A Novel Synthesis of 6-Hydroxyalkyl- and 6-Hydroxyaralkyl-6*H*-dibenz[*c*,*e*][1,2]oxaphosphorin 6-Oxides [1]

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A new strategy for the synthesis of 6-hydroxyalkyl- and 6-hydroxyaralkyl-6*H*-dibenz[*c*,*e*][1,2]oxaphosphorin 6-oxides **3** was achieved by the reaction of 2-(2-hydroxyphenyl)phenylphosphonic acid (**1**) with various carbonyl compounds **2**. The desired products **3** were obtained in acceptable yields.

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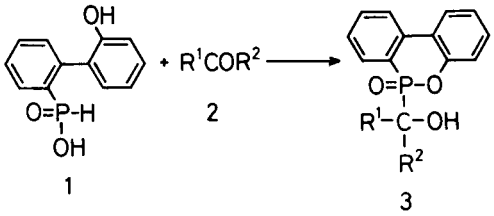
Cyclic organophosphorus compounds are useful intermediates in organic synthesis [2-6]. The synthesis of 6-hydroxyalkyl-6*H*-dibenz[*c*,*e*][1,2]oxaphosphorin 6-oxides **3**, a new class of compounds having stabilizing activity for organic polymers, from the reaction of 6*H*-dibenz[*c*,*e*][1,2]-oxaphosphorin 6-oxides and some carbonyl compounds has been disclosed in the patent literature [7-8]. No experimental details and physical data were given. Recently, similar reactions have appeared in the literature [9-10]. In connection with our synthetic studies using organophosphorus compounds, we have now developed a novel and convenient procedure for the synthesis of oxaphosphorin derivatives **3** from the reaction of 2-(2-hydroxyphenyl)-phenylphosphonic acid (**1**) with a variety of carbonyl compounds **2** without the presence of bases usually required.



1 3

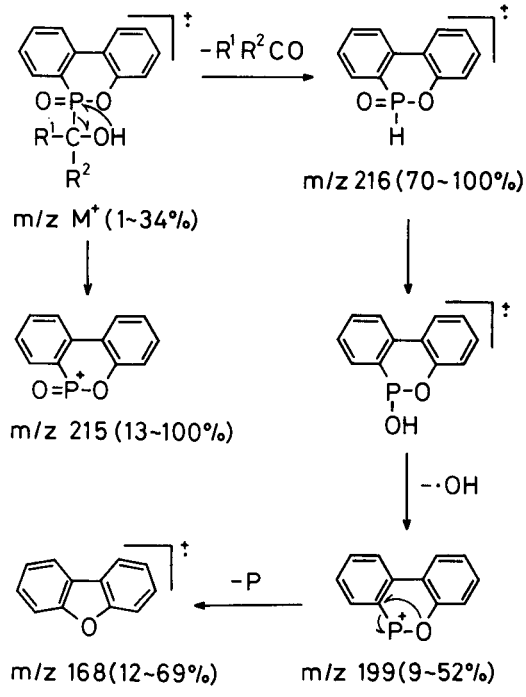
We report herein our results with complete experimental and physical data. The reaction was carried out by heating the phosphonic acid **1** with the appropriate carbonyl compound neat or in acetonitrile.

The reaction proceeds smoothly at 80°, and was complete within 0.5-3 hours with a few exceptions. Pure products **3** were obtained after three or four recrystallizations from suitable solvents. In general, aldehydes are more reactive than ketones in these reactions.

Exceptionally, in the synthesis of 6-hydroxymethyl-6*H*-dibenz[*c*,*e*][1,2]oxaphosphorin 6-oxide (**3aa**), a longer reaction time (heating for 9 hours) was required to achive satisfactory condensation because of a very low decomposition rate of paraformaldehyde to formaldehyde in acetonitrile.

A main limitation of the present procedure was observed. Four aliphatic ketones such as methyl isopropyl, methyl *t*-butyl, diisopropyl and diisobutyl ketones were completely inert even after a prolonged reaction period at reflux temperature of the ketone used. This would be attributed to the bulkiness of the alkyl group. In contrast, isobutyraldehyde, isovaleraldehyde and pivalaldehyde gave the desired products, **3ae**, **bb**, **bc**, in excellent yields, compared with the above mentioned four ketones.

Scheme



The oxaphosphorin structure assigned to the products **3** is based on analytical and spectroscopic data (Tables 1-6). The ir spectra of the products **3** investigated show the OH stretching vibration in the region between 3400-3050 cm^{-1}, a hydrogen-bonded P=O absorption band near 1200 cm^{-1} and P-O-C (aromatic) absorption band near 1220 cm^{-1}, respectively. The ^1H and ^{13}C nmr spectra clearly suggest the 6-substituted oxaphosphorin structure. The structure of **3**

