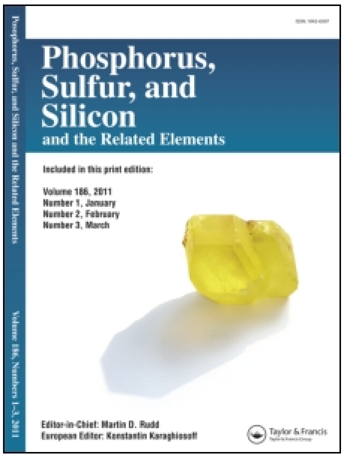


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

12H-DIBENZO[d,g][1,3,2]DIOXAPHOSPHOCINS: Synthesis and Evidence for Long-Range Coupling to Phosphorus

Paul A. Odorisio[a]; Stephen D. Pastor[a]; John D. Spivack[a]; Leander Steinhuebel[a]; Ronald K. Rodebaugh[b]
[a] Research and Development Laboratories Plastics & Additives Division, CIBA-GEIGY Corp., Ardsley, New York [b] Analytical Research Services, CIBA-GEIGY Corp., Ardsley, New York

To cite this Article Odorisio, Paul A. , Pastor, Stephen D. , Spivack, John D. , Steinhuebel, Leander and Rodebaugh, Ronald K.(1983) '12H-DIBENZO[d,g][1,3,2]DIOXAPHOSPHOCINS: Synthesis and Evidence for Long-Range Coupling to Phosphorus', Phosphorus, Sulfur, and Silicon and the Related Elements, 15: 1, 9 — 13

To link to this Article: DOI: 10.1080/03086648308073275

URL: http://dx.doi.org/10.1080/03086648308073275

Phosphorus and Sulfur, 1983, Vol. 15, pp. 9–13
0308-664X/83/1501-0009/$18.50/0

12H-DIBENZO[d,g][1,3,2]DIOXAPHOSPHOCINS: Synthesis and Evidence for Long-Range Coupling to Phosphorus

PAUL A. ODORISIO, STEPHEN D. PASTOR,*
JOHN D. SPIVACK and LEANDER STEINHUEBEL

Research and Development Laboratories, Plastics & Additives Division, CIBA-GEIGY Corp., Ardsley, New York 10502

RONALD K. RODEBAUGH

Analytical Research Services, CIBA-GEIGY Corp., Ardsley, New York 10502

(Received August 3, 1982; in final form September 14, 1982)

The synthesis of the 12H-dibenzo[d,g][1,3,2]dioxaphosphocin ring system from 2,2′-alkylidene bisphenols and phosphorus trichloride is described. The ^{1}H NMR shows evidence for long range through-space coupling of the C-12 methine proton to phosphorus.

INTRODUCTION

Although the 12H-dibenzo[d,g][1,3,2]dioxaphosphocin ring system has appeared in the chemical[1,2] and patent[3–7] literature, neither a detailed account of their synthesis nor spectral characterization has been given. Prior synthetic procedures utilized the reaction of alkylidene bisphenols with phosphorodichloridous esters,[1] phosphorus trichloride followed by reaction with alcohols[3] or sec-amines,[7] and transesterification with triaryl or triaklyl phosphites.[1,4,6] We describe in this paper, the synthesis of the 12H-dibenzo[d,g][1,3,2]dioxaphosphocin ring system and NMR spectral data.

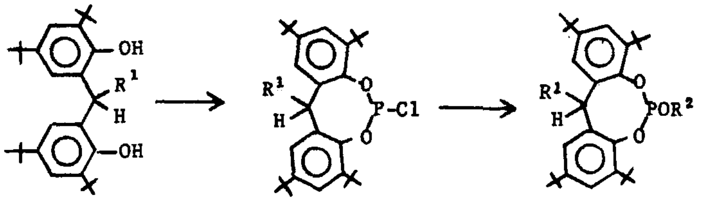
RESULTS AND DISCUSSION

The reaction of 2,2′-methylenebis(4,6-di-*tert*-butylphenol) (**1**)[8] with phosphorus trichloride[3] was found to give the phosphorochloridite (**4**) in 45% recrystallized yield. The chloridite was found to be relatively stable to normal laboratory handling, suggesting that the ortho *tert*-butyl groups sterically hinders hydrolysis of **4** in atmospheric moisture. The steric retardation of associate displacements by large substituents at phosphorus has been studied by Haake *et al.*[9–11]

The reaction of **4** with methyl alcohol utilizing pyridine as an acid scavanger gave the corresponding ester **7**. Alternately, the chloridite could be generated *in situ*, providing a convenient one-pot synthesis of **7**. Similarly, the chloridites **5** and **6** were

---

*Author to whom correspondence should be addressed.



