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Synthesis and Crystal Structure of Stable Oxyphosphoranes

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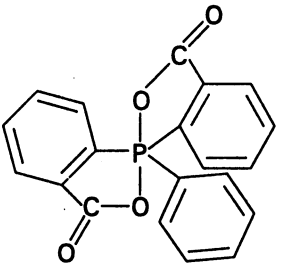
Exceptionally stable spiro cyclicoxyphosphoanes were prepared by potassium permanganate oxidation of bis(*o*-tolyl)phenylphosphine oxide followed by acidification probably involving nucleophilic attack by phosphine oxygen atom on a carboxylic carbonyl group. And its structure was determined by single-crystal X-ray diffraction.

Key Words: Spiro cyclicoxyphosphoanes, Nuclephilic attack, Crystal structure.

INTRODUCTION

Nucleophilic attack of a phosphine oxide oxygen atom on the carbonyl group of acetic anhydride followed by formation of an unstable oxyphosphorane has been postulated to account for the racemization of optically active phosphine oxides[1,2]. Relatively stable spirocyclic oxyphosphoranes have been reported through the ^{31}P NMR analysis earlier[3,4], but its crystal structure has never been reported. This paper deals with a novel synthesis of exceptionally stable spiro cyclicoxyphosphoranes involving a similar mechanism.

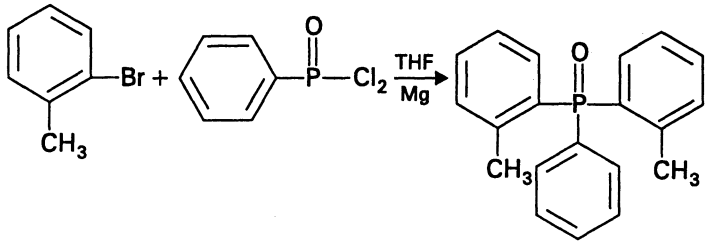


EXPERIMENTAL

Synthesis of bis(o-tolyl)phenyl phosphine oxide

To a magnetically stirred suspension 5.1 g (0.43 mol) of magnesium turnings in 100 mL of dry THF was added dropwise at a rate sufficient to maintain gentle reflux a solution of 37.5 g (0.22 mol) of 2-bromotoluene in 100 mL of dry THF. After the addition was complete, the reaction mixture was refluxed for 2 h, and cooled to 25°C, and to this dark brown reaction mixture was added dropwise a

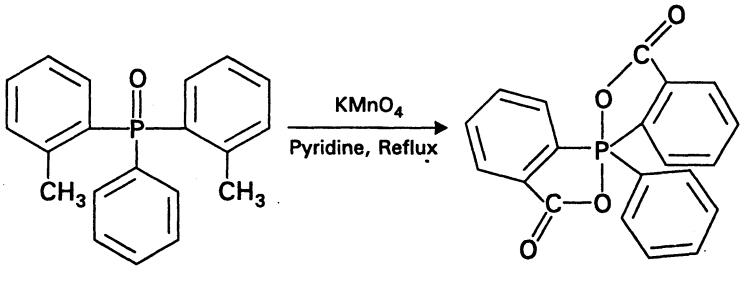
solution of 21.3 g (0.11 mol) of phenylphosphonic dichloride in 100 mL of dry THF. After the addition was complete, the reaction mixture was refluxed for 2 h, stirred at 25°C for 12 h, and poured into an ice-cold aqueous ammonium chloride solution. The resulting white precipitate was collected and recrystallized from THF + ether; m.p.: 82–85 °C; ^{1}H NMR ($CDCl_3$) δ 6.8–7.8 (m, ArH, 13H) and 2.5 (s, $ArCH_3$, 6H).