Table 1

Physical, Analytical and High Resolution Mass Spectral Data for Products 3

Compound	R^1	R^2	Method	Crude Yield (%)	Mp (°C)	Recrystallization solvent	Formula	Analysis (%) Calcd. C	Calcd. H	Found C	Found H	HRMS(m/z) Calcd.	Found
3aa	H	H	C [a]	69	170-171	acetonitrile	$C_{13}H_{11}O_3P$	63.42	4.50	63.13	4.22	246.0445	246.0464
ab	CH_3	H	A [b]	90	195.5-197	acetonitrile	$C_{14}H_{13}O_3P$	64.61	5.03	64.56	5.06	260.0560	260.0591
ac	C_2H_5	H	A	78	163.5-164.5	acetonitrile	$C_{15}H_{15}O_3P$	65.69	5.51	65.29	5.78	274.0758	274.0774
ad	*n*-C_3H_7	H	A	81	150-152	acetonitrile	$C_{16}H_{17}O_3P$	66.66	5.94	66.25	5.87	288.0914	288.0874
ae	*i*-C_3H_7	H	A	94	152-155	acetonitrile	$C_{16}H_{17}O_3P$	66.66	5.94	66.27	5.91	288.0914	288.0891
ba	*n*-C_4H_9	H	A	40	106.5-108.5	ether/dioxane	$C_{17}H_{19}O_3P$	67.54	6.33	67.62	6.27	302.1070	302.1088
bb	*i*-C_4H_9	H	A	82	164-165.5	ether/hexane	$C_{17}H_{19}O_3P$	67.54	6.33	67.28	6.03	302.1070	302.1031
bc	*t*-C_4H_9	H	A	93	160-161.5	acetonitrile	$C_{17}H_{19}O_3P$	67.54	6.35	67.40	6.45	302.1070	302.1069
bd	*n*-C_5H_{11}	H	A	28	104-107	acetonitrile	$C_{18}H_{21}O_3P$	68.34	6.69	68.09	6.78	316.1226	316.1203
be	2-furyl	H	A	79	160.5-162.5	acetonitrile	$C_{17}H_{13}O_4P$	65.38	4.19	65.31	4.35	312.0551	312.0566
ca	2-thienyl	H	A	91	178.5-180.5	acetonitrile	$C_{17}H_{13}O_3PS$	62.18	3.99	61.93	3.82	328.0323	328.0352
cb	CH_3	CH_3	B [c]	73	181.5-182.5	chloroform	$C_{15}H_{15}O_3P$	65.69	5.51	65.66	5.53	274.0758	274.0831
cc	C_2H_5	CH_3	B	51	166.5-167.5	acetonitrile	$C_{16}H_{17}O_3P$	66.66	5.94	66.68	5.95	288.0914	288.0954
cd	*n*-C_3H_7	CH_3	B	64	159-160	acetonitrile	$C_{17}H_{19}O_3P$	67.54	6.33	67.63	6.12	302.1070	302.1002
ce	*n*-C_4H_9	CH_3	B	32	169-170.5	acetonitrile	$C_{18}H_{21}O_3P$	68.34	6.69	68.39	6.69	316.1227	316.1342
da	*i*-C_4H_9	CH_3	B	38	167-168.5	acetonitrile	$C_{18}H_{21}O_3P$	68.34	6.69	68.36	6.96	316.1227	316.1214
db	C_2H_5	C_2H_5	B	56	164.5-165	acetonitrile	$C_{17}H_{19}O_3P$	67.54	6.33	67.55	6.36	302.1070	302.1035
dc	*n*-C_3H_7	*n*-C_3H_7	B	53	161-162	acetonitrile	$C_{19}H_{23}O_3P$	69.07	7.01	69.09	6.71	330.1384	330.1418
dd	*n*-C_4H_9	*n*-C_4H_9	B	69	151-152	acetonitrile	$C_{21}H_{27}O_3P$	70.37	7.59	70.30	7.61	358.1696	358.1747
de	-$(CH_2)_4$-		B	65	186.5-187.5	dioxane	$C_{17}H_{17}O_3P$	67.99	5.70	67.75	5.78	300.0914	300.0955
ea	-$(CH_2)_5$-		B	97	192-193	acetonitrile	$C_{18}H_{19}O_3P$	68.78	6.09	68.60	5.89	314.1071	314.1113
eb	C_6H_5	H	A	96	196-196.5	acetonitrile	$C_{19}H_{15}O_3P$	70.80	4.69	70.59	4.67	322.0758	322.0762
ec	*o*-HOC_6H_4	H	A	98	191.5-193	ether/hexane	$C_{19}H_{15}O_4P$	67.45	4.46	67.08	4.34	338.0706	338.0686
ed	*m*-HOC_6H_4	H	C	97	205.5-207.5	acetonitrile	$C_{19}H_{15}O_4P$	67.45	4.46	67.37	4.74	338.0706	338.0706
ee	*p*-HOC_6H_4	H	C	98	208.5-210.5	acetonitrile	$C_{19}H_{15}O_4P$	67.45	4.46	67.40	4.51	338.0706	338.0702
fa	*o*-$CH_3C_6H_4$	H	C	74	197-199.5	acetonitrile	$C_{20}H_{17}O_3P$	71.42	5.09	71.56	4.93	336.0914	336.0929
fb	*m*-$CH_3C_6H_4$	H	A	83	158-159.5	acetonitrile	$C_{20}H_{17}O_3P$	71.42	5.09	71.24	5.00	336.0914	336.0968
fc	*p*-$CH_3C_6H_4$	H	C	86	181-182.5	acetonitrile	$C_{20}H_{17}O_3P$	71.42	5.09	71.46	5.23	336.0914	336.0894
fd	*o*-$CH_3OC_6H_4$	H	C	88	205-206.5	ether/hexane	$C_{20}H_{17}O_4P$	68.18	4.86	68.20	5.12	352.0863	357.0846
fe	*m*-$CH_3OC_6H_4$	H	C	75	176-178	acetonitrile	$C_{20}H_{17}O_4P$	68.18	4.86	68.22	5.12	352.0863	352.0884
ga	*p*-$CH_3OC_6H_4$	H	C	98	186-186.5	acetonitrile	$C_{20}H_{17}O_4P$	68.18	4.86	68.08	4.93	352.0863	352.0820
gb	*o*-ClC_6H_4	H	C	89	213-214	acetonitrile	$C_{19}H_{14}O_3ClP$	63.96	3.95	63.96	3.95	356.0328	356.0368
gc	*m*-ClC_6H_4	H	C	72	155-156	acetonitrile	$C_{19}H_{14}O_3ClP$	63.96	3.95	63.92	3.66	356.0328	356.0333
gd	*p*-ClC_6H_4	H	C	94	202-205	acetonitrile	$C_{19}H_{14}O_3ClP$	63.96	3.95	63.51	4.14	356.0328	356.0356
ge	*o*-$NO_2C_6H_4$	H	C	92	181.5-183	ether/hexane	$C_{19}H_{14}O_5NP$	62.13	3.84	62.09	4.09	367.0608	367.0719
ha	*m*-$NO_2C_6H_4$	H	C	98	192.5-195	acetonitrile	$C_{19}H_{14}O_5NP$	62.13	3.84	61.80	3.95	367.0608	367.0633
hb	*p*-$NO_2C_6H_4$	H	C	79	192-192.5	ether/hexane	$C_{19}H_{14}O_5NP$	62.13	3.84	61.72	3.86	367.0608	367.0607
hc	*o*-CNC_6H_4	H	C	98	211.5-214	acetonitrile	$C_{20}H_{14}O_3NP$	69.16	4.06	69.06	3.84	347.0709	347.0716
hd	*p*-CNC_6H_4	H	C	98	185-187	acetonitrile	$C_{20}H_{14}O_3NP$	69.16	4.06	69.25	4.15	347.0709	347.0692
he	C_6H_5	CH_3	B	36	179.5-180.5	acetonitrile	$C_{20}H_{17}O_3P$	71.42	5.09	71.32	5.09	336.0914	336.0994

