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Synthesis and Characterization of 2,4-*di*-methyl-, and 3,4-*di*-methyl-phenol Derivatives of Hexachlorocyclotriphosphazatriene

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Abstract: In this study, the reactions of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$ (**1**) with bulky phenols (**2a** and **2b**) have been reported. For this purpose, two different phenols [2,4-*di*-methyl-phenol (**2a**) and 3,4-*di*-methyl-phenol **(2b)**] were selected. Reactions were carried out preparing sodium salts of phenols in tetrahydrofuran (THF) solvent at a 1:1 molar ratio and under argon atmosphere. Two new mono phenoxy-substituted phosphazene compounds [($N_3P_3Cl_5OC_6H_3$-Me-2,4 (**3**) and $N_3P_3Cl_5OC_6H_3$-Me-3,4 **(4)**] were separated and purified from the reaction mixtures using thin layer and column chromatography techniques. The molecular structures of new compounds were characterized by ^{1}H, ^{13}C, ^{31}P NMR spectroscopy and elemental analyses.

Bulky phenols are widely used as antioxidant. Therefore, it can be expected that the new compounds obtained may show antioxidant activity. Moreover, since the obtained new mono phenoxy-phosphazene derivatives contain five P-Cl bonds, these compounds have potential use in the preparation of new small organocyclophosphazene derivatives.

Hekzaklorosiklotrifosfazatrienin 2, 4-*di*-metil ve 3, 4-*di*-metil-fenol Türevlerinin Sentezi ve Karakterizasyonu

Anahtar Kelimeler
Hekzaklorosiklotrifosfazatrien,
2, 4-*di*-metil-fenol,
3, 4-*di*-metil-fenol,
NMR,
Kromatografi

Öz: Bu çalışmada hacimli fenoller ile hekzaklorosiklotrifosfazatrienin reaksiyonları rapor edildi. Bu amaç için, iki değişik fenol [2,4-*di*-metil-fenol (**2a**) ve 3,4-*di*-metil-fenol **(2b)**] seçildi. Reaksiyonlar argon atmosferi altında 1:1 mol oranında tetrahidrofuran (THF) çözücüsü içinde fenollerin sodyum tuzları hazırlanarak gerçekleştirildi. İki yeni mono fenoksi-sübstitüe fosfazen bileşiği **[**$N_3P_3Cl_5OC_6H_3$-Me-2, 4 **(3)** and $N_3P_3Cl_5OC_6H_3$-Me-3, 4 **(4)]** ince tabaka ve kolon kromatografisi teknikleri kullanılarak reaksiyon karışımlarından ayrıldı ve saflaştırıldı. Yeni bileşiklerin moleküler yapıları ^{1}H, ^{13}C, ^{31}P NMR spektoskopisi ve elemental analiz yöntemleri ile karakterize edildi.

Hacimli fenoller antioksidan olarak yaygın bir şekilde kullanılmaktadır. Bu nedenle elde edilen yeni bileşiklerin antioksidan aktivite göstermesi beklenebilir. Ayrıca elde edilen yeni mono fenoksi-fosfazen türevleri beş tane P-Cl bağı içerdiğinden bu bileşikler yeni küçük organosiklofosfazen türevlerinin hazırlanmasında potansiyel kullanıma sahiptir.

1. INTRODUCTION

One of the most studied and best known heterocyclic compounds are cyclophosphazenes [1-4]. Hexachlorocyclotriphosphazene [$N_3P_3Cl_6$, trimer **(1)**] is a very important compound due to used in synthesis of most halophosphazenes. This compound in the most popular compound in the cyclophosphazene series, and its reactions have been investigated in great detail [5-10]. The physical and chemical properties of cyclotriphosphazene derivatives, depending on of the substituted groups. These derivatives are used in the preparation of functional materials in many fields (science, technology, medical) as antimicrobial, anticancer, antifungal, antibacterial, antitumor, liquid crystals, organic light emitting diodes (OLEDs), flame retardant properties, electrical conductivity, fluorescent chemosensors [11-28].

