

Synthesis and Characterization of Novel Organotin–Phosphorus Compounds

SALEM S. AL-DIAB

Chemistry Department, College of Science, King Saud University, Riyadh-11451, P.O. Box 2455 (Saudi Arabia)

(Received October 12, 1988)

Abstract

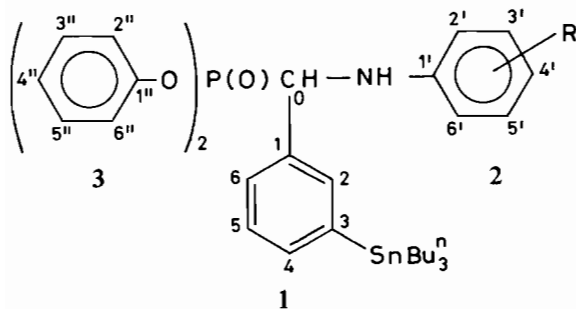
A new organotin substituted alpha-anilino methylphosphonate was prepared and was characterized by ^1H and ^{13}C NMR spectroscopy.

Introduction

Organic phosphorus compounds have become increasingly important in recent years, being used as antioxidants, corrosion-resistance stabilizers and plasticizers, as well as insecticides [1–3]. Introducing biocidal organotin groups [4] into phosphorus compounds could possibly enhance their biocidal activities.

Results and Discussion

A series of novel tri-*n*-butyl stannyl phenyl substituted methylphosphonates via Schiff base have been prepared (X).

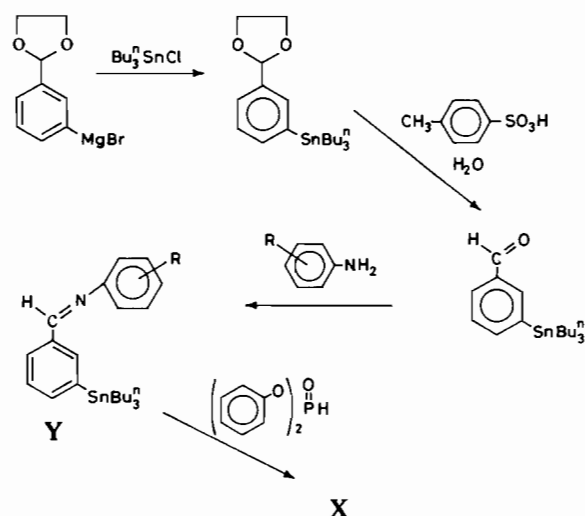


X

when R = H I
 = 3-Cl II
 = 3-Br III
 = 4-Br IV
 R = 3-NO₂ V
 = 3-CH₃ VI
 = 4-CH₃ VII
 = 3,4,5-OCH₃ VIII

The active tin alkyl groups were first attached to the *meta* position of the benzene ring [5] and the resulting aldehyde was then allowed to react with aniline and with a selected substituted aniline [6] such as aniline, *m*-chloroaniline, *m*-bromoaniline, *p*-bromoaniline, *m*-nitroaniline, *m*-toluidine, *p*-tolu-

idine and 3,4,5-trimethoxyaniline giving a highly substituted Schiff base (imines) which is reacted directly with a phosphited ester such as diphenyl phosphite resulting in a solid product (see Scheme 1 and Table 1).



Scheme 1.

TABLE 1. Physical properties of the title compounds

Number	R	Melting point (°C)	Yield (%)
I	H	37–40	55
II	3'-Cl	94.6	43
III	3'-Br	97.7	56
IV	4'-Br	84.4	65
V	3'-NO ₂	86.9	62
VI	3'-CH ₃	58	47
VII	4'-CH ₃	80.6	50
VIII	3',4',5'-OCH ₃	67	63

The title compounds have been isolated in almost quantitative yield. The stoichiometry of the compounds was established by elemental analysis; further evidence was obtained from ^1H and ^{13}C spectra.

Generally the assignments of the ^{13}C resonances for tin-phosphorus compounds (Table 2) in which more than three benzene rings are found are very much more difficult than for the starting compounds [tri-*n*-butyltin chloride, benzaldehyde, *m*-(tri-*n*-butylstannyl)benzaldehyde, aniline, *m*-chloroaniline, *m*-bromoaniline, *p*-bromoaniline, *m*-nitroaniline, *m*-toluidine, *p*-toluidine, 3,4,5-trimethoxyaniline, and diphenyl phosphite] (Table 3), because, excluding the quaternary carbons, the ^{13}C chemical shifts for the ring carbons in 1, 2, and 3 and its derivatives are spread over *c.* 18 ppm, compared with the ^{13}C of the starting material in which only one benzene ring is found.