[a] Paraformaldehyde was used, and the reaction mixture was heated for 9 hours at 80°. [b] Paraldehyde was used. [c] The reaction mixture was heated for 3 hours at 55°.

is amply supported by mass spectral data. The main mode of cleavage is a rearrangement process leading to the elimination of hydroxyalkyl or hydroxyaralkyl moiety from the primary mode of molecular ion fragmentation (m/z M^+). Two significant fragment ions are formed, and their production is due to simple P-C bond cleavage with (m/z 216) and without (m/z 215) hydrogen migration. Loss of OH from the m/z 216 ion could then lead to the ion at m/z 199. Further decomposition by explusion of the phosphorus atom from the m/z 199 ion yields the dibenzofuran ion (m/z 168).

Table 2

Infra-red Spectral Data (Potassium bromide, cm^{-1})

Compound	OH	P-O-C [a]	P=O [b]	Other Characteristic Vibrations				
3aa	3205	1218	1195	1118	1050	938	745	512
ab	3285		1198	1104	1060	914	752	524
ac	3245	1231	1200	1110	1040	918	750	545
ad	3110		1218	1112	1070	895	748	504
ae	3265	1225	1200	1115	1040	905	750	550
ba	3258	1227	1195	1114	1078	926	748	512
bb	3298	1245	1230	1114	1058	905	750	520
bc	3135	1216	1200	1116	1072	898	750	552
bd	3245	1215	1200	1115	1075	905	748	550
be	3200	1226	1194	1116	1050	925	745	535
ca	3180		1224	1114	1038	930	750	532
cb	3255	1225	1205	1114	1040	912	748	500
cc	3258	1226	1204	1115	1040	914	754	534
cd	3230	1220	1200	1116	1042	925	752	508
ce	3300	1230	1200	1112	1034	958	752	514
da	3295	1230	1200	1116	1038	912	750	545
db	3295		1205	1115	1045	920	750	535
dc	3202	1225	1200	1134	1066	920	748	538
dd	3100	1225	1195	1115	1075	925	748	538
de	3250	1220	1205	1118	1055	920	748	550
ea	3255		1200	1116	1048	920	750	550
eb	3205	1235	1223	1112	1040	930	750	534
ec	3390		1175	1115	1025	928	746	504
ed	3280		1212	1140	1040	930	748	525
ee	3232	1230	1195	1115	1040	928	748	538
fa	3250		1194	1112	1034	930	760	545
fb	3208	1230	1226	1116	1055	932	750	530
fc	3250		1196	1115	1040	928	750	540
fd	3222		1194	1118	1032	930	746	515
fe	3232	1220	1234	1118	1034	932	752	530
ga	3180		1210	1116	1025	925	746	540
gb	3238	1220	1234	1112	1030	920	755	540
gc	3172	1235	1200	1115	1042	928	748	528
gd	3175		1204	1115	1040	924	752	540
ge	3175		1224	1112	1032	928	745	535
ha	3200	1228	1196	1114	1045	918	752	525
hb	3205	1228	1200	1116	1055	925	750	558
hc	3400		1195	1116	1035	928	750	558
hd	3240	1228	1196	1116	1040	928	750	558
he	3200		1205	1115	1075	930	750	545

[a] Aromatic carbon. [b] Hydrogen-bonded.