A large number of reactions of phenols with hexachlorocyclotriphosphazatriene,[$N_3P_3Cl_6$, **(1)**] have been investigated [29-31]. Phenoxy derivatives of compound **(1)** are potentially used in the preparation of many organophosphazene derivatives. These derivatives found variety of applications in science and technology including, nonlinear optical properties, thermal and electrochemical properties, flame retardant, thermal stability [32-35].

In this study, the bulky phenols have been selected as a nucleophile. Bulky phenols are widely used as antioxidants. Because bulky phenols are interested in preparation of stable phenoxyl radicals and biologically active compounds such steric factors of substituents also play a major role in determining the biological activity and effective antioxidant activity of these kind of chemicals via inhibiting lipid peroxidation and lowering the oxidative stress of the organism [36-37].

We have previously reported the reactions of $N_3P_3Cl_6$ with 2, 6-*di*-*tert*-butylphenoxide, 2, 6-*di*-*tert*-butyl-4-methylphenoxide, 2, 4, 6-*tri*-*tert*-butylphenoxide, 2, 4, 6-*tri*-methyl-phenoxide and $N_4P_4Cl_8$ with 2,6-*di*-*tert*-butyl-4-methylphenoxide [38-42].

In the present work have been reported the reactions of $N_3P_3Cl_6$ with the sodium salts of 2, 4-*di*-methyl-phenol, 3, 4-*di*-methyl-phenol. Two new mono- (2,4-*di*-methyl- and 3,4-*di*-methyl-) phenoxy-substituted phosphazene compounds were obtained as majör products. The structures of these obtained compounds were determined by elemental analysis, ^1H, ^{13}C and ^{31}P NMR spectroscopy techniques.

2. MATERIAL AND METHOD

2.1. Experimental

Synthetic steps were carried out under an inert atmosphere by using standard schlenk techniques. Hexachlorocyclotriphosphazatriene, [$N_3P_3Cl_6$], **(1)**, was provided by Aldrich and purified recrystallization from *n*-hexane. 2,4-*Di*-methyl-phenol and 3,4-*di*-methyl-phenol (Aldrich Chemical Co. Ltd.) were used as supplied. The tetrahydrofuran (THF) used as solvent was distilled under argon from sodium benzophenone prior to use. Reactions were observed by using silica gel 60 F_{254} pre-coated Thin Layer Chromatography (TLC) plates (Merck, Kieselgel 60, 0.25 mm thickness) and the separating conditions were determined. The separation of compounds **3** and **4** was achieved by column chromatography using silica gel (Merck, Kieselgel 60, 230–400 mesh, for 3 g crude product, 100 g silica gel in a column, of 3 cm in diameter and 60 cm in lenght).

The structures of **3** and **4** were determined by elemental analyses, ^1H, ^{13}C, ^{31}P NMR spectroscopy and purity of the new compounds was checked by TLC. Microanalysis were carried out with a LECO 932 CHNS-O apparatus. Melting points were measured in open capillary tubes with an Elektrothermal-9100 melting point apparatus and were uncorrected.

^1H (300.13 MHz), ^{13}C (75.47 MHz), and ^{31}P (121.49 MHz) spectra were recorded in $CDCl_3$ solutions a BRUKER 300 MHz spectrometer using 85% H_3PO_4 as an external reference for ^{31}P and TMS as internal reference for ^1H NMR. All data were recorded for solutions in $CDCl_3$. The ^1H- and ^{13}C-NMR chemical shifts were measured using $SiMe_4$ ($\delta=0$) as an internal standard, and the ^{31}P chemical shifts were measured using 85% H_3PO_4 as an external standard.

2.1.1. Synthesis of 2-(2,4-*di*-methylphenoxy)-2,4,4,6,6-pentachlorocyclo-2λ^5, 4λ^5, 6λ^5-triphosphazatriene (3)

General method for the preparation, of phenoxy substituted phosphazenes derivatives 3 and 4 (Figure 1.).