1 R^1 = H
2 R^1 = methyl
3 R^1 = n-propyl

4 R^1 = H
5 R^1 = methyl
6 R^1 = n-propyl

7 R^1 = H, R^2 = methyl
8 R^1 = H, R^2 = benzyl
9 R^1 = R^2 = methyl
10 R^1 = n-propyl, R^2 = methyl
11 R^1 = n-propyl, R^2 = n-octadecyl

formed *in situ* by reaction of the corresponding bisphenol **2**[8] and **3**[12] with phosphorus trichloride and used without further purification.

In the ^{1}H NMR spectrum of **7**, the C-12 (bridging methylene carbon) protons were observed to be non-equivalent, appearing as two doublets. The downfield doublet was further split into a doublet of doublets by phosphorus with $^5J_{HP} = 2.9$ Hz. In a decoupling experiment, irradiation of the aromatic region had no effect on the methylene resonance, demonstrating that the observed coupling is *not* due to the aromatic protons.

Similarly in the ^{1}H NMR spectrum of **9**, the C-12 methine was observed as a doublet of quartets (1 : 3 : 3 : 1 relative intensity) with a $^5J_{HP} = 2.4$ Hz. The chloridite **4** and all of the phosphites showed similar coupling behavior to phosphorus.

The ^{1}H NMR spectra data are consistent with a single conformational isomer being formed, with only one methylene (or methine) proton being coupled to phosphorus. Examination of molecular models suggest a rigid boat-like conformation with one methylene (or methine) proton pointing in towards the lone-pair electron on phosphorus (Figure 1). The larger C-12 and phosphorus substituents appear to point outward to avoid steric interactions.[18] Examination of the reaction mixture prior to workup by TLC shows no evidence for formation of other isomers.

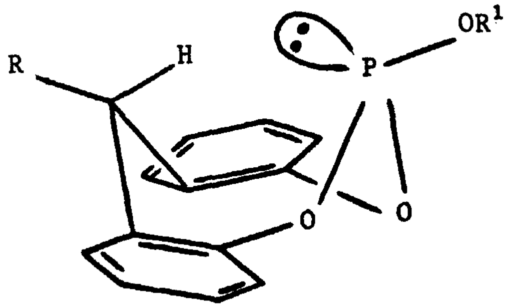


FIGURE 1

The alternate explanations of a mixture of *cis* and *trans* isomers or of two distinct (or interconverting slowly on the NMR time scale) conformational isomers are ruled out by the fact that the sole evidence for it would have to be the methine signal, *no other* signal being split into two separate regions. In accord with this interpretation, the proton decoupled ^{31}P NMR obtained for compounds **7–11** show only a single absorption. Recently, Quin *et al.* have reported a similar non-equivalence of ring carbons in the ^{13}C spectrum of a 9-membered dibenzophosphonin ring.[13] The authors interpreted the NMR non-equivalence as being due to severely restricted motion in the ring imposed by the benzo groups resulting in seemingly equivalent ring carbons being "frozen in a different position with respect to the groups on phosphorus." An additional steric restraint in the present study is imposed by the bulky *tert*-butyl substituents.

The operation of a through-space[14] or a through-bond coupling mechanism has not been established in this study. In phosphorus heterocycles, $^4J_{HP}$ of 3 Hz have been reported and are known to be controlled by steric factors.[15] A large $^4J_{PH}$ of 7.2 Hz was reported by Verkade *et al.* in a 2,6,7-trioxa-1-phosphabicyclo[2.2.2] octane, for which a through-space mechanism was speculated upon.[16] Whereas, Denney *et al.* have reported a $^4J_{HP}$ of 2 Hz in a cyclic six membered phosphate, no coupling was observed in the corresponding phosphite.[17] The large $^5J_{HP}$ along with the interpretation of a rigid ring conformation in the present study suggest the operation of a through-space mechanism.