EXPERIMENTAL

All melting points are uncorrected. The proton nuclear magnetic resonance (^1H nmr) spectra were recorded on a Varian VXR-300 or a JEOL C 60-HL spectrometer using dimethyl sulfoxide-d_6. The ^{13}C nmr spectra were run on a Varian VXR-300. Infrared spectra were taken on a Perkin-Elmer 283 infrared spectrophotometer. High resolution mass spectra were obtained with Hitachi M-80 mass spectrometer at an ionizing voltage of 70 eV. The tlc were carried out on a silica gel 60 F_{254} plates (Merck). The hplc were performed by using a Nippon Seimitsu apparatus with an ODS Column (4.6 x 250 mm) and a RI detector. All melting points were measured with a Yamato MP-21 apparatus.

6-(1-Hydroxy-2-methylpropyl)-6*H*-dibenz[*c*,*e*][1,2]oxaphosphorin 6-Oxide (**3ae**). Typical Procedure.

Method A. (In the cases of aldehydes) without using solvent.

A mixture of 2-(2-hydroxyphenyl)phenylphosphonic acid (**1**, 0.50 g, 2.14 mmoles) and excess isobutyraldehyde (1.5 ml) is heated at 80° with magnetic stirring in an oil bath for 0.5 hour. The reaction mixture, on cooling, was triturated with cold ether/-*n*-hexane (1:1, 4 ml). The white solid thus formed is collected, washed with cold ether/*n*-hexane (2 ml), and air-dried to give practically pure **3ae** (0.58 g, 94%). Analysis by tlc and hplc indicated a single component. Three recrystallizations from acetonitrile gave an analytical sample.

6-(2-Hydroxy-2-butyl)-6*H*-dibenz[*c*,*e*][1,2]oxaphosphorin 6-Oxide (**3cc**). Typical Procedure.

Method B. (In the cases of ketones) without using solvent.

A mixture of **1** (0.50 g, 2.14 mmoles) and excess methyl ethyl ketone (1.5 ml) was heated at 80° with magnetic stirring in an oil bath for 3 hours. The reaction mixture was kept in the refrigerator overnight. The resulting precipitate was collected, washed with cold acetonitrile (2 ml) and air-dried, yielding the desired product **3cc** as white crystals (0.71 g, 98%). The tlc and hplc analyses in a variety of solvents revealed the presence of only one compound. An analytical sample was obtained by three recrystallization from acetonitrile.

6-[1-Hydroxy-1-(*p*-hydroxyphenyl)methyl]-6*H*-dibenz[*c*,*e*][1,2]oxaphosphorin 6-Oxide (**3ee**). Typical Procedure.

Method C. In acetonitrile solution.

A mixture of **1** (0.50 g, 2.14 mmoles) and *p*-hydroxybenzaldehyde (0.26 g, 2.14 mmoles) in acetonitrile (1.5 ml) was stirred at 80° in an oil bath for 3 hours. After removal of the solvent, the residue was collected, washed with cold acetonitrile (2 ml) and air-dried, giving the desired product **3ee** as a white solid (0.71 g, 98%). The tlc and hplc analyses indicate complete absence of two starting materials and the presence of a new product. Purification for the analysis was performed by three recrystallization from acetonitrile.

6-Chloro-6*H*-dibenz[*c*,*e*][1,2]oxaphosphorin.

This compound was prepared by our published procedure [2]. An efficiently stirred mixture of 2-hydroxybiphenyl (20.4 g, 0.12 mole) and phosphorus trichloride (20.6 g, 0.15 mole) was heated at 50° for 0.5 hour. Immediately, hydrogen chloride gas evolution was evident. The mixture was further stirred at 140° for an additional 2.5 hours. The hydrogen chloride evolved was trapped by passage over water. Subsequently, zinc chloride (0.12 g) was carefully added, and the mixture was stirred at 140-210° for 5 hours wth gradual heating from 140 to 210° over that interval. Again hydrogen chloride evolved vigorously. After the completion of the reaction, the excess phosphorus trichloride was remov-

Table 3

Mass Spectral Data (m/z (%))