To a solution of the respective phenol (1.05 g; 8.62 mmol) in THF (15 mL) at 20 °C during 0.5 h, metallic Na (0.99 g; 43 mmol) were added under argon atmosphere. The excess of Na was removed by filtration and the solution of the sodium phenoxide was cooled and then frozen with a liquid nitrogen-acetone mixture. To this mixture $N_3P_3Cl_6$ **(1)** (3 g; 8.62 mmol) in 10 mL of THF was added and the resulting mixture was stirred to come to an ambient temperature. The mixture was stirred 48 hour at room temperature, after the precipitated salt (NaCl) was filtered and the solvent was removed with rotary evaporator. Column chromatography was applied to the remaining white solid. The reaction mixture was chromatographed on silica gel: 100 g [eluent: acetone : *n*- hexane 1:3 (for **3**); dichloromethane : *n*- hexane 1:10 (for **4**)].

2-(2, 4-*di*-methylphenoxy)-2,4,4,6,6-pentachlorocyclo-2λ^5, 4λ^5, 6λ^5-triphosphazatriene (3)

Viscous oil; Yield: 0.856 g (23 %). Found: C, 22.60; H, 2.36; N, 9.23 % Calcd for $N_3P_3Cl_5C_8H_9O$ (433.5 g/mol) : C, 22.16; H, 2.07; N, 9.69 %. NMR ($CDCl_3$): ^1H, δ 2.12 (s, 3H, CH_3-*ortho*), 2.33 (s, 3H, CH_3-*para*), 7.00-7.28 (m, 3H, Ar-*H*) (**Figure 3.**); ^{13}C, δ 16.55 (s, 1C, CH_3-*ortho*), 20.82 (s, 1C, CH_3-*para*), 120.63; (s, C(6), phenyl), 127.68; (s, C(2), phenyl), 129.91; (s, C(5), phenyl), 132.38; (s, C(4), phenyl), 136.28; (s, C(3), phenyl), 146.24 (s, 1C, C-ipso) (**Figure 4.**); ^{31}P, AB_2 pattern, δ_A=12.43, δ_B=22.53, $^2J_{AB}$ =59.9 Hz. (**Figure 2.**).

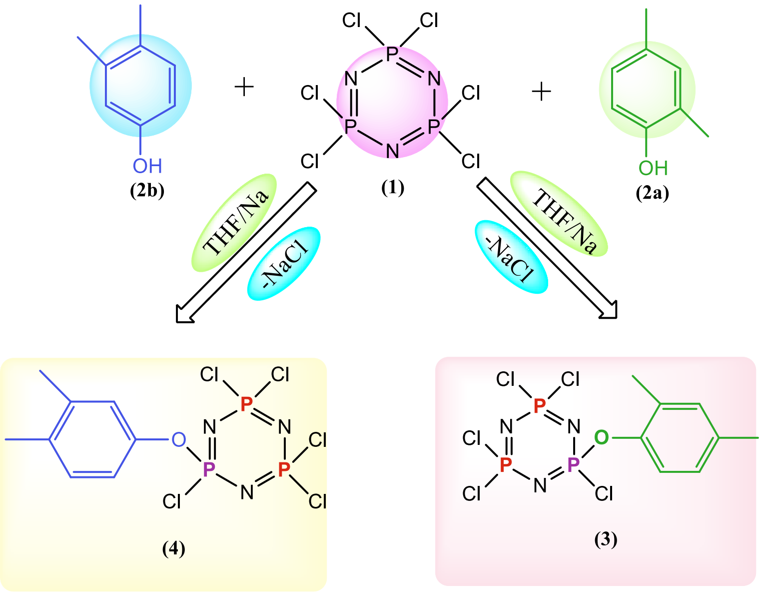

Figure 1. Synthesis of compounds **3** and **4**

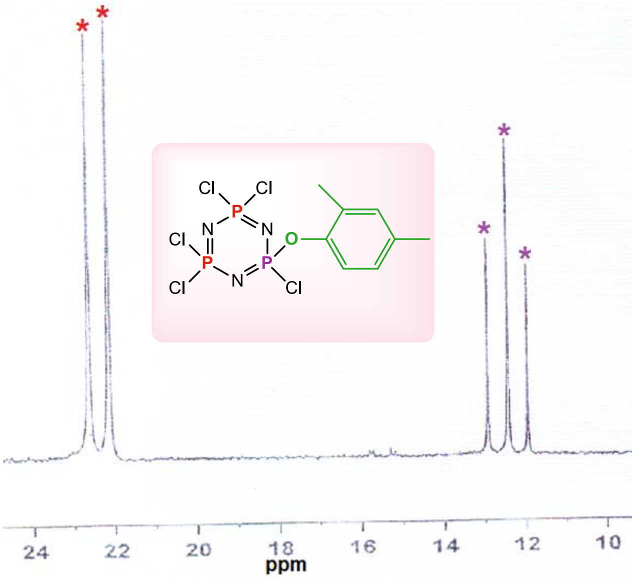

Figure 2. ^{31}P NMR spectra of compound (**3**)

