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Synthesis and Characterization of Diphenyl 1-[3-(Tri-n-butylstannyloxy)phenyl]-1-(aryl and alkyl amino) Methyl Phosphonates

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Abstract. Preparation of new organophosphorus compounds containing an active alkyltin group such as diphenyl 1-[3-(tri-n-butylstannyloxy) phenyl]-1-(aryl and alkyl amino) methyl phosphonates compounds was achieved. The process of preparation involved the reaction of (3-hydroxy-n-benzylidene) aryl or alkyl amines with bis(tri-n-butylstannyl) oxide, giving new imines which were then reacted with diphenyl phosphite. The resulting phosphonates were studied mainly by ^{13}C NMR spectroscopy.

Introduction

Organophosphorus compounds are important compounds because of their practical use in various applications, such as antioxidants, and corrosion-resistance stabilizers and plasticizers [1] [2, p. 164]. Introducing biocidal organotic groups such as a n-butyltin-moiety into phosphorus compounds [2-4] [5, p. 958] could possibly enhance their activities; for this reason, some organotin-phosphorus compounds in the form of phosphonates have been synthesized earlier in which a tri-n-butyltin group was attached directly to a benzene ring [1]. In this work related new compounds (2) have been prepared. The method of preparation involved the preparation of imines (Schiff bases) containing a tri-n-butylstannyloxy group followed by the reaction of the new imines with diphnyl phosphite.

Experimental

General procedure for the preparation of imines and phosphonates containing trialkyltin group.

Preparation of N-(3-tri-n-butylstannyloxy benzylidene) aryl or alkyl amine (la-e)

m-Hydroxy salicylaidehyde [5 g (41 mmole)] in 35 ml methanol has been reacted under reflux with one equivalent of an appropriate aliphatic or aromatic amine for about 1 h. Then the mixture was cooled down and the solvent was evaporated; the remaining liquid was washed with dried petroleum ether and then weighed, dissolved in 150 ml of benzene, and reacted under reflux with one equivalent of bis (tri-n-butyltin) oxide for 3 hr. The reaction mixture was washed twice with (50 ml) of cold water. The organic layer was separated and the aqueous layers were combined and extracted with 50 ml of benzene. The combined organic layers were dried over anhydrous $MgSO_4$, the solvent were stripped off using a vaccum as- pirator, and the remaining liquid was washed with dried petroleum ether giving the desired imines in a quantitative yield.

The crude imines obtained by this procedure were utilized in the next reaction without further purification.

Preparation of diphenyl-1-[3-(tri-n-butylstannyloxy phenyl]-1-[substituted amino] methyl phosphonate (2a-e)

In a 25 ml conical flask, one equivalent of an appropriate imine (containing the trialkyltin group) was placed and to this was added one equivalent of diphenyl phosphite. The resulting mixture was stirred until the viscosity of the media increased. The mixture was then washed with warm petroleum ether several times. The resulting produce was obtained as a highly viscous material in up to 83% yield.

Materials

All the materials used were commercially available compounds.

Instruments

^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 (25°C). The compounds were dissolved in $CDCl_3$.