Compound	
3aa	246 (M^+,34), 216 (72), 215 (100), 199 (10), 169 (11), 168 (64), 139 (28)
ab	260 (M^+,4), 216 (100), 199 (10), 168 (19), 139 (11)
ac	274 (M^+,2), 217 (14), 216 (100), 215 (13), 199 (11), 168 (17), 139 (8)
ad	288 (M^+,13), 217 (75), 216 (100), 215 (40), 199 (52), 169 (25), 168 (69), 152 (20), 141 (11), 139 (41)
ae	288 (M^+,2), 217 (15), 216 (100), 215 (12), 199 (10), 168 (12), 139 (5)
ba	302 (M^+,1), 217 (13), 216 (100), 199 (12), 168 (24), 139 (17)
bb	302 (M^+,3), 217 (29), 216 (100), 215 (26), 199 (22), 169 (14), 168 (32), 139 (18)
bc	302 (M^+,1), 217 (27), 216 (100), 199 (18), 139 (11)
bd	316 (M^+,4), 217 (92), 216 (100), 215 (32), 199 (45), 169 (26), 168 (51), 152 (14), 141 (11), 139 (25)
be	312 (M^+,9), 217 (13), 216 (100), 215 (15), 199 (12), 168 (21), 139 (12), 115 (12)
ca	328 (M^+,9), 217 (14), 216 (100), 199 (15), 169 (10), 168 (23), 139 (12), 110 (18)
cb	274 (M^+,2), 217 (14), 216 (100), 199 (13), 152 (9), 139 (30), 115 (10)
cc	288 (M^+,13), 217 (75), 216 (100), 215 (40), 199 (52), 169 (25), 168 (69), 152 (20), 141 (11), 139 (41)
cd	320 (M^+,3), 217 (29), 216 (100), 215 (26), 199 (22), 169 (14), 168 (32), 139 (18)
ce	316 (M^+,7) 217 (54), 216 (100), 215 (32), 199 (35), 169 (18), 168 (46), 139 (24)
da	316 (M^+,5), 217 (36), 216 (100), 215 (22), 199 (24), 169 (12), 168 (30), 139 (15)
db	302 (M^+,4), 217 (32), 216 (100), 215 (22), 199 (24), 169 (13), 168 (30), 139 (16)
dc	330 (M^+,9), 217 (60), 216 (100), 215 (36), 199 (37), 169 (16), 168 (49), 152 (13), 139 (25), 115 (15)
dd	358 (M^+,4), 217 (46), 216 (100), 215 (32), 199 (28), 169 (16), 168 (36), 139 (18)
de	300 (M^+,6), 217 (34), 216 (100), 215 (20), 199 (22), 169 (12), 168 (32), 139 (17)
ea	314 (M^+,5), 217 (19), 216 (100), 215 (13), 199 (12), 168 (18), 139 (10)
eb	322 (M^+,5), 217 (12), 216 (100), 215 (17), 199 (11), 168 (16), 139 (8), 106 (13)
ec	338 (M^+,4), 216 (100), 215 (22), 199 (16), 169 (12), 168 (23), 139 (14), 122 (28), 121 (28)
ed	338 (M^+,4), 217 (13), 216 (100), 215 (27), 199 (16), 169 (12), 168 (23), 139 (14), 122 (28), 121(28)
ee	338 (M^+,1), 232 (10), 216 (100), 215 (18), 199 (13), 169 (10), 168 (21), 139 (13), 120 (19), 119 (18)
fa	336 (M^+,1), 217 (15), 216 (100), 215 (18), 199 (13), 169 (10), 168 (21), 139 (13), 120 (19), 119 (18)
fb	336 (M^+,5), 217 (14), 216 (100), 215 (17), 199 (12), 168 (18), 139 (9)
fc	336 (M^+,8), 217 (43), 216 (100), 215 (21), 199 (28), 169 (16), 168 (33), 139 (19), 120 (35), 119 (40)
fd	352 (M^+,1), 217 (15), 216 (100), 215 (21), 199 (14), 169 (11), 168 (23), 139 (15), 136 (18)
fe	352 (M^+,1), 217 (14), 216 (100), 215 (12), 199 (10), 168 (19), 139 (13), 136 (11), 135 (11)
ga	353 (M^+,9), 217 (13), 216 (100), 215 (15), 199 (10), 168 (22), 139 (14), 137 (21), 136 (20), 135 (23)
gb	356 (M^+,4), 217 (13), 216 (100), 215 (13), 199 (10), 168 (17), 139 (9)
gc	356 (M^+,4), 217 (14), 216 (100), 199 (9), 169 (9), 168 (17), 139 (10)
gd	356 (M^+,3), 217 (13), 216 (100), 199 (9), 169 (9), 168 (17), 139 (10)
ge	367 (M^+,4), 233 (34), 232 (100), 217 (51), 216 (100), 215 (39), 199 (43), 169 (21), 168 (68), 139 (34)
ha	367 (M^+,1), 232 (12), 217 (14), 216 (100), 215 (27), 199 (15), 169 (13), 168 (28), 151 (24), 139 (17)
hb	367 (M^+,2), 233 (9), 232 (61), 216 (100), 215 (30), 199 (11), 168 (38), 139 (17)
hc	347 (M^+,18), 217 (13), 216 (100), 215 (67), 199 (12), 168 (38), 139 (15), 133 (20), 132 (10)
hd	347 (M^+,3), 217 (14), 216 (100), 215 (33), 199 (13), 169 (11), 168 (28), 139 (16), 131 (21), 130 (29)
he	347 (M^+,10), 217 (21), 216 (100), 215 (19), 199 (10), 169 (11), 168 (24), 139 (13)

Table 4

^{1}H NMR Spectral Data [δ–value (ppm), J-value (Hz)]