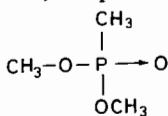
Assignments of the ^{13}C chemical shifts of ring 1, 2 and 3 are based on comparisons with those reported [7–16].

The quaternary carbons C-1, C-3, C'-1, C'-3, C'-4, C'-5 and C"-1 are readily identified since they are less intense and almost invariant in position, compared with other signals as a result of long relaxation times of the quaternary carbons [17, 18]. The ^{13}C spectrum of diphenyl-1-(4-bromoanilino)-1-[3-(tri-*n*-butylstannyl)phenyl]methyl phosphonate in CDCl_3 (Fig. 1), shows that the ^{13}C signal of C_0 appears at δ 53.15 and 59.32 ppm, which indicates a clear spin-spin coupling between ^{31}P and ^{13}C . $^1J(^{31}\text{P}-^{13}\text{C})$, 154 Hz was obtained from the NOE spectrum.

The carbon rings values were confirmed by using the substituent chemical shift (SCS) effect of the $-\text{SnBu}_3$, $-\text{N}-\text{R}$, $(\phi\text{O})_2\text{P}(\text{O})-\text{CH}$ groups on the ring carbons, in comparison with the parent compounds.

However it has been found that the substituent chemical shift (SCS) effects for the above mentioned groups are additive in all positions. It is worth noting that the ^{13}C chemical shift of C_0 in which the phosphorus atom directly, bonded to it generally appears as a doublet centered at δ 55.50 ppm. This doublet is separated by 154.00 Hz. As expected the carbon of C_0 , appears as a single peak coupled with the adjacent phosphorus-31 atom ($I = \frac{1}{2}$, 100%).

^{13}C spin-spin coupling constants involving ^{31}P have been used during the rapid growth of organophosphorus chemistry, particularly for biological molecules such as the nucleotides, phospholipids and the title compounds which contain phosphorus. $^{13}\text{C}-^{31}\text{P}$ spin-spin interactions have frequently been used as a probe and also used to identify carbons near the phosphorus atom. 1J values $^1J(^{31}\text{P}-^{13}\text{C})$ for phosphonates (of analogous system) e.g.



have been reported [19, 20]; $^1J_{\text{CH}}$, 128 Hz; $^1J_{\text{PC}}$, 142.0 Hz ($\text{P}-\text{CH}_3$). The $^1J_{\text{PC}}$ value lower than that observed for the title compounds, $^1J_{\text{PC}}$ 154.00 Hz,

TABLE 2. ^{13}C NMR of the title compounds^a

R group	Sn-CH ₂	-CH ₂ CH ₂ -	-CH ₃	C ₀	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C' ₁	C' ₂	C' ₃	C' ₄	C' ₅	C' ₆	C''	C _{2,6} ^b	C _{3,5} ^b	C ₄	
H	20.01	27.31 13.68	9.57 53.21	59.38 53.21	134.03	136.44	145.71	142.55	129.21	129.68	146.30	114.12	129.50	118.76	126.50	114.12	150.59	150.24	120.76 120.46	129.68 129.68	128.28
3'-Cl	28.96	27.75 13.57	9.57 52.98	59.20 52.98	136.02	136.50	146.82	143.25	128.33	129.51	147.43	113.88	134.98	118.10	129.68	112.24	150.42	150.42	120.70 120.52	130.15 130.15	127.25
3'-Br	29.01	27.31 13.62	9.63 53.98	59.14 53.98	136.20	136.50	142.38	142.32	128.39	129.57	147.13	116.82	123.11	121.52	130.30	112.65	150.53	150.12	120.58 120.34	130.39 130.39	127.80
4'-Br	29.01	27.29 13.63	9.57 53.15	59.32 53.15	136.08	136.61	142.78	142.66	128.33	129.54	144.78	115.64	131.92	110.54	131.64	115.64	150.53	150.42	120.37 120.17	129.74 129.74	127.88
3'-NO ₂	28.96	27.25 13.57	9.57 52.92	59.11 52.92	136.2	136.85	143.13	143.13	128.57	129.97	147.31	107.84	149.18	113.24	129.74	120.46	150.40	150.01	129.22 129.05	120.74 120.74	127.81
3'-CH ₃	29.01	27.31 13.63	9.57 53.21	59.38 53.21	136.44	136.97	142.43	142.43	128.33	129.50	146.37	115.06	138.97	119.26	129.03	120.81	150.53	150.12	120.63 120.40	129.53 129.53	127.92
4'-CH ₃	29.01	27.31 13.62	9.57 53.57	59.73 53.57	134.20	136.44	143.37	142.49	128.214	129.51	143.95	129.51	114.30	127.98	114.51	129.68	150.65	150.53	120.64 120.40	129.69 129.69	127.67
3',4',5'-OCH ₃ ^c	28.96	27.25 13.50	9.57	60.08 53.98	134.27	136.30	142.43	142.43	127.85	128.33	142.61	91.92	153.77	120.35	153.77	91.92	150.53	150.42	120.71 120.58	130.92 130.92	127.81

^a δ c, ppm from TMS. ^bC'_{2,6} and C'_{3,5}, two non-equivalent carbons. ^cC₃ and 5-OCH₃ = 55.74; 4-OCH₃ = 60.97.