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

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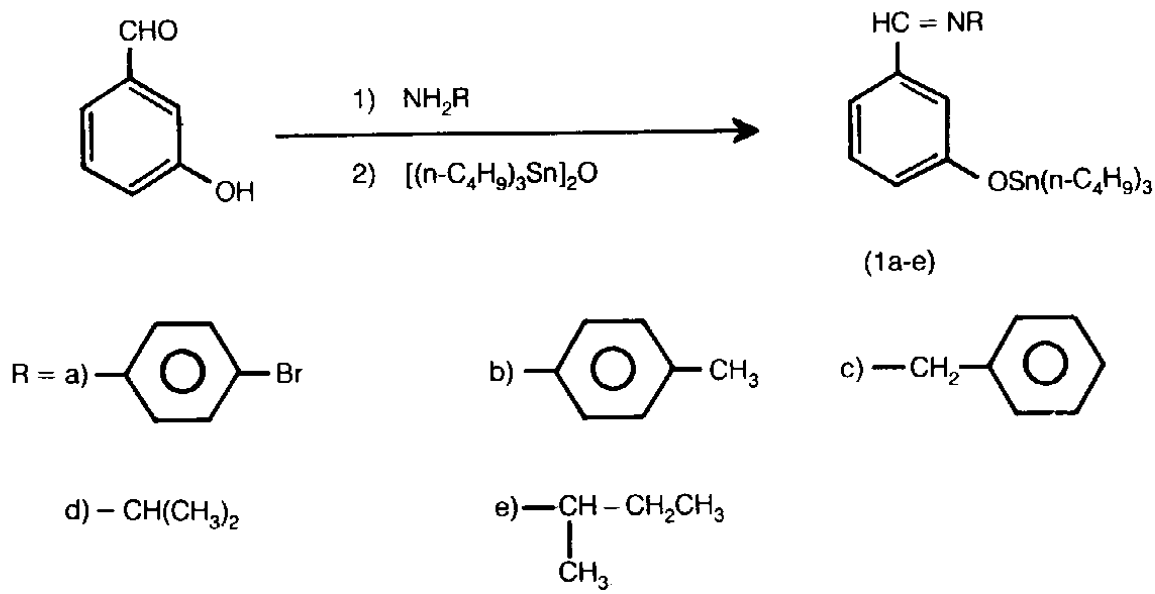
Results and Discussion

Introducing a bulky tri-n-butyltin group to imines has been achieved by reacting N-(3-hydroxy-n-benzylidene) aryl or alkyl amines with bis (tri-n-butyltin) oxide according to the following Scheme.



Scheme 1

The new imines have been studied by uv, ^1H NMR and ^{13}C NMR spectroscopy. The uv spectra have a characteristic absorption band for C = N group (ca. 255-268 nm in CH_2Cl_2). The IR data shows that the absorption of the C=N stretching of the imines occurred in the region 1615-1650 cm^{-1} as one band of each imine. ^1H NMR spectra of the imines show that the CH = N signals appear as a single peak at δ 8.20–8.30 ppm and one set of N-alkyl signals in $CDCl_3$ at 0.92–3.86 ppm. For the case C = N-CH_2-Ph, the CH_2 group occurs at 4.70 ppm. Alkytin signals were spread over 0.80–1.65 ppm and aryl signal spread over δ 6.3–7.3 ppm. ^{13}C NMR chemical shifts show a single peak of the CH = N groups and one set of N-alkyl signals which indicate the existence of only one stereoisomer for the imines in solution.

Study of the chemical shift for C_α(C=N) carbons shows that the C_α carbon is sensitive to the type of groups attached to the nitrogen of imine group (Table 1). Of interest, when the R-group is an aryl group, a considerable down field shift occurred for C_α, δ 161.28 ppm (1a) compared with the compounds where R- is an alkyl group,

= 158.85 ppm. This result comes from the ability of the benzene ring to increase the polarization of (C=N) in the imine bond as a result of delocalization of the unshared electron pair of the nitrogen over the ring and shift the carbon resonance to a lower field. In constrast, the alkyl group will increase the electron density on C_α (more than that of aromatic ring) and shift the carbon resonance to a higher field, Table 1. The ^{13}C NMR chemical shift of the butyl carbons bonded to tin atom of imine compounds are as expected and vary little within the series, Table 2.

Table 1. ^{13}C NMR chemical shift (ppm from TMS) of imine compounds containing trialkyl gorup

Compound No.	C_α	C_1	C_2	C_3	C_4	C_5	C_6	C_1'	$C_{2,6}'$	$C_{3,5}'$	C_4'
1a	161.2	137.3	119.4	162.7	119.6	129.7	123.4	151.4	122.7	132.9	119.2
1b	160.2	137.3	119.4	162.6	120.9	129.7	123.0	149.8	120.9	129.3	135.5
1c*	158.3	137.7	118.8	160.6	121.1	130.0	121.8	138.9	128.4	127.9	126.8
1d	148.8	138.4	118.4	162.6	119.0	129.3	121.7	−CH=61.4		$-CH_3$=24.2	
1e	158.9	138.2	118.5	160.2	119.2	129.4	122.0	−CH=68.0	$-CH_2$ = 22.2	$-CH_3$ =	30.8 11.0