Compound	
3aa	3.20 (br s, 1H, OH), 4.19 (d, 1H, J_{PH} = 14.5, C*H*H), 430 (dd, 1H, J_{PH} = 15.1, J_{HH} = 4.5, C*H*H), 7.26 (d, 1H, Ar), 7.27 (td, 1H, Ar), 7.40 (t, 1H, Ar), 7.55 (tdd, 1H, Ar), 7.74 (t, 1H, Ar), 7.95 (dd, 1H, Ar), 8.01 (ddd, 1H, Ar), 8.02 (dd, 1H, Ar)
ab	1.55 (dd, J_{PH} = 16.6, J_{HH} = 7.1 CH_3), 2.01 (br s, 1H, OH), 4.24 (q, J = 7.2 CH), 7.24 (d, 1H, Ar), 7.73 (t, 1H, Ar), 7.94 (d, 1H, Ar), 8.01 (dd, 1H, Ar), 8.05 (ddd, 1H, Ar),

ac 1.07 (t, 3H, J = 7.5, CH_3), 1.73-2.03 (m, 2H, CH_2), 3.20 (br s, 1H, OH), 3.96-4.00 (m, 1H, CH), 7.22 (dd, 1H, Ar), 7.24 (dd, 1H, Ar), 7.37 (tt, 1H, Ar), 7.52 (tdd, 1H, Ar), 7.72 (tt, 1H, Ar), 7.93 (dd, 1H, Ar), 7.99 (dd, 1H, Ar), 8.04 (ddd, 1H, Ar)

ad 0.91 (t, 3H, J = 7.4, CH_3), 1.34-1.51 (m, 1H, C*H*HCH$_3$), 1.54-172 (m, 1H, C*H*HCH$_3$), 1.72-1.95 (m, 2H, CH_2CH_3), 2.78 (br s, 1H, OH), 4.10 (dd, 1H, J = 3.6, 10.3, CH), 7.23 (d, 1H, Ar), 7.25 (t, 1H, Ar), 7.38 (tt, 1H, Ar), 7.53 (tdd, 1H, Ar), 7.73 (t, 1H, Ar), 7.93 (d, 1H, Ar), 8.00 (dd, 1H, Ar), 8.04 (ddd, 1H, Ar)

ae 0.99 (dd, 3H, J = 6.8, 1.7, CH_3), 1.11 dd, 3H, J = 6.6, 2.2, CH_3), 213-2.24 (m, 1H, $(CH_3)_2CHCH_2$), 2.42 (br s, 1H OH), 3.95-4.00 (m, 1H, CHC*H*P), 7.24 (d, 1H, Ar), 7.25 (t, 1H, Ar), 7.38 (t, 1H, Ar), 7.53 (t, 1H, Ar), 7.73 (t, 1H, Ar), 7.95 (d, 1H, Ar), 7.98-8.04 (m, 2H, Ar)

bb 0.85, 0.94 (2d, 3H, each, J = 6.4 and 6.6 respectively, $2CH_3$), 1.62-1.72 (m, 1H, $(CH_3)_2CHCH_2$), 1.76-1.94 (m, 3H, CH_2 and OH), 4.18 (d, 1H, J = 10.0, CH_2CHP), 7.23 (d, 1H, Ar), 7.26 (t, 1H, Ar), 7.38 (tt, 1H, Ar), 7.53 (tdd, 1H, Ar), 7.73 (t, 1H, Ar), 7.93 (d, 1H, Ar), 8.00 (dd, 1H, Ar), 8.04 (ddd, 1H, Ar)

bc 1.15 (s, 9H, $3CH_3$), 1.66 (br s, 1H, OH), 3.73 (d, 1H, J_{PH} = 82.8, CC*H*P), 7.22 (d, 1H, Ar), 7.27 (t, 1H, Ar), 7.38 (t, 1H, Ar), 7.52 (tt, 1H, Ar), 7.70 (t, 1H, Ar), 7.94 (dd, 1H, Ar), 7.99 (dd, 1H, Ar), 8.06 (ddd, 1H, Ar)

be 2.21 (br s, 1H, OH), 5.19, 5.22 (2d, 1H, J = 22.3 and 25.3 respectively, PC*H*), 6.25 (ddd, 1H, J_{PH} = 52.1, J_{HH} = 3.5, 2.1, furyl group), 6.32 (dt, 1H, J_{PH} = 62.0, J = 62.0, J_{HH} = 3.1, furyl group), 7.14 (dd, 1H, J = 8.20, 1.5, Ar), 7.23 (td, 1H, J = 7.6, 1.3, Ar), 7.32-7.38 (m, 1H, Ar), 7.50 (dtdd, 1H, J_{PH} = 14.5, J_{HH} = 7.2, 3.2, 1.0, Ar), 7.68-7.77 (m, 1H, Ar), 7.88 (ddd, 1H, J_{PH} = 14.7, J_{HH} = 8.1, 1.7, Ar), 7.90-8.01 (m, 2H, Ar)