EXPERIMENTAL

All melting points were determined in open capillary tubes on a Thomas-Hoover melting point apparatus and are uncorrected. Infrared Spectra (1% solution–potassium bromide cells) were recorded on a Perkin-Elmer 710 spectrophotometer. ^1H NMR spectra were taken on Varian model XL-100, T-60 and CFT-20 spectrophotometers. All chemical shifts are reported in ppm relative to tetramethylsilane. ^{31}P NMR spectra were run on a Varian model FT-80 spectrometer and chemical shifts are reported in ppm relative to 85% phosphoric acid (external), where a positive sign is downfield from the standard. Unless noted otherwise, reagents were purchased from Aldrich Chemical Company.

2,4,8,10-Tetra-tert-Butyl-6-Chloro-12H-Dibenzo[d,g][1,3,2]dioxaphosphocin (**4**). In a flame-dried flask under a dry nitrogen atmosphere, a solution of 6.87 g (0.05 mol) of phosphorus trichloride in 100 ml toluene was cooled to 5°C and was treated with a solution of 21.27 g (0.05 mol) of 2,2′-methylenebis(4,6-di-*tert*-butylphenol) and 10.12 g (0.10 mol) of triethylamine in 80 ml of toluene. The reaction mixture was stirred at rt until disappearance of the phenolic OH absorption in the IR spectrum (approximately 2–4 hours) occurred. The resultant suspension was filtered to remove triethylamine hydrochloride and the solvent was removed *in vacuo*.

The residue was recrystallized from heptane to give 11.00 g (45%) of fine white needles, mp 213–218°C; ^1H NMR (deuteriochloroform): δ 1.24 and 1.44 (2 singlets, *tert*-butyls, 18H each), 3.68 (doublet, $^2J_{HCH}$ = 13 Hz, 1H), 4.16 (doublet of doublets, $^2J_{HCH}$ = 13 Hz, $^5J_{HP}$ = 2 Hz, 1H), 7.26 (complex, aromatic, 4H) ^{31}P NMR (benzene-d_6): δ 136.3. Anal. Calcd. for $C_{29}H_{42}ClPO_2$: C, 71.2; H, 8.7. Found: C, 71.4; H, 8.6.

2,4,8,10-Tetra-tert-Butyl-6-Methoxy-12H-Dibenzo[d,g][1,3,2]dioxaphosphocin (**7**). In a flame-dried flask under a dry nitrogen atmosphere, a solution of 13.37 g (0.1 mole) of phosphorus trichloride in 100 ml of toluene was cooled to 5°C and treated with a solution of 42.47 g (0.1 mole) of 2,2′-methylenebis(4,6-di-*tert*-butylphenol) and 20.24 g (0.2 mole) of triethylamine in 150 ml of toluene. The reaction mixture was stirred at rt until disappearance of the phenolic OH absorption in the IR spectrum (approximately 2–4 hours) occurred, and then was cooled to 5°C. The reaction mixture was treated with a mixture of 3.20 g (0.1 mole) of dry methyl alcohol and 7.91 g (0.1 mole) of pyridine. The reaction mixture was stirred 15 hours at rt and the suspension was filtered to remove triethylamine hydrochloride. The solvent was removed *in vacuo*. The residue was recrystallized from heptane/toluene to give 11.13 g (23%) of a white solid, mp 245–248°C; IR (carbon tetrachloride): 1040 cm^{-1} (POC aliphatic stretch); ^{1}H NMR (deuteriochloroform): δ 1.30 and 1.42 (2 singlets, *tert*-butyls, 18H each), 3.42 (doublet, $^{2}J_{HCH}$ = 12.7 Hz, 1H), 4.04 (doublet, methoxy $^{3}J_{POCH}$ = 8.1 Hz, 3H), 4.16 (doublet of doublets, $^{2}J_{HCH}$ = 12.7 Hz, $^{5}J_{HP}$ = 2.9 Hz, 1H), 7.24 (complex, aromatic, 4H); ^{31}P NMR (benzene-d$_6$): δ 129.5. Anal. Calcd. for $C_{30}H_{45}O_3P$: C, 74.4; H, 9.4. Found: C, 74.2; H, 9.3.

6-Benzyloxy-2,4,8,10-Tetra-tert-Butyl-12H-Dibenzo[*d,g*][*1,3,2*]*dioxaphosphocin* (**8**). By the procedure used to prepare compound **7**, compound **8** was prepared from 41.6 g (0.098 mole) of 2,2′-methylenebis(4,6-di-*tert*-butylphenol), 13.4 g (0.098 mole) of phosphorus trichloride, 10.6 g (0.098 mole) of benzyl alcohol, and 29.7 g (0.294 mole) of triethylamine (triethylamine substituted for pyridine). The residue was recrystallized from acetonitrile to give 32 g (58%) of a white solid, mp 178–180°C; IR (carbon tetrachloride): 1020 cm^{-1} (POC aliphatic stretch); ^{1}H NMR (deuteriochloroform): δ 1.33 and 1.45 (2 singlets, *tert*-butyls, 18H each), 3.46 (doublet, $^{2}J_{HCH}$ = 13 Hz, 1H), 4.43 (doublet of doublets, $^{2}J_{HCH}$ = 13 Hz, $^{5}J_{HP}$ = 2 Hz, 1H), 5.49 (doublet, benzylic H, $^{3}J_{POCH}$ = 6 Hz, 2H), 7.36 (complex, aromatic, 9H); ^{31}P NMR (deuteriochloroform): δ 128.7. Anal. Calcd. for $C_{36}H_{49}O_3P$: C, 77.1; H, 8.8; P, 5.5. Found: C, 77.1; H, 9.0; P, 5.4.

2,4,8,10-Tetra-tert-Butyl-6-Methoxy-12-Methyl-12H-Dibenzo[*d,g*][*1,3,2*]*dioxaphosphocin* (**9**). By the procedure used to prepare compound **7**, compound **9** was prepared from 13.73 g (0.1 mole) of phosphorus trichloride, 43.87 g (0.1 mole) of 2,2′-ethylidenebis (4,6-di-*tert*-butylphenol), 3.20 g (0.1 mole) of methyl alcohol, 20.23 g (0.2 mole) of triethylamine, and 7.91 g (0.1 mole) of pyridine. The residue was recrystallized twice, from acetonitrile/toluene and heptane/toluene respectively, to give 6.55 g (13%) of white solid, mp 238–240°C; IR (carbon tetrachloride): 1040 cm^{-1} (POC aliphatic stretch); ^{1}H NMR (deuteriochloroform): δ 1.32 and 1.44 (2 singlets, *tert*-butyls, 18H each), 1.60 (doublet, methyl, $^{3}J_{HCCH}$ = 8 Hz, 3H), 4.08 (doublet, methoxy, $^{3}J_{POCH}$ = 8 Hz, 3H), 4.92 (doublet of quartets, methine, $^{3}J_{HCCH}$ = 8 Hz, $^{5}J_{HP}$ = 2.4 Hz, 1H), 7.28 (complex, aromatic, 4H); ^{31}P NMR (deuteriochloroform$_3$): δ 129.0. Anal. Calcd. for $C_{31}H_{47}O_3P$: C, 74.7, H, 9.5; P, 6.2. Found: C, 74.6; H. 9.3; P, 6.2.

*2,4,8,10-Tetra-tert-Butyl-6-Methoxy-12-*n*-Propyl-12H-Dibenzo*[*d,g*][*1,3,2*]*dioxaphosphocin* (**10**). By the procedure used to prepare compound **7**, compound **10** was prepared from 4.12 g (0.03 mole) of phosphorus trichloride, 14.00 g (0.03 mole) of 2,2′-butylidenebis (4,6-di-*tert*-butylphenol), 0.96 g (0.03 mole) of methyl alcohol, 6.07 g (0.06 mole) of triethylamine, and 2.37 (0.03 mole) of pyridine. The residue was recrystallized from acetonitrile to give 11.28 (71%) of a white crystalline solid, mp 170–175°C; IR (carbon tetrachloride): 1040 cm^{-1} (POC aliphatic stretch); ^{1}H NMR (deuteriochloroform): δ 0.86 (triplet, methyl, 3H), 1.32 and 1.44 (2 singlets, *t*-butyls, 18H each), 2.02 (complex, methylene, 4H), 4.04 (doublet, methoxy, J_{POCH} = 8 Hz, 3H), 4.71 (doublet of triplets, methine, $^{3}J_{HCCH}$ = 8 Hz, $^{5}J_{HP}$ = 2 Hz, 1H), 7.24 (complex, aromatic, 4H). ^{31}P NMR (deuteriochloroform): δ 129.9. Anal. Calcd. for $C_{33}H_{51}PO_3$: C, 75.3; H, 9.8. Found: C, 75.4; H, 9.7.

*2,4,8,10-Tetra-tert-Butyl-6-(*n*-Octadecyloxy)-12-Propyl-12H-Dibenzo*[*d,g*][*1,3,2*]*dioxaphosphocin* (**11**). By the procedure used to prepare compound **7**, compound **11** was prepared from 6.87 g (0.05 mole) of phosphorus trichloride, 23.34 g (0.05 mole) of 2,2′-butylidenebis (4,6-di-*tert*-butylphenol), 13.52 g (0.05 mole) of *n*-octadecyl alcohol, 3.96 g (0.05 mole) of pyridine, and 10.12 g (0.1 mole) of triethylamine. The residue was recrystallized from acetonitrile to give 34.7 g (91%) of a white solid, mp 58–62°C; IR (carbon tetrachloride): 1020 cm^{-1} (POC aliphatic stretch) ^{1}H NMR (deuteriochloroform): δ 0.86 (overlapping triplets, two methyls, 6H), 1.00–2.20 (complex, *t*-butyls and methylenes, 72H) 4.44 (doublet of triplets, $POCH_2$—, $^{3}J_{POCH}$ = 6 Hz, 2H), 4.70 (doublet of triplets, $^{3}J_{HCCH}$ = 8 Hz, $^{5}J_{HP}$ = 2 Hz, methine, 1H), 7.22 (complex, aromatic, 4H) ^{31}P NMR (deuteriochloroform): δ 129.1. Anal. Calcd. for $C_{50}H_{85}O_3P$: C, 78.5; H, 11.2. Found: C, 78.2; H, 11.3.

ACKNOWLEDGEMENT

We thank CIBA-GEIGY Corporation for support and permission to publish this work. The author thanks Drs. Dorothy Z. and Donald B. Denney for reading the manuscript and offering helpful suggestions, and Alice Tarlaian and Teresa Bjorkback for preparation of the manuscript.

REFERENCES AND NOTES

1. V. Kh. Kadyrova, P. A. Kirpichnikov, N. A. Mukmenva, G. P. Gren, and N. S. Kolyubakina, *Z. Obshchei Kim.*, **41**, 1688 (1971).

2. D. G. Pobedimskii and P. A. Kirpichnikov, *J. Polym. Sci., Chem. Ed.*, **18**, 815 (1980).
3. J. D. Spivack, M. Dexter and S. D. Pastor, U.S. Patent #4,318,845 (1982).
4. H. -J. Buysch, B. Brassat, E. Eimers, and K. H. Hermann, U.S. Patent #4,252,750 (1981).
5. S. F. Naumova, M. V. Balykina, Z. I. Akulich, L. V. Velikanova, and T. N. Bolbotunova, U.S.S.R. Patent #749,844; *CA*, **94**, 208613 (1981).
6. D. E. Brown and R. I. McDougall, U.S. Patent #3,297,631 (1967).
7. M. Rasberger, U.S. Patent #4,322,527 (1982).
8. Commercially available from Schenectady Chemicals, Inc., Schenectady, New York 12301.
9. J. Rahil and P. Haake, *J. Org. Chem.*, **46**, 3048 (1981).
10. P. Haake and P. S. Ossip, *J. Amer. Chem. Soc.*, **93**, 6924 (1971) and references cited therein.
11. P. Haake and P. S. Ossip, *Tetrahedron Lett.*, 4841 (1970).
12. G. E. Smith and C. A. Pearson, British Patent #893,162 (1962); *CA*, **57**, 8503 (1962).
13. L. D. Quin, E. D. Middlemas, N. S. Rao, R. W. Miller, and A. T. McPhail, *J. Amer. Chem. Soc.*, **104**, 1893 (1982).
14. For a discussion see (a) F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," p. 146 (Academic Press, 1969, New York); (b) J. Hilton and L. H. Sutcliffe, *Prog. in NMR Spectroscopy*, **10**, 27 (1975).
15. L. D. Quin, "The Heterocyclic Chemistry of Phosphorus," pp. 325–330 (John Wiley, 1981, New York) and references therein.
16. E. J. Boros, K. J. Coskran, R. W. King, and J. G. Verkade, *J. Amer. Chem. Soc.*, **88**, 1140 (1966).
17. D. Z. Denney and D. B. Denney, *J. Amer. Chem. Soc.*, **88**, 1830 (1966).
18. A referee has pointed out that temperature dependent ^1H NMR studies could provide information on isomer interconversion.