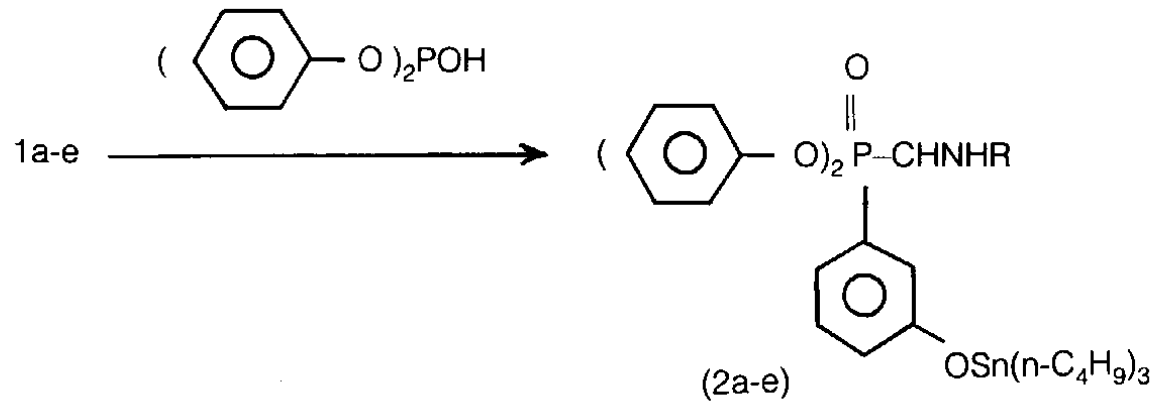
See Table 2

*CH_2 δ = 64.96 **CH_3 δ = 20.96

Table 2. ^{13}C NMR chemical shift (ppm from) of tri-n-butyltin group in various imine compounds

Compound	α $SnCH_2$	β CH_2	γ CH_2	δ CH_3
$[(CH_3CH_2CH_2CH_2)Sn]_2O$	27.96	27.13	16.03	13.63
1a	27.73	27.13	16.21	13.73
1b	27.34	27.07	16.15	13.58
1c	27.71	27.08	16.21	13.63
1d	27.78	27.08	16.27	13.63
1e	27.72	27.08	16.21	13.96

The new organotin-phosphorus compounds were prepared by reacting diphenyphospite with appropriate imines, Scheme 2.



Scheme 2

The yield obtained varied according to the type of R-group, Table 3. Of interest, when R- is an aryl group the products are isolated in a yield up to 83%, however when R is an alkyl group the yields were less (48-55%) for the same reaction conditions.

^{1}H-NMR spectra for phosphonates compounds (2a-e) showed that the α-proton (-CH-NH-) is observed as a doublet of doublet around δ 4.6–5.1 ppm. The coupling is due to the adjacent proton on the nitrogen and the phosphorus atom.

^{13}C-NMR spectra show that the chemical shift of C_α resonates down field [compared to C_α for corresponding imines (1a-e) $^{13}C_\alpha \sim 159.0$, Table 1] and appears as doublet around 52.90 and 59.50 ppm which indicates a clear spin-spin coupling between ^{31}p and ^{13}C, [1] Table 3.

Assignment of ^{13}C chemical shifts of aromatic carbons are straightforward as well as for butyl carbons directly bounded to tin except that the ^{13}C chemical shift of the methylene carbon δ from Sn in phosphonate compounds resonates at a lower field ($^{13}C_\alpha \sim 18.5$ ppm) than that of the starting imine compounds (1a-e)($^{13}C_\alpha \sim 16.2$ ppm, Table 1).

An interesting point which was investigated is the ^{13}C chemical shift of methylene and methyl carbons (γ and δ from Sn atom) in phosphonate compounds (2a-e) (see Table 3) in which the -$SnBu^n_2$ group was attached to the ring through an oxygen atom. The ^{13}C chemical shifts of γ and δ carbons resonate at lower field ($^{13}C_\gamma \sim 18.5$ ppm; $^{13}C_\delta \sim 13.6$ ppm) than that of analogous phosphonate compounds, in which the -$SnBu^n_3$ group was attached directly to the meta position of the phenyl ring ($^{13}C_\gamma \sim 13.7$ ppm, $^{13}C_\delta \sim 9.6$ ppm) [1]. The explanation may relate to the effect of the oxygen atom in the present work which increases the distance between the phenyl