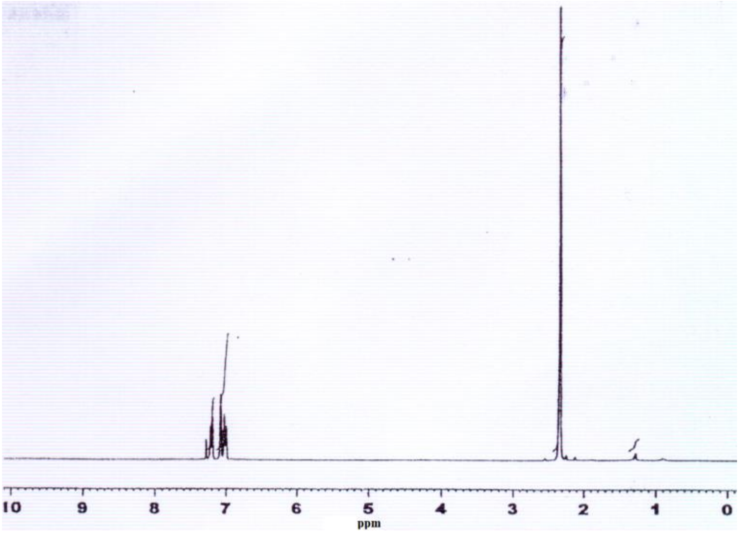

Figure 3. ^{1}H NMR spectra of compound (**3**)

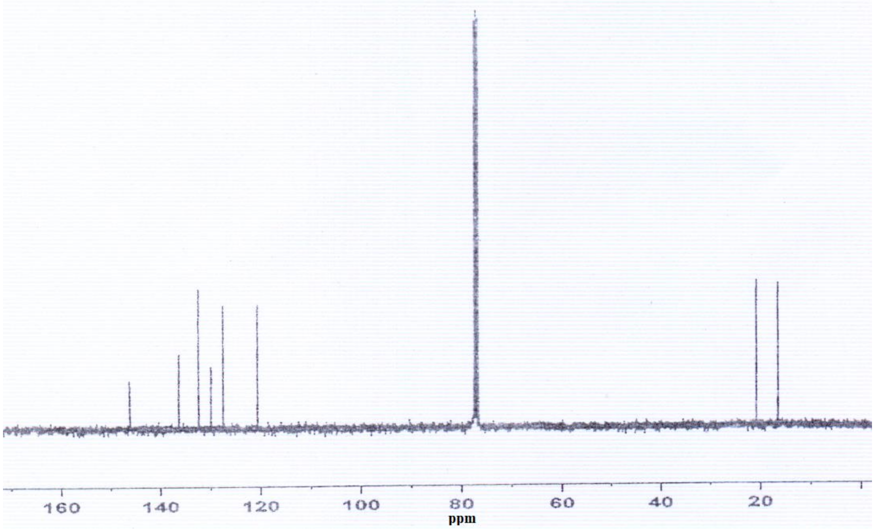

Figure 4. ^{13}C NMR spectra of compound (**3**)

2-(3, 4-*di*-methylphenoxy)-2,4,4,6,6-pentachlorocyclo-2λ^5, 4λ^5, 6λ^5-triphosphazatriene (4)

Viscous oil; Yield: 0,969 g (26 %). Found: C, 22.72; H, 2.54; N, 9.33 % Calcd for