Synthesis of the stable oxyphosphoranes[5]

In a dry 150 mL flask, 5.0 g bis(*o*-tolyl)phenyl phosphine oxide was dissolved in 25 mL pyridine and 50 mL water. 25 g $KMnO_4$ was added in batches; the mixture was heated at reflux temperature for 6 h and was slowly cooled down, washed withEtOAC (25 mL × 2), concentrated, acidified to around pH = 2 with dense hydrochloride acid to give a white precipitate, filtered, washed with water to give a white solid in 45% total yield; m.p. 218–220°C; ^{1}H NMR ($CDCl_3$) : δ 8.2–8.60 (t, ArH, 2H), δ (8.17–8.22), (t, 2H), δ (7.84–7.90) (t, 6H), δ (7.34–7.78) (t, 4H). ^{13}C NMR, δ 127.03, 127.33, 128.35, 128.69, 131.58, 131.79, 131.87, 132.17, 134.28, 134.57, 134.72, 135.21, 135.28, 136.11, 136.29, 136.74, 137.10.

Anal. calcd. (%) for $C_{20}H_{13}O_4P$: C = 68.47, H = 3.72; Found (%): C = 68.47, H = 3.72.



Structure determination

A colourless and block monoclinic crystal of the title compound with approximate dimensions of 0.50 × 0.20 mm × 0.20 mm was selected for data collection on a Bruker Smart diffractometer with graphite monochromated M_0K_α radiation (λ = 0.71073 Å). A total of 7564 reflections were collected in the range of $2.52° < \theta < 27.48°$ by using "phi and omega" scans technique at 293(2) K, of which 3733 independent reflections were unique for 12221 reflections observed, R_{int} = 0.0409, LP corrections were applied to the data.

The structure was solved by direct methods and difference Fourier map techniques by using Bruker SMART Program, and refinement on F^2 was performed using Bruker Smart program by full-matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen positions were located in calculation positions antisotropically refined. The refinement converged to final R = 0.0372, wR = 0.0658, $(\Delta/\sigma)_{max}$ = 0.001, $(\Delta/\sigma)_{mean}$ = 0.000, and the minimum peak is 0.224 e/Å^3. The maximum peak in the final difference Fourier map is 0.179 e/Å^3. Molecular graphics were drawn with the program package SHELXTL 97[6].

RESULTS AND DISCUSSION

In the title compound $C_{20}H_{13}O_4P$, atom P is located at the centre, it is connected with three phenyl and two oxygen atoms from the carboxylic carbonyl group, P(1)-O(3), P(1)-O(1), P(1)-C(10), P(1)-C(15), P(1)-C(7) are as expected for [1.899(2) Å], [1.910 Å], [1.802(2) Å], [1.804(2) Å], [1.801(2) Å]. One of the dimensions of phenyl ring C(2) ~ C(7) distances ranging from 1.378(2) ~ 1392(2) Å, C—C—C angle (113.0 ~ 121.5°), the distances and the angles of other two phenyls are similar. These three aromatic rings in the molecule do not show any unusual features and the bond angles and lengths are within the range of normal values. The angle of O(1)-P(1)-C(7) and O(3)-P(1)-C(10); O(3)-P(1)-C(15) and O(1)-P(1)-C(15); C(1)-O(1)-P(1) and C(8)-O(3)-P(1) are similar, they are 88.28(7), 88.03(7), 90.66(6), 90.02(6), 116.06(10), 116.09(10), respectively. The final atomic coordinates and thermal parameters are listed in Table-1, and the selected bond lengths and bond angles in Tables 2 and 3. Their molecular structures are shown in Figs. 1 and 2, respectively.

