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Synthesis of New 2-(1,3-Dithianyl)phenols and Hexakis-[*p*-(1,3-dithian-2-yl)phenoxy]cyclotriphosphazene

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Abstract: 2-Chloro-1,3-dithiane was obtained by the chlorination of 1,3-dithiane with *N*-chlorosuccinimide. Reactions of 2-chloro-1,3-dithiane with various substituted phenols lead to 2-(1,3-dithianyl)phenols (**3**). Hexakis-[*p*-(1,3-dithian-2-yl)phenoxy]cyclotriphosphazene (**6**) was obtained by reaction with hexachlorotriazacyclotriphosphazene (**5**).

Keywords: 1,3,5,2,4,6,-Triazatriphosphorine, 1,3-dithiane, phenol, electrophilic substitution.

Introduction

Only a few examples of direct introduction of a 2-(1,3-dithianyl) group into aromatic compounds were found in literature. Electrophilic aromatic substitution reactions of 2-chloro-1,3-dithiane is of interest since a protected formyl group is introduced in one step. 1,3-Dithiane was used as the sulfide for the preparation of o-aminobenzaldehyde derivatives [1]. Japanese authors described some interesting reactions of 2-chloro-1,3-dithiane with excess phenol or *N*,*N*-dimethylaniline [2]. The highly specific method for the ortho formylation of p-substituted phenols via corresponding 1,3-dithiane was described [3]. Kruse reported on the reactions of 2-chloro-1,3-dithiane with phenols and electron-rich aromatic compounds [4]. The most obvious route to the synthesis of functionalized organophosphazenes is one that involves the reaction of a halogenophosphazene with a functional reagent. Many aryloxyphosphazenes are already known [5,6] , but none has been prepared that bears 1,3-dithianyl units. Trying to use 1,3-dithiane in the chemistry of cyclotriphosphazenes we studied the reaction of 2-(*p*-hydroxyphenyl)-1,3-dithiane, prepared according to lit. [2], with hexachlorocyclotriphosphazene. The nucleophilic reactions of substituted phenols with halophosphazenes in THF in the presence of sodium hydride and catalytical amount of tetrabutylammonium bromide [7] and using 2-butanone as a solvent in the presence of potassium hydrogen carbonate [6] are described. Also the reaction of phosphazenes with sodium or potassium salt of the corresponding phenols in THF [8] or in the mixture THF-DMF [9] are known.

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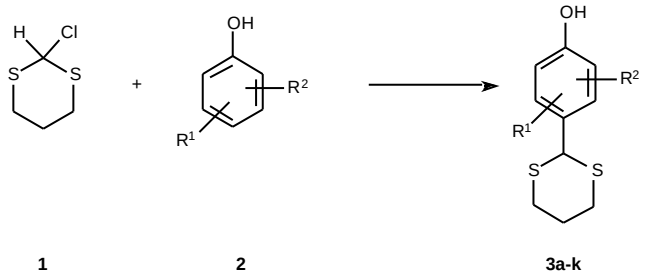


1 **2** **3a-k**

Scheme 1.

Results and Discussion

We found, that using the above mentioned reaction conditions for the preparation of hexasubstituted derivative **6** the reaction did not yield the expected product. In our hands the best results were obtained in a mixture of solvents DMF-acetonitrile in the ratio 2:1, the presence of potassium carbonate and a catalytical amount of sodium iodide. The procedure for preparation of hexakis-[p-(1,3-dithian-2-yl)phenoxy]cyclotriphosphazene using the above conditions led to the required product. The structure of the obtained compound was confirmed by ^{31}P, ^{1}H, ^{13}C NMR spectroscopy and by IR spectra and elemental analysis.

The reaction of 2-chloro-1,3-dithiane with o-, m- and two p-substituted phenols using modified conditions made possible the preparation of new 2-(1,3-dithian-2-yl) phenol derivatives **3a-3k** (Table 1). The synthetized compounds were isolated by column chromatography in 20–40 % yields. Besides the products of electrophilic substitution on aromatic phenol ring we observed also the formation of the well known 1,3-bis(1´,3´-dithian-2-yl-2´-thio) propane and *S*-[3-(1´,3´-dithian-2-yl-2´-thio)]propyl thioformate.

The reaction course was controlled by TLC, after the starting phenol was consumed and the reaction mixture was worked up. The reactions took from 16 to 88 hrs to complete depending on the phenol substituent and its position. 2,6-Dimethylphenol was observed to be the most reactive of all used phenols, m- and p- halo substituted phenols showed unexpected low reactivity. In the case of 4-unsubstituted phenols the reaction took place in that free position. The observed chemical shifts were compared with the calculated ones by ACD/Labs™ for chemistry method with PC computer. They were also compared with chemical shifts, calculated depending on effect of substituent and its position at

Table 1. *Physicochemical data of compounds **3a-k.** The given positions in numbers of the groups are relative to the OH group.*

Compound	R^1	R^2	R	Formula M_r	M.p. °C	Yield %	Calcd/found C	H	S
3a	2-CH_3	6-CH_3	4-dithianyl	$C_{12}H_{16}OS_2$ 240.24	182-185	43	60.00 59.78	6.71 6.56	26.69 26.20
3b	3-CH_3	4-CH_3	6-dithianyl	$C_{12}H_{16}OS_2$ 240.24	129-132	23	60.00 59.45	6.71 6.42	26.69 26.34
3c	3-CH_3	5-C_2H_5	4-dithianyl	$C_{13}H_{18}OS_2$ 254.25	139-141	24	61.42 61.05	7.14 6.88	25.22 25.05
3d	2-*sec*-C_4H_9	H	4-dithianyl	$C_{14}H_{20}OS_2$ 268.26	96-98	19	62.68 62.51	7.51 7.33	23.90 23.85
3e	3-*tert*-C_4H_9	H	6-dithianyl	$C_{14}H_{20}OS_2$ 268.26	112-114	43	62.68 62.44	7.51 7.24	23.90 23.57
3f	2-C_6H_{12}	H	4-dithianyl	$C_{16}H_{22}OS_2$ 294.23	120-123	30	65.31 65.11	7.48 7.50	21.79 21.66
3g	2-CH_3O	H	4-dithianyl	$C_{11}H_{14}O_2S_2$ 242.23	140-143	29	54.54 54.74	5.83 5.67	26.47 26.25
3h	3-*iso*-C_3H_7O	H	4-dithianyl	$C_{13}H_{18}O_2S_2$ 270.25	119-121	19	57.78 57.26	6.71 6.48	23.73 23.60
3i	2-Cl	H	6-dithianyl	$C_{10}H_{11}ClOS_2$ 246.67	103-106	17	48.69 48.30	4.49 4.45	25.99 25.75
3j	4-Br	H	2-dithianyl	$C_{10}H_{11}BrOS_2$ 291.20	136-138	33	41.25 40.97	3.81 3.34	22.02 21.74
3k	3-F	H	4-dithianyl	$C_{10}H_{11}FOS_2$ 231.09	122-123	22	51.98 51.59	4.80 4.78	27.75 27.58

phenol ring [10] using index of ^{13}C NMR Spectra Data. All these data were also used for determination of phenol ring position attacked by the 1,3-dithian-2-yl electrophilic group.

2-(4-Hydroxyphenyl)-1,3-dithiane reacted with hexachlorocyclotriphosphazene in DMF-acetonitrile (2:1) using potassium carbonate as a base and a new hexasubstituted cyclotriphosphazene was prepared in 85% yield. The others prepared 1,3-dithian-2-yl substituted phenols reacted with hexachlorocyclotriphosphazene in a more complicated fashion and these reactions are under study.

Experimental

Melting points were determined on the Kofler hot stage. ^{1}H NMR spectra were obtained with a Tesla BS 487 (80 MHz) instrument and ^{13}C NMR spectra with a Varian VXR-300 (75 MHz) in deuteriochloroform with tetramethylsilane as an internal standard. ^{31}P NMR spectra were measured on a Jeol FX 100 (46 MHz) with phosphoric acid as an internal standard. Chemical shifts are given in ppm (δ-scale). IR spectra were recorded on FTIR PU 9802/25 (Philips) spectrophotometer using KBr technique (ν in cm^{-1}). The TLC analyses were carried out on Silufol 60 F_{254} sheets in the following solvent system: chloroform-methanol 7:3, or 1:1, for phosphazene cyclohexane-benzene 9:1. Spots were detected by UV light at 254 nm, or by spraying with mixture aniline-pyridine 2:1. For column chromatography, silica gel 60–120 μm was used. Starting hexachlorotriazacyclotripho-sphazene (m.p.=113–115°C) was prepared from phosphorus pentachloride by treatment ammonium chloride according to a described procedure [11].

*General procedure for preparation of 2-(1,3-dithianyl)-phenols (**3a-k**)*

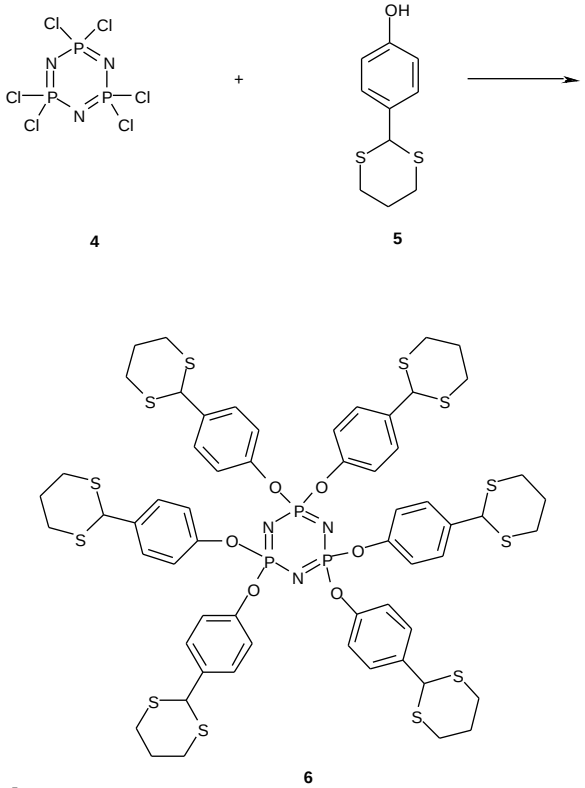
A well stirred solution of 1,3-dithiane (25 mmol) in benzene (60 ml) was cooled to 10 °C, and *N*-chlorosuccinimide (27 mmol) was added under atmosphere of nitrogen. After stirring for 15 min at room temperature the solution of corresponding phenol (25 mmol) in benzene (40 ml) was dropwise added so that the temperature remained within 20 °C to 30 °C. Then the mixture was stirred another 24–96 h at room temperature. The precipitated *N*-succinimide was filtered off and the solvent was evaporated *in vacuo*, the residue was chromatographed on silica gel column (250 g) in chloroform or in chloroform/methanol (7:3,v/v). Yields and spectroscopic data were given in the Tables.

*Hexakis-[*p*-(1,3-Dithian-2-yl)phenoxy]cyclotriphosphazene (**6**)*

A solution of hexachlorotriazacyclotriphosphazene (5 mmol) in acetonitrile (30 ml) was added dropwise during 20 min to a stirred suspension of 2-(*p*-hydroxyphenyl)-1,3-dithiane (30 mmol) potasium carbonate (30 mmol) and sodium iodide (0.2

Table 2. *Measured ^{13}C NMR spectral data of compounds **3a-k***

Compound	^{13}C NMR chemical shifts, δ in ppm
3a	152.3, 130.7, 127.9, 123.3, 51.0, 32.3, 25.2, 15.9
3b	151.6, 138.5, 129.6, 128.6, 120.8, 118.1, 46.4, 31.7, 24.8, 19.4
3c	154.7, 141.1, 137.3, 115.2, 113.6, 48.4, 33.0, 28.1, 25.6, 21.4, 15.6
3d	153.2, 133.6, 131.3, 126.7, 125.9, 115.4, 51.2, 34.0, 32.3, 29.6, 25.0
3e	153.7, 153.5, 128.5, 120.5, 117.8, 114.3, 46.7, 34.5, 31.5, 31.1, 24.7
3f	152.8, 133.9, 131.3, 126.4, 125.9, 115.4, 51.1, 37.2, 32.8, 32.2, 26.9, 26.2
3g	146.5, 145.7, 131.0, 120.8, 114.4, 110.2, 55.9, 51.2, 32.2, 25.0
3h	156.2, 155.7, 130.1, 120.4, 115.0, 102.6, 71.1, 47.7, 43.0, 32.4, 26.8
3i	151.3, 132.4, 128.4, 128.0, 119.4, 116.3, 50.0, 32.0, 24.9
3j	153.6, 132.8, 131.7, 125.8, 119.1, 112.5, 46.6, 31.5, 24.6
3k	164.3, 157.0, 130.2, 118.4, 112.0, 102.7, 42.7, 32.2, 24.9



Scheme 2.

mmol) in dimethylformamide (60 ml). The mixture was heated at 70 °C for 12 h under stirring and exclusion of moisture. The solvent was evaporated *in vacuo* and the residue