Table 3. Yield and ^{13}C NMR data of organotinphosphorus compounds (2a-e) s containing trialkyl gorup

Compound No.	Yield %	C_α	C_1	C_2	C_3	C_4	C_5	C_6	C'_1	$C'_{2,6}$	$C'_{3,5}$	C'_4	C''_1	$C''_{2,6}$	$C''_{3,5}$	C''_4	$C^{*}\gamma$ $-CH_2-$
2a	83	53.3 59.7	136.6	120.6	156.9	120.0	129.5	125.6	145.0	129.8	115.3	120.3	149.4 –	120.5 119.8	130.0 130.0	127.0 127.0	19.0
2b	78	53.2 59.4	136.4	120.3	156.7	120.3	129.8	125.3	143.9	129.5	114.3	128.3	149.3 149.0	–	130.1 130.0	127.2 127.1	18.3
2c	52	52.9 59.7	136.6	120.8	156.9	120.6	129.7	125.6	138.7	128.9	128.3	126.8	149.7 149.3	129.2 129.5	129.8 129.6	126.8 126.8	18.5
2d	48	53.2 59.0	136.0	120.7	156.8	120.1	129.7	124.9	$-CH=59.8$	$-CH_3=24.9$			150.0 149.5	–	–	127.1 127.1	17.9
2e	55	53.4 59.7	136.3	120.6	156.8	120.2	127.6	126.2	$-CH=68.01$	$-CH_2=$	$-CH_3=$	30.8 11.00	149.8 149.4	129.1 129.0	– –	127.0 127.0	18.9

*^{13}C NMR Chemical shift for α,β,δ carbons are the same of those presented in Table 2.

ring and carbons of the alkyl group attached to Sn-atom which help weakening the ring effect on the resonance of $^{13}C_{\gamma}$ and $^{13}C_{\delta}$ for Ar-o-$SnBu^{n}_{3}$

C,H,N analysis for compounds 2a-e (Table 3) was as follows:

2a (found % C: 56.10; H: 5.63; N: 1.72; $C_{37}H_{47}NPO_4Sn$; requires % C: 55.75; 5.95; N: 1.76).

2b (found % C: 61.53; H: 6.61; N: 1.96; $_{38}H_{50}NPO_4Sn$; requires C: 61.30; H: 6.87; N: 1.91).

2c (found % C: 66.63; H: 7.56; N: 2.03; $C_{34}M_{50}NPO_4Sn$; requires % C: 66.47; H: 7.35; N: 2.04).

2d (found % C: 59.10; H: 7.41; N: 2.02; $C_{34}M_{50}NOP_4Sn$; requires % C: 59.51; H: 7.29; N: 2.04).

2e (found % C: 60.08; H: 7.73; N: 2.02; $C_{35}H_{52}NPO_4Sn$; requires % C: 60.03; H: 7.43; N: 2).

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تحضير ودراسة مركب ١- [٣- (تراي - ن - بيوتيل ستانايل أوكس) فينيل] -١- (أريل والكيل أمينو) ميثيل فوسفونات

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(سُلِّمَ في ١ جمادي الأول ١٤١٣هـ؛ وقُبل للنشر في ٢٥ ذي الحجة ١٤١٣هـ)

ملخص البحث. لقد تم تحضير مركبات عضوفوسفورية جديدة تحتوي على الكيلات القصدير ذات الفعالية الحيوية مثل ١- [٣- (تراي - ن - بيوتيل ستانايل أوكس) فينيل] -١- (أريل والكيل أمينو)، ميثيل فوسفونات وتتضمن طريقة التحضير تفاعل (٣- هيدروكس - ن - بنزايليدين) أريل أو الكيل أمين مع بس (تراي - ن - بيوتيل - ستانايل) أكسيد معطيًا أمينات جديدة ينتج بتفاعلها مع داي فينيل فوسفايت، مركبات الفوسفونات، ولقد تمت دراسة هذه الفوسفونات بشكل رئيس بوساطة طيف الرنين المغناطيس النووي للكربون - ١٣.