

Synthesis and Spectral Studies of 8-Alkyl/Phenyl-16H-Dinaphtho [2,1-*d*:1',2'-*g*][1, 3, 2] Dioxaphosphocin 8-oxides and 2,10-Dichloro-6-Alkyl/Phenyl-12H-Dibenzo [*d*, *g*][1, 3, 2] Dioxaphosphocin 6-Oxides

C. DEVENDRANATH REDDY*, R. SURYANARAYANA REDDY
and C. NAGA RAJU

Department of Chemistry, S. V. University College of Engineering
Tirupati-517 502, India

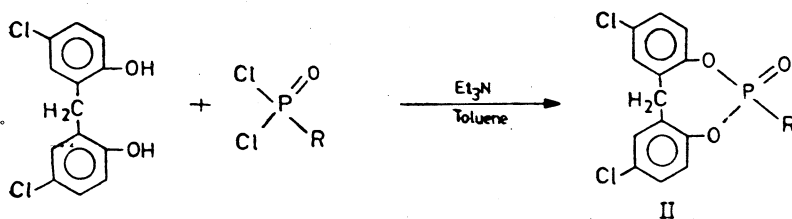
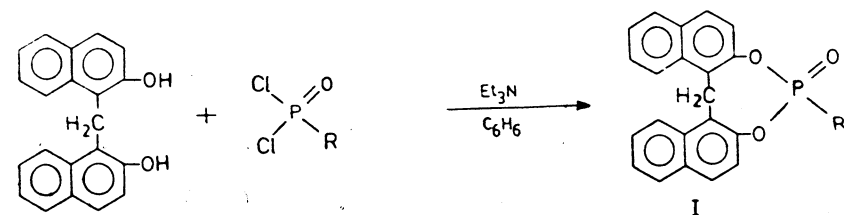
Two series of novel 8-alkyl/phenyl-16H-dinaphtho [2,1-*d*:1',2'-*g*][1, 3, 2] dioxaphosphocin 8-oxides and 2,10-dichloro-6-alkyl/phenyl-12H-dibenzo [*d*, *g*][1, 3, 2] dioxaphosphocin 6-oxides were synthesised and their structures established by IR, ¹H NMR and mass spectral data. A few of these compounds were also evaluated for their toxicity in insects.

INTRODUCTION

In view of the various applications of organophosphorus compounds in agriculture¹, medicine² and industry^{3,4}, series of 8-alkyl/phenyl-16H-dinaphtho [2,1-*d*:1',2'-*g*][1, 3, 2] dioxaphosphocin 8-oxides and 2,10-dichloro-6-alkyl/phenyl-12H-dibenzo [*d*, *g*][1, 3, 2] dioxaphosphocin 6-oxides have been synthesised and their spectral characteristics and toxicity are evaluated.

RESULTS AND DISCUSSION

Synthesis of dioxaphosphocin 8-oxides (I) and dioxaphosphocin 6-oxides (II) were accomplished by the reaction of bis(2-hydroxy-1-



In I & II

	R	R	
a	C ₂ H ₅	d	n-C ₆ H ₅
b	C ₃ H ₇	e	C ₆ H ₁₁
c	i-C ₃ H ₇	f	C ₆ H ₅

naphthyl) methane and 5,5'-dichloro-2,2'-dihydroxy-diphenyl methane with various alkyl and phenyl phosphonic dichlorides in equimolar quantities in the presence of triethylamine.

All the title compounds are crystalline and colourless solids with melting points in the range of 180–246°C and the yields were moderate (35–72%). The characterization data of these compounds are given in Table 1. In IR, the title compounds showed characteristic bands in the regions 1260–1310 ($\nu_{\text{P=O}}$)⁵, 1195–1250 and 930–965 ($\nu_{\text{P-O-C}_{\text{aromatic}}}$)⁶, 730–745 cm^{-1} ($\nu_{\text{P-C}_{\text{aliph}}}$)⁷ and 1440–1485 and 990–995 cm^{-1} ($\nu_{\text{P-Ph}}$)⁸.