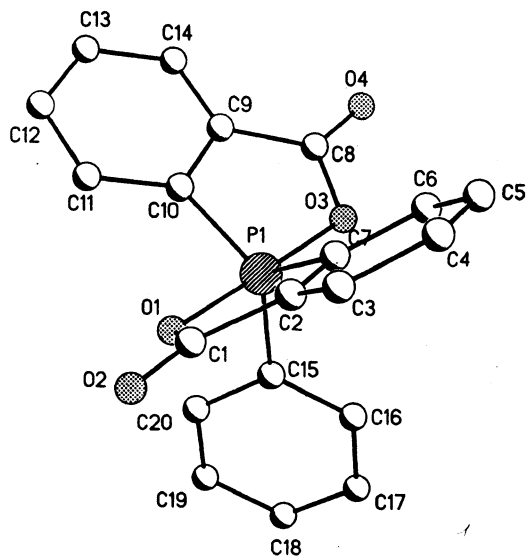


Fig. 1. The molecular structure of $C_{20}H_{13}O_4P$

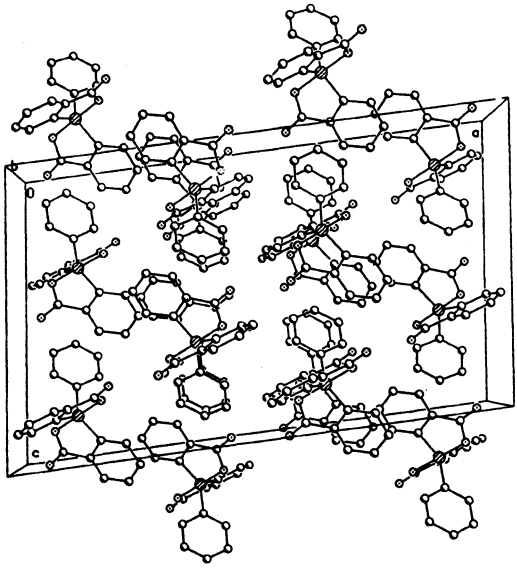


Fig. 2. The packing diagram of the unit cell

TABLE-1
ATOMIC COORDINATES (X 10^4) AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS ($A^2 \times 10^3$) FOR $C_{20}H_{13}O_4P$

atom	x	y	z	U (eq)	atom	x	y	z	U (eq)
P (1)	3741 (1)	501 (1)	6555 (1)	39 (1)	C (9)	3538 (1)	-1048 (2)	5047 (1)	43 (1)
O (1)	3232 (1)	1614 (1)	6973 (1)	45 (1)	C (10)	3289 (1)	-110 (2)	5612 (1)	42 (1)
O (2)	3027 (1)	3994 (2)	7422 (1)	58 (1)	C (11)	2755 (1)	263 (2)	5400 (1)	58 (1)
O (3)	4247 (1)	-601 (1)	6124 (1)	44 (1)	C (12)	2484 (1)	-324 (3)	4623 (1)	67 (1)
O (4)	4417 (1)	-2056 (2)	4976 (1)	64 (1)	C (13)	2738 (1)	-1249 (3)	4068 (1)	69 (1)
C (1)	3335 (1)	3129 (2)	7111 (1)	43 (1)	C (14)	3265 (1)	-1628 (2)	4277 (1)	60 (1)
C (2)	3859 (1)	3545 (2)	6838 (1)	40 (1)	C (15)	3797 (1)	-716 (2)	7527 (1)	37 (1)
C (3)	4071 (1)	5033 (2)	6854 (1)	54 (1)	C (16)	4280 (1)	-920 (2)	8051 (1)	49 (1)
C (4)	4561 (1)	5241 (2)	6561 (1)	60 (1)	C (17)	4314 (1)	-1868 (2)	8790 (1)	62 (1)
C (5)	4828 (1)	3983 (2)	6260 (1)	54 (1)	C (18)	3873 (1)	-2644 (2)	8991 (1)	67 (1)
C (6)	4619 (1)	2489 (2)	6247 (1)	46 (1)	C (19)	3393 (1)	-2451 (2)	8473 (1)	65 (1)
C (7)	4124 (1)	2272 (2)	6536 (1)	37 (1)	C (20)	3350 (1)	-1467 (2)	7753 (1)	49 (1)
C (8)	4106 (1)	-1312 (2)	5352 (1)	46 (1)					