ca 3.43, 3.88 (2 br s, 1H, OH), 5.48, 5.49 (2d, 1H, J_{PH} = 28.5, 31.4 respectively, C*H*P), 6.85 (ddd, 1H, J_{PH} = 57.8, J_{HH} = 5.1, 3.7, thienyl group), 6.97 (dt, 1H, J_{PH} = 59.0, J_{HH} = 3.4, thienyl group), 7.10-7.16 (m, 1H, Ar), 7.18-7.28 (m, 2H, Ar), 7.34 (t, 1H, J = 7.6, Ar), 7.48 (td, 1H, J = 7.5, 3.1, Ar), 7.71 (dt, 1H, J_{PH} = 12.2, J_{HH} = 7.8, Ar), 7.83 (ddd, 1H, J_{PH} = 12.0, J_{HH} = 7.7, 1.3, Ar), 7.88-8.00 (m, 2H, Ar)

cb 1.29, 1.60 (2d, 3H, J = 15.9 and 14.2 respectively, $2CH_3$), 2.88 (d, 1H, J = 2.5, OH), 7.22 (d, 1H, Ar), 7.23 (t, 1H Ar), 7.37 (tt, 1H, Ar), 7.53 (tdd, 1H, Ar), 7.73 (tt, 1H, Ar), 7.94 (d, 1H, Ar), 8.02 (dd, 1H, Ar), 8.12 (ddd, 1H, Ar)

cc 1.06 (t, 3H, J = 7.5, CH_2CH_3), 1.21 (d, 3H, J = 16.7, CCH_3), 1.92-2.01 (m, 2H, $CHCH_3$), 2.49 (br s, 1H, OH), 7.20 (dd, 1H, J = 8.0, 1.1, Ar), 7.23 (td, 1H, J = 7.6, 1.4, Ar), 7.36 (tt, 1H, J = 7.7, 1.3, Ar), 7.55 (tdd, 1H, J_{PH} = 3.0, J_{HH} = 7.5, 1.0, Ar), 7.72 (tt, 1H, J = 7.76, 1.2, Ar), 8.01 (dd, 1H, J_{PH} = 5.0, J_{HH} = 7.9, Ar), 8.10 (ddd, 1H, J_{PH} = 11.4, J_{HH} = 7.6, 1.4, Ar)

cd 0.81 (t, 3H, J = 6.9, CH_2CH_3), 1.32-1.70 (m, 4H, $CH_2CH_2CH_3$), 1.54 (d, 3H, J_{PH} = 15.1, CCH_3), 2.80 (br s, 1H, OH), 7.21 (dd, 1H, Ar), 7.22 (td, 1H, Ar), 7.36 (t, 1H, Ar), 7.52 (tdd, 1H, Ar), 7.72 (tt, 1H, Ar), 7.93 (dd, 1H, Ar), 8.02 (dd, 1H, Ar), 8.10 (ddd, 1H, Ar)

ce 0.93 (t, 3H, J = 7.3, CH_2CH_3), 1.22 (d, 3H, J_{PH} = 16.9, CCH_3), 1.36 (sex, 2H, J = 7.1, $CH_2CH_2CH_3$), 1.44-1.53 (m, 2H, $CCH_2CH_2C_2H_5$), 1.88-1.96 (m, 2H, CCH_2CH_2), 2.48 (d, 1H, OH), 7.21 (d, 1H, Ar), 7.22 (t, 1H, Ar), 7.36 (td, 1H, Ar), 7.52 (td, 1H, Ar), 7.93 (dd, 1H, Ar), 8.01 (dd, 1H, Ar), 8.10 (ddd, 1H, Ar),

da 1.00, 1.01 (2d, J = 6.6 and 6.4 respectively, $CH(CH_3)_2$; 1.27 (d, 3H, J_{PH} = 17.1, CCH_3); 1.79-2.05 (m, 2H, CCH_2CH), 2.27 (br s, 1H, OH), 4.42-4.57 (m, 1H, $CH_2CH(CH_3)_2$), 7.21 (d, 1H, Ar), 7.22 (t, 1H, Ar), 7.36 (td, 1H, Ar), 7.52 (td, 1H, Ar), 7.72 (td, 1H, Ar), 7.93 (d, 1H, Ar), 8.01 (dd, 1H, Ar), 8.10 (dd, 1H, Ar)

db 0.87, 1.09 (2t, 3H, J = 7.5 and 7.6 respectively, $2CH_3$), 1.58-1.77 (m, 2H CH_2), 1.77-1.96 (m, 1H , C*H*H), 2.00-2.26 (m, 1H, C*H*H), 2.28 (br s, 1H, OH), 7.19 (dd, 1H, Ar), 7.22 (td, 1H, Ar), 7.36 (td, 1H, Ar), 7.52 td, 1H, Ar), 7.71 (td, 1H, Ar), 9.93 (dd, 1H, Ar), 8.01 (dd, 1H, Ar), 8.08 (ddd, 1H, Ar)

de 1.60-1.97 (m, 8H, $4CH_2$), 2.36 (br s, 1H, OH), 7.22 (d, 1H, Ar), 7.23 (t, 1H, Ar), 7.36 (tt, 1H, Ar), 7.51 (tdd, 1H, Ar), 7.71 (tt, H, Ar), 7.94 (dd, 1H, Ar), 8.01 (dd, 1H, Ar), 8.11 (ddd, 1H, Ar)

ea 1.45-171 (m, 10, $5CH_2$), 2.29 (br s, 1H, OH), 7.21 (d, 1H, Ar), 7.23 (td, 1H, Ar), 7.37 (td, 1H, Ar), 7.51 (tdd, 1H, Ar), 7.71 (td, 1H, Ar), 7.93 (dd, 1H, Ar), 8.01 (dd, 1H, Ar), 8.07 (ddd, 1H, Ar)

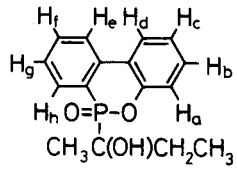
eb 3.06 (br s, 1H, OH), 5.23 (d, 1H, J = 6.8, C*H*P), 7.10 (d, 1H, J = 6.8, Ar), 7.18 (t, 1H, J = 7.2, Ar), 7.23-7.29 (m, 5H, Ar), 7.32(t, 1H, J = 7.6, Ar), 7.43 (td, 1H, J = 7.5, 3.1, Ar), 7.65 (dd, 1H, J_{PH} = 12.0, J_{HH} = 6.2, Ar), 7.71 (t, 1H, J = 7.8, Ar), 7.85 (dd, 1H, J = 8.1, 1.5, Ar), 7.96 (dd, 1H, J = 8.1, 5.4, Ar)

fc 2.20 (d, 3H, J_{PH} = 2.0, CH_3), 3.52 (dd, 1H, J_{PH} = 10.1, J_{HH} = 4.8, OH), 5.24 (dd, 1H, J $_{PH}$ = 8.5, J_{HH} = 4.7, C*H*P), 6.88 (d, 1H, J = 8.1, Ar), 7.00 (dd, 1H, J = 8.2, 2.1, Ar), 7.06-7.20 (m, 2H, Ar), 7.31 (tt, 1H, J = 7.6, Ar), 7.46 (tdd, 1H, J = 7.5, 3.3, 1.0, Ar), 7.66 (tt, 1H, J = 7.7, 1.1, Ar), 7.72 (dd, 1H, J = 7.9, 1.4, Ar), 7.85 (dd, 1H, J = 7.7, 4.6, Ar), 7.89 (ddd, 1H, J_{PH} = 12.1, J_{HH} = 7.6, 1.3, Ar)

he 1.92 (d, 3H J_{PH} = 14.4, CH_3), 2.47 (d, 1H, J_{PH} = 8.8, OH), 7.16 (d, 1H, Ar), 7.18 (td, 1H, Ar), 7.21-7.36 (m, 6H, Ar), 7.38-7.43 (m, 2H, Ar), 7.65 (td, 1H, Ar), 7.86 (dd, 1H, Ar), 7.95 (dd, 1H, Ar)

Table 5

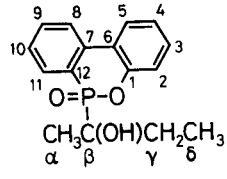
^{1}H NMR Spectral Data for **3cc**



	δ-value (ppm)	J-value (Hz)
Ha,	7.20	Jab = 7.8, Jac = 1.3
Hb,	7.36	Jbc = 7.7, Jbd = 1.5
Hc,	7.23	Jcd = 7.7
Hd,	7.93	
He,	8.01	J_{PH} = 5.0, Jef = 7.9, Jeg = 1.1
Hf,	7.72	Jfg = 7.6, Jfh = 1.3
Hg,	7.55	J_{PH} = 3.0, Jgh = 7.6
Hh	8.10	J_{PH} = 11.4

Table 6

^{13}C NMR Spectral Data for **3cc**



	δ-value (ppm)	J-value (Hz)		δ-value (ppm)	J-value (Hz)
C-1,	150.20, d	J_{CP} = 9.4	C-9,	133.46, d	J_{CP} = 2.3
C-2,	119.86, d	J_{CP} = 6.0	C-10,	128.36, d	J_{CP} = 12.4
C-3,	130.51, s		C-11,	132.41, d	J_{CP} = 9.6
C-4,	124.30, s		C-12,	121.12, d	J_{CP} = 81.6
C-5,	124.98, s		C-α	20.00, d	J_{CP} = 6.6
C-6,	136.62, d	J_{CP} = 5.7	C-β	74.72, d	J_{CP} = 115.5
C-7,	122.00, d	J_{CP} = 18.5	C-γ	28.62, d	J_{CP} = 6.4
C-8,	123.38, d	J_{CP} = 9.3	C-δ	6.61, d	J_{CP} = 8.0

ed under reduced pressure, and the residue was subjected to fractional distillation, and a fraction distilling at 180-190°/20 mm Hg was collected. The distillate which soon solidifies on standing (mp 87°, quantitative yield). The 6-chloro derivative thus obtained was sufficiently pure for use in the following reaction step.

2-(2-Hydroxyphenyl)phenylphosphonic Acid (**1**).

The above 6-chloro derivative (40.6 g, 0.17 mole) was mixed with a solution of methanol/water (1:1, 100 ml). The mixture was heated under reflux for 1 hour and then poured into water (100 ml) under vigorous stirring. The resulting precipitate was collected, washed with water. Two recrystallizations from ethanol/water (1:2) afforded pure **1**, mp 105-106° dec (38 g, 94%).

Anal. Calcd. for $C_{12}H_{11}O_3P$: C, 61.54; H, 4.70. Found: C, 61.67; H, 4.91.

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