TABLE I
CHARACTERIZATION DATA OF Ia-f AND IIa-f

Compound No.	M.pt. °C	Yield %	Molecular formula	Analysis	
				Found C	Calculated H
Ia	184–85	67 ^a	C ₂₃ H ₁₉ O ₃ P	73.86 (73.80)	5.12 (5.08)
Ib	223–24	64 ^a	C ₂₄ H ₂₁ O ₃ P	74.28 (74.23)	5.49 (5.41)
Ic	245–46	72 ^a	C ₂₄ H ₂₁ O ₃ P	74.40 (74.23)	5.47 (5.41)
Id	176–77	64 ^a	C ₂₃ H ₂₃ O ₃ P	74.76 (74.63)	5.83 (5.72)
Ie	196–97	65 ^b	C ₂₇ H ₂₅ O ₃ P	75.86 (75.70)	5.80 (5.84)
If	189–90	63 ^c	C ₂₇ H ₁₉ O ₃ P	76.89 (76.78)	4.58 (4.50)
IIa	120–21	49 ^d	C ₁₅ H ₁₃ O ₃ Cl ₂ P	52.72 (52.48)	3.90 (3.79)
IIb	180–81	52 ^d	C ₁₆ H ₁₃ O ₃ Cl ₂ P	53.98 (53.78)	4.27 (4.20)
IIc	172–73	56 ^e	C ₁₆ H ₁₃ O ₃ Cl ₂ P	53.97 (53.78)	4.18 (4.20)
IId	146–48	48 ^e	C ₁₇ H ₁₇ O ₃ Cl ₂ P	55.20 (54.99)	4.58 (4.58)
IIe	242–44	55 ^a	C ₁₉ H ₁₉ O ₃ Cl ₂ P	57.54 (57.43)	4.69 (4.79)
IIf	182–83	35 ^a	C ₁₉ H ₁₃ O ₃ Cl ₂ P	58.30 (58.31)	3.28 (3.32)

Recrystallized from (a) methanol-benzene (2 : 1), (b) 1-butanol, (c) tetrahydrofuran, (d) Petroleum ether-benzene, (e) ethanol.

The bridged methylene protons of dioxaphosphocin 8-oxides (Ia-f) resonated as a multiplet in the region 4.70–5.48 ppm (Table 2). In dioxaphosphocin 6-oxides (IIa-f) these protons appeared as a doublet ($J=13.3\text{--}13.5$ Hz) in the region 3.60–3.63 ppm and a doublet of doublet ($J=13.3\text{--}13.5, 2.5\text{--}2.6$ Hz) in the range of 4.29–4.31 ppm. The coupling

TABLE 2
¹H NMR CHEMICAL SHIFTS OF Ia-f AND IIa-f

Compound No.	Aromatic-H	Bridged methylene-H	R-H
Ia	7.01-8.30 (m, 12H)	4.76-5.20 (m, 2H)	1.20-1.60 (m, 3H, CH ₃), 1.90-2.40 (m, 2H, CH ₂)
Ib	7.00-8.30 (m, 12H)	4.70-5.30 (m, 2H)	1.10-1.40 (m, 3H, CH ₃), 1.60-2.50 (m, 4H, CH ₂)
Ic	7.10-8.40 (m, 12H)	4.70-5.35 (m, 2H)	1.30-1.75 (m, 6H, CH ₃), 2.10-2.70 (m, 1H, CH)
Id	7.00-8.40 (m, 12H)	4.70-5.30 (m, 2H)	0.90-1.20 (t, 3H, CH ₃), 1.40-2.50 (m, 6H, CH ₂)
Ie	7.18-8.23 (m, 12H)	4.87-5.12 (m, 2H)	1.32-2.26 (m, 11H, Cyclohexyl-H)
I	7.11-8.47 (m, 17H)	4.86-5.48 (m, 2H)	—
IIa	7.02-7.29 (m, 6H) *	4.31 (13.5, 2.5 Hz) 3.63 (13.5 Hz)	1.35-1.50 (m, 3H, CH ₃), 2.20-2.30 (m, 2H, CH ₂)
IIb	7.01-7.29 (m, 6H)	4.29 (13.4, 2.6 Hz) 3.63 (13.4 Hz)	1.21-1.41 (t, 3H, CH ₃), 1.90-1.95 (m, 2H, CH ₂), 2.12-2.22 (m, 2H, CH ₂)
IIc	6.93-7.43 (m, 6H)	3.61-4.35 (dd)	1.31-1.74 (m, 6H, CH ₃), 2.12-2.75 (m, 1H, CH)
IIId	7.02-7.29 (m, 6H)	4.30 (13.3, 2.6 Hz) 3.60 (13.4 Hz)	0.98-1.04 (t, 3H, CH ₃), 1.52-1.61 (m, 2H, CH ₂), 1.80-2.00 (m, 2H, CH ₂), 2.13-2.20 (m, 2H, CH ₂)
IIe	7.01-7.33 (m, 6H)	3.32-4.36 (dd)	1.22-2.46 (m, 11H, Cyclohexyl-H)
IIIf	6.80-7.80 (m, 11H)	3.30-4.30 (dd)	—

constant $J=13.3-13.5$ Hz is readily attributed as geminal coupling ($^2J_{H,H}$). The small coupling constant ($J=2.5-2.6$ Hz) is ascribed to the long range coupling ($^3J_{H,P}$) with phosphorus⁹. Based on the 1H NMR data and a study of the molecular model, a rigid boat like conformation for the central eight membered dioxaphosphocin 6-oxide ring has been proposed as shown in Fig. B, which facilitates the coupling between the phosphorus and methylene protons.

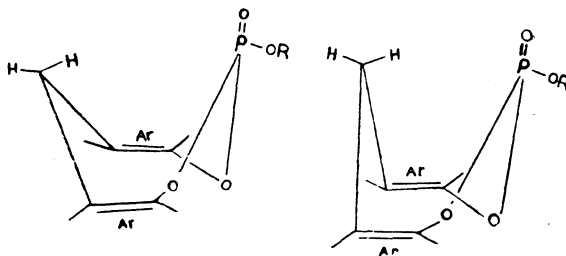


Fig. A

Fig. B

It is of interest to note the absence of long range coupling ($^3J_{H,P}$) in dinaphtho analogues (Ia-f) which is attributed to a distorted boat like conformation of the molecule (Fig. A)¹⁰.

Aromatic protons of the naphthyl and phenyl moieties resonated in the expected range. The chemical shifts of ethyl, n-propyl, iso-propyl and butyl groups were located in the slightly downfield region (Table 2) and these signals appeared as complex multiplets due to coupling with phosphorus. The cyclohexyl protons (Ie, IIe) exhibited signals in the region 1.22–2.46 ppm, as complex multiplet due to coupling with phosphorus as expected.

TOXICITY EVALUATION

Different concentrations of test compounds (IIa, IIb and IIc) were prepared in tetrahydrofuran and the solutions were sprayed on the cuticle surface of the insect (*P. americana*) by a micro syringe. The mortality was observed after 24 hours. The observed data was subjected to the Finney's¹¹ statistical treatment to arrive at the following graphs: (1) log concentration vs. per cent kill and (2) log concentration vs. probit kill. The LD₅₀ values of the test compounds (IIa, IIb and IIc) were 29.90, 29.40 and 29.16 respectively.

EXPERIMENTAL

Melting points were taken on a Mel-Temp apparatus, Tempo Instruments, India and were uncorrected. Central Drug Research Institute, Lucknow, has performed the micro-analysis. Infrared spectra (ν_{max} in

TABLE 3
 IMPORTANT MASS FRAGMENTS OF Ia-f AND IIa-f

Compound No.	M ⁺	m/z (relative intensity)
Ie	428.1555(15)	345(1.5, M-R), 327(3), 282(4.5), 281(18), 265(3.2), 252(4.1), 239(1.4), 226(0.6), 213(0.8), 155(2.2), 143(2.7), 83(0.5), 69(100)
If	422.1072(1.3)	345(0.1, M-R), 344(0.1, M-RH), 329(1.0), 327(1.2), 298(0.2), 282(0.7), 281(4.7), 265(0.4), 252(0.4), 239(0.3), 213(0.6), 155(1.9), 143(2.6), 77(0.6), 69(100)
IIb	356(100)	358(78, M+2), 343(40), 341(55), 328(9), 321(18, M-C1), 314(58), 310(42), 298(35), 296(58), 279(24), 267(18), 251(40), 249(69), 233(26), 215(55), 202(11), 197(11), 186(27), 173(12), 168(19), 152(39), 139(36), 125(10), 42(49)
IIc	356(76)	358(57, M+2), 340(12.5), 338(19), 321(17), 315(13), 314(37), 313(46), 298(35), 296(52), 279(22), 267(15), 261(31), 260(25), 251(46), 250(15), 249(60), 233(23), 231(15), 217(24), 216(15), 215(48), 197(12), 188(21), 186(43), 173(19), 168(27), 153(15), 152(52), 151(42), 150(33), 140(15), 139(53), 126(13), 125(13), 113(16), 99(16), 89(19)
IId	370(93)	372(66, M+2), 371(20), 355(6, M-C1), 341(60), 328(20), 314(13), 310(19), 296(15), 279(10), 267(6), 249(19), 233(12), 215(48), 187(7), 186(19), 173(12), 168(20), 152(70), 139(60), 55(100)
IIe	396(100)	398(65, M+2), 361(2, M-C1), 355(1.5), 343(3.5), 328(1.3), 314(70), 296(35), 279(14), 277(0.7), 267(6), 249(19), 233(7.2), 215(12), 197(2), 186(7), 173(7), 168(3.5), 163(1.3), 152(8), 139(6.3), 81(7)
IIf	390(62)	392(32, M+2), 372(16), 355(12, M-C1), 337(11), 313(6), 277(25), 249(62), 233(9), 215(65), 197(9), 186(30), 173(10), 168(20), 163(9), 152(62), 139(52), 77(100)

cm⁻¹) in KBr pellets were recorded on a Perkin-Elmer model 683 spectrophotometer, pmr spectra on Jeol FX 90 MHz NMR spectrometer using TMS as internal standard, mass spectra on DS-50S and JMS-D300 spectrometers using ionization potential of 70 eV and a direct inlet system.

8-Cyclohexyl-16H-dinaphtho [2,1-d : 1',2'-g][1, 3, 2] dioxaphosphocin 8-oxide (Ie)

To a stirred solution of bis (2-hydroxy-1-naphthyl) methane (0.01 mole)

and triethylamine (0.02 mole) in benzene (50 ml), cyclohexylphosphonic dichloride (0.01 mole) in benzene (30 ml) was added dropwise at room temperature. The reaction temperature was then gradually raised to 50–60° and stirred for 4 hrs. The progress of the reaction was removed by TLC. The triethylamine hydrochloride salt was removed by filtration and the solvent was distilled under reduced pressure. The residue was washed with water and recrystallized from methanol-benzene mixture (2 : 1) to yield 2.34 g (55%) of Ie as colourless crystals, m.pt. 196–97°C.

Other dioxaphosphocin 8-oxides (Ia-d and If) were synthesized by adopting the above procedure.

2,10-Dichloro-6-iso-propyl-12H-dibenzo [*d*, *g*][1, 3, 2] dioxaphosphocin 6-oxide (IIc)

Iso-propylphosphonic dichloride (0.01 mole) in toluene (30 ml) was added dropwise to a stirred solution of 5,5'-dichloro-2,2'-dihydroxy-biphenyl methane (0.01 mole) and triethylamine (0.02 mole) in toluene (60 ml) at a warm (40–50°) temperature. The reaction mixture was refluxed with stirring for 2 hr. The progress of the reaction was followed by TLC. Triethylamine hydrochloride was removed by filtration and the solvent concentrated in a rotaevaporator. The residue was washed with water and recrystallized from ethanol to obtain 1.99 g (56%) of Ic as colourless crystals, m.pt. 172–173°C.

Other dioxaphosphocin 6-oxides (IIa-b and II-d-f) were synthesized by following the above procedure.

ACKNOWLEDGEMENTS

The authors are thankful to Hindustan Lever Research Foundation, Bombay, for their financial help to CDRI, Lucknow for analytical and spectral data and to Prof. K. D. Berlin of Oklahoma State University, USA, for high resolution mass spectra.

REFERENCES

1. D. F. Heath, *Organophosphorus Poisons*, Pergamon, Oxford (1961).
2. D. L. Hill, *A Review of Cyclophosphamide*, Charles C. Thomas, Springfield, Illinois (1975).
3. S. D. Pastor, J. D. Spivack, P. L. Steishuebel and C. Matzura, *Phosphorus and Sulphurs*, 15, 253 (1983).
4. R. Ismail (Dynamit Nobel), German Patent, 543539, *Chem. Abstr.*, 83, 97416q (1975).
5. L. C. Thomas and R. A. Chittenden, *Chem. Ind.*, (London), 1913 (1951).
6. ———, *Spectrochim Acta*, 20, 489 (1964).
7. M. Halmann, *Spectrochim Acta*, 16, 407 (1960).

8. L. W. Daash and D. C. Smith, *Anal. Chem.*, **23**, 853 (1951).
9. P. A. Odorisio, S. D. Pastor and J. D. Spivack, *Phosphorus and Sulphur*, **15**, 9 (1989).
10. R. Suryanarayana Reddy, Ph.D. thesis, Sri Venkateswara University, Tirupati, India, 1988.
11. D. F. Finney, *Probit Analysis*, Cambridge University Press, London, 20 (1964).

[Received: 11 September 1989; Accepted 10 March 1990]

AJC-149

FIRST INTERNATIONAL CONFERENCE ON FRONTIERS OF POLYMER RESEARCH

First International Conference on Frontiers of Polymer Research is being held at New Delhi during 20-25 January 1991.

For details:

Dr. J. K. Nigam
Director, Shriram Institute for Industrial Research
19, University Road
New Delhi-110 007

SYNTHETIC MEMBRANES AND THEIR APPLICATIONS

A two-day national conference on "Synthetic membranes and their applications" will be organized by the Central Salt & Marine Chemicals Research Institute, Bhavnagar, during 29-30 November 1991 at Bhavnagar.

For further information contact:

Dr. A. V. Rao
Organizing Secretary
National Conference on Synthetic
Membranes and their Applications
Central Salt & Marine Research Institute
Gijubhai Badheka Road
Bhavnagar-364 002, India