TABLE-2
BOND LENGTHS [A] FOR $C_{20}H_{13}O_4P$

Bond	Distance (Å)	Bond	Distance (Å)	Bond	Distance (Å)
P (1)-O (3)	1. 7805 (11)	C (1)-C (2)	1. 480 (2)	C (12)-C (13)	1. 376 (3)
P (1)-O (1)	1. 7829 (11)	C (2)-C (3)	1.381 (2)	C (13)-C (14)	1. 370 (2)
P (1)-C (7)	1. 8006 (17)	C (2)-C (7)	1. 388 (2)	C (15)-C (20)	1. 380 (2)
P (1)-C (10)	1. 8024 (17)	C (5)-C (6)	1. 380 (2)	C (15)-C (16)	1. 388 (2)
P (1)-C (15)	1. 8039 (16)	C (6)-C (7)	1. 392 (2)	C (16)-C (17)	1. 384 (2)
O (1)-C (1)	1. 335 (2)	C (8)-C (9)	1. 472 (2)	C (17)-C (18)	1. 366 (3)
O (2)-C (1)	1. 2118 (18)	C (9)-C (10)	1. 384 (2)	C (18)-C (19)	1. 376 (3)
O (3)-C (8)	1. 3360 (19)	C (10)-C (11)	1. 388 (2)	C (19)-C (20)	1. 378 (2)
O (4)-C (8)	1. 2144 (19)	C (11)-C (12)	1. 389 (2)		

TABLE-3
BOND ANGLES [DEG] FOR $C_{20}H_{13}O_4P$

Angle	(o)	Angle	(o)	Angle	(o)
O (3)-P(1)-O(1)	179.29(6)	C(3)-C(2)-C(1)	125.24(16)	C(9)-C(10)-P(1)	111.96(12)
O(3)-P(1)-C(7)	91.54(7)	C(7)-C(2)-C(1)	113.01(15)	C(11)-C(10)-P(1)	128.55(14)
O(1)-P(1)-C(7)	88.28(7)	C(4)-C(3)-C(2)	118.48(17)	C(10)-C(11)-C(12)	118.67(18)
O(3)-P(1)-C(10)	88.03(7)	C(3)-C(4)-C(5)	120.30(18)	C(13)-C(12)-C(11)	121.06(18)
O(1)-P(1)-C(10)	91.47(7)	C(4)-C(5)-C(6)	121.54(17)	C(14)-C(13)-C(12)	120.45(19)
C(7)-P(1)-C(10)	121.32(7)	C(5)-C(6)-C(7)	118.49(16)	C(13)-C(14)-C(9)	118.91(18)
O(3)-P(1)-C(15)	90.66(6)	C(2)-C(7)-C(6)	119.45(15)	C(20)-C(15)-C(16)	119.14(16)
O(1)-P(1)-C(15)	90.02(6)	C(2)-C(7)-P(1)	111.87(12)	C(20)-C(15)-P(1)	119.45(13)
C(7)-P(1)-C(15)	120.78(7)	C(6)-C(7)-P(1)	128.66(13)	C(16)-C(15)-P(1)	121.41(13)
C(10)-P(1)-C(15)	117.90(8)	O(4)-C(8)-O(3)	122.55(16)	C(17)-C(16)-C(15)	120.37(17)
C(1)-O(1)-P(1)	16.06(10)	O(4)-C(8)-C(9)	126.67(17)	C(18)-C(17)-C(16)	119.89(18)
C(8)-O(3)-P(1)	116.09(10)	O(3)-C(8)-C(9)	110.78(14)	C(17)-C(18)-C(19)	120.03(18)
O(2)-C(1)-O(1)	122.15(16)	C(14)-C(9)-C(10)	121.42	C(18)-C(19)-C(20)	120.56(18)
O(2)-C(1)-C(2)	127.13(17)	C(14)-C(9)-C(8)	125.47(16)	C(19)-C(20)-C(15)	119.93(17)
O(1)-C(1)-C(2)	110.72(14)	C(10)-C(9)-C(8)	113.10(15)		
C(3)-C(2)-C(7)	121.73(15)	C(9)-C(10)-C(11)	119.48(16)		

REFERENCES

1. B.Y. Segall and I. Granoth, *J.C.S. Chem. Comm.*, 399 (1975).
2. L. Horner and H. Winker, *Tetrahedron Letters*, 3271 (1964).
3. D.B. Denney and A.K. Tsolis, *J. Am. Chem. Soc.*, **86**, 4486 (1964).
4. D. Hellvinkel and W. Krapp, *Angew. Chem. Int. Edn.*, **13**, 542 (1974).
5. L.G. Kaplan, G.R. Weisman and D.J. Cram, *J. Org. Chem.*, 2226 (1979).
6. G.M. Sheldrick, Shelxs-97, Program for crystal structure solution, University of Gottingen, Germany (1990 and 1997).

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