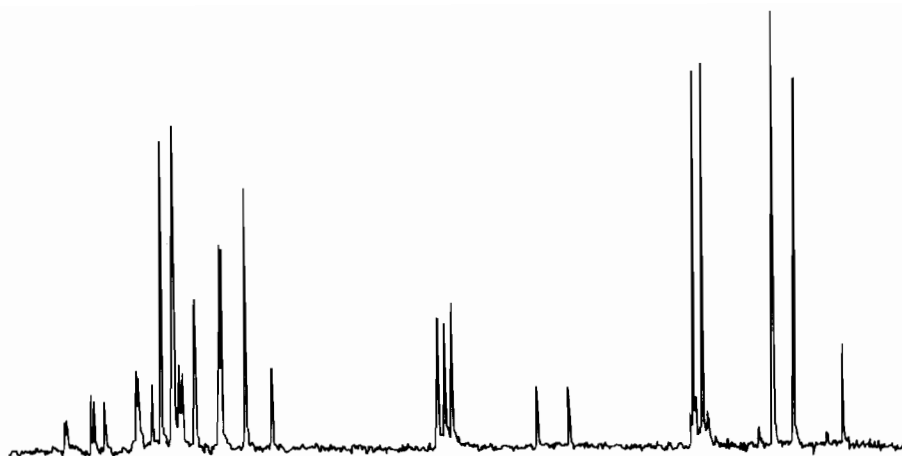


Fig. 1. ^{13}C NMR spectra for diphenyl-1-(4-bromoanilino)-1-[3-(tri-n-butylstannyl)phenyl]methylphosphonate.

The ^{13}C signal of the imine group $-\text{C}=\text{N}$ of compound **Y** (Scheme 1) shows only one signal at δ 161.0 ppm, which indicates the existence of one isomer.

Experimental

Organotin substituted alpha-aniline methyl phosphonate such as diphenyl-1-(4-chloroaniline)-1-[3-(tri-n-butylstannyl)phenyl]methylphosphonate was prepared as follows.

Preparation of 2-[3-(Tri-n-butylstannyl)]1,3-dioxolane

Ten g (0.03 mol) of tri-n-butyl stannyl chloride in 30 ml THF was allowed to react with an equivalent amount of a Grignard reagent prepared from 2-(3-bromophenyl)-2,3-dioxolane. After the reaction was completed the mixture was hydrolyzed and washed with saturated ammonium chloride solution. The organic layer was separated and the aqueous layer was extracted twice with 70 ml of benzene and the combined organic layers were dried over MgSO_4 . The solvents were stripped off using a vacuum aspirator and the remaining liquid was twice fractionally distilled under reduced pressure to give 9.93 g (73% yield).

Preparation of 3-(Tri-n-butylstannyl)benzaldehyde

This was prepared by dissolving 2-[3-(tri-n-butylstannyl)]1,3-dioxolane in 100 ml THF, 50 ml of water and 1 g of *p*-toluenesulfonic acid; the solution was gently refluxed under an inert atmosphere. After 48 h, the organic layer was separated and the aqueous layer was extracted twice with 50 ml portions of benzene and the combined organic layers were dried over MgSO_4 . The solvents were stripped

off and the remaining liquid was fractionally distilled at reduced pressure to give 89–93% yield of a colorless compound, b.p. 140–142 $^\circ\text{C}/0.07$ mmHg.

Preparation of Diphenyl-1-(4-chloroaniline)-1-[3-(tri-n-butylstannyl)phenyl]methylphosphonate

In a 25 ml conical flask, 1.0 g (0.003 mol) of *m*-(tri-n-butylstannyl)benzaldehyde was placed and to this was added one equivalent 0.58 g (0.003 mol) of *p*-bromoaniline. The mixture was gently heated on a hot plate, with occasional stirring to give a Schiff base which was reacted directly with one equivalent 0.7 g (0.003 mol) of diphenyl phosphite, the resulting mixture was stirred until the viscosity of the media increased. After a few ml of methanol were added, the solution was stored in a refrigerator for a few days until a precipitate was formed which was filtered and recrystallized two times from methanol. The resulting product was obtained as a white solid substance in yield up to 63%, m.p. 84.4 $^\circ\text{C}$.

