoclinic crystals, mp 104–104.5°.

Crystal Data. $C_{20}H_{16}BrO_2P$, M = 399.21. Monoclinic, a = 8.853(4) Å, b = 18.799(10) Å, c = 10.554(4) Å, β = 96.34(3)°, V = 1746(1) Å^3. D_x = 1.519 g.cm^{-3}, Z = 4, F(000) = 872. Space Group $P2_1/c$. MoKα radiation, λ = 0.7107 Å.

Three-dimensional intensity data were recorded on a Syntex $P2_1$ four-circle computer-controlled automatic diffractometer using graphite monochromatized MoKα radiation; accurate cell dimensions were determined by a least squares fit of the 2θ values for 15 accurately-centered medium-angle reflections. Intensity data were recorded at ambient temperatures by the θ-2θ scan technique out to a maximum of 2θ = 60°, using standard techniques.[10] A total of 4137 reflections were measured, of which 2298 were considered above background.

Data were processed and the structure solved and refined with programs in the Stewart Xray72 package. In the final model, the carbon, oxygen, phosphorus and bromine atoms were refined anisotropically and the hydrogen atoms were refined isotropically, with a total of 282 parameters varied. The final value of R was 0.072.[11]

ACKNOWLEDGEMENTS

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