$N_3P_3Cl_5C_8H_9O$ (433.5 g/mol) : C, 22.16; H, 2.07; N, 9.69 %. NMR ($CDCl_3$): ^{1}H, δ 2.25 (s, 3H, CH_3-*para*), 2.28 (s, 3H, CH_3-*meta*), 6.92-7.28 (m, 3H, Ar-*H*); ^{13}C, δ 19.21 (s, 1C, CH_3-*meta*), 19.89 (s, 1C, CH_3-*para*), 118.14 (s, C(6), phenyl), 118.21 (s, C(2), phenyl) , 122.18 (s, C(5), phenyl) , 134.44 (s, C(4), phenyl) , 138,27 (s, C(3), phenyl), 147.87 (s, 1C, C-ipso); ^{31}P, AB_2 pattern, $\delta_A = 12.46$, $\delta_B = 22.43$, $^2J_{AB} = 59.9$ Hz.

3. RESULTS

The reacions of **1** with an equimolar amount of **2a** and **2b** in THF gave the mono-substituted products **3** and **4.** New compounds were isolated as a highly viscous oil from the reaction mixtures by column chromatography. The structures of compounds **3** and **4** were identified by using elemental analyses; ^{1}H-, ^{13}C-, and ^{31}P- NMR spectroscopy. The elemental analyses and NMR results are consisted with the predicted structures as explained in the experimental section. The results of elemental analyses of compounds **3** and **4** showed that one chlorine atoms in phosphazene was replaced by an phenol reactive.

^{1}H NMR spectra of compounds **3** and **4** are relatively simple, but informative. The methyl protons resonate at δ =2.12 (s, 3H, CH_3-para) and 2.33 (s, 3H, CH_3-ortho) (in a 1:1 ratio), 7.00-7.28 (m, 3H, Ar-H) for **3**. For **4**, the protons of methyl group at the meta position and methyl group at the para position gave singlets at δ =2.25 (s, 3H, CH_3-para) and 2.28 (s, 3H, CH_3-ortho) (in a 1:1 ratio), 6.92-7.28 (m, 3H, Ar-H) respectively. The **^{13}**C NMR signals for **3**, (*C*H_3-orto), (*C*H_3-para), (*C*(6)-phenyl, *C*(2)-phenyl, *C*(5)-phenyl, *C*(4)-phenyl, *C*(3)-phenyl and *C*-ipso are observed at 16.55, 20.82, 120.63, 127.68, 129.91, 132.38, 136.28, and 146.24 respectively.

The **^{13}**C NMR signals for **4**, (*C*H_3-meta), (*C*H_3-para), (*C*(6)-phenyl, *C*(2)-phenyl, *C*(5)-phenyl, *C*(4)-phenyl, *C*(3)-phenyl and *C*-ipso are observed at 19.21, 19.89, 118.14, 118.21, 122.18, 134.44, 138.27, and 147.87 respectively.

The ^{31}P NMR spectra of the compounds **3** and **4** showed an AB_2 type spin system because of two differernt phosphorus environments within the molecules. The proton-decoupled ^{31}P NMR spectral data of compounds **3** and **4** were very similar. Chemical shifts were δ PCl(OPh) = 12.43, δ PCl_2= 22.53 in **3**, δ PCl(OPh) = 12.46, δ PCl_2 = 22.43 in **4**. Two bond-coupling constants $^2J_{pp}$ of compounds are the same. This value is 59.9 Hz. All these data are in good agreement with the literature values [43-46].

4. DISCUSSION AND CONCLUSION

In this study, reactions of hexachlorocyclotriphosphazatriene (**1**) with bulky phenols were investigated. The reaction of **1** with an equimolar amount of sodium salts of **2a-b** in THF gave the monosubstituted products (**3** and **4**). Products were isolated by column chromatography.

The structures of two mono-phenoxy-substituted phosphazene derivative compounds (**3** and **4**) are described by ^{1}H, ^{13}C, ^{31}P NMR spectroscopy, and elemental analyses.
The compounds prepared are important. Because bulky phenols have effective antioxidant properties. Therefore, the antioxidant effect of these compounds (**3** and **4**) can be examined in the future.

Additionally, since these compounds contain five P-Cl bonds, they can be used in the synthesis of new phosphazene derivative compounds by interacting with different nucleophiles.

Ethic

There are no ethical issues with the publication of this article.

Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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