^1H NMR Spectra

^1H NMR spectra were measured on a Jeol JNM FX-100 spectrometer operating in the Fourier transform mode. All the spectra were recorded at ambient temperature.

^{13}C NMR Spectra

Natural abundant ^{13}C NMR spectra were recorded at 25 MHz using a Jeol JNM FX-100 instrument system operating in the Fourier transform mode.

All the spectra were recorded at ambient temperature 25 $^\circ\text{C}$, the compounds dissolved in CDCl_3 (concentration 50 to 100 mg in 2 ml solvent using a 10 mm diameter NMR tube).

Chemical shift data of the ^{13}C NMR spectra were determined relative to the internal standard TMS.

Nuclear Overhouse Enhancement (NOE) Measurements

The absolute NOE determined at 25 MHz was recorded after gating the decoupler to allow interrupted (pulse modulated) ^1H decoupling. Using the technique of decoupling just before the short ^{13}C pulses and during short (≥ 1 s) acquisitions of the free-induction decays, while leaving the decoupler off for the longer ($\leq 4 T_1$) pulse intervals, allowed direct measurements of the NOE values from the ^1H decoupled spectra [17].

Acknowledgements

This research (Chem/1407/03) was supported by the Research Center, College of Science, King Saud University, Riyadh, Saudi Arabia. I would like to thank Dr I. M. Al-Najjar for helpful discussion and M. S. Bakkar for his assistance.

References

- 1 W. Lange and G. Kruegen, *Chem. Ber.*, **65** (1932) 1598.
- 2 H. McCombie, B. C. Saunders and G. J. Stacey, *J. Chem. Soc.*, (1945) 921.
- 3 G. Schrader, *Die Entwicklung Neuer Insektizider Phosphorsäure-Ester*, Verlag Chemie, 1963.
- 4 (a) S. A. Al-Diab, M. A. Barcelon, J. E. Mark and H. Zimmer, paper presented at the 186th American Chemical Society Meeting, March 1983; (b) S. S. Al-Diab, *J. Chem. Res. S*, (1987) 90.
- 5 S. S. Al-Diab, *J. Chem. Res. S*, (1986) 306.
- 6 S. S. Al-Diab, *Ph.D. Thesis*, 1982.
- 7 R. J. Abraham and W. C. Jankowski, *Carbon-13 NMR Spectra*, Wiley Interscience, New York, 1972.
- 8 G. L. Nelson, G. C. Levy and J. D. Carjioli, *J. Am. Chem. Soc.*, **94** (1972) 3088.
- 9 G. H. Yoder, F. K. Shelfey, R. Howell, R. E. Hess, L. Paceta, C. D. Schaeffer and J. J. Zucherman, *J. Org. Chem.*, **41** (1976) 1511.
- 10 D. R. Coulson, *J. Am. Chem. Soc.*, **98** (1976) 3111.
- 11 J. Bromilow, R. T. C. Brownie, R. D. Jopson and R. W. Taft, *J. Am. Chem. Soc.*, **98** (1976) 2020.
- 12 K. Isomura, H. Taniguchi, M. Mishima, N. Fugis and Y. Tsumo, *Org. Magn. Reson.*, **9** (1977) 559.
- 13 B. M. Lynch, *Can. J. Chem.*, **55** (1977) 541.
- 14 G. M. Bodner and M. M. Gaul, *J. Organomet. Chem.*, **101** (1975) 63.
- 15 M. Bullpitt, W. Kitching, W. Adcock and D. Doddrell, *J. Organomet. Chem.*, **116** (1975) 161, 187.
- 16 G. A. Olah and D. J. Donoven, *J. Org. Chem.*, **43** (1978) 880.
- 17 I. M. Al-Najjar and H. B. Amin, *Spectrochim. Acta, Part A*, **43** (1987) 1307.
- 18 S. S. Al-Showiman, A. M. Al-Shalan and I. M. Al-Najjar, *Arab Gulf. Math. Phys. Sci.*, **A5**(3) (1987) 359.
- 19 F. W. Wehrli, *Applications Note*, Varian Assoc., Palo Alto, CA, 1973.
- 20 F. W. Wehrli and T. Wirthlin, *Interpretation of Carbon-13 NMR Spectrum*, Heyden, London, 1978, Ch. 3.
- 21 S. Sorenson, R. S. Hanson and H. J. Jackobsen, *J. Am. Chem. Soc.*, **94** (1972) 5900.
- 22 G. A. Gray and S. C. Remer, *Tetrahedron Lett.*, (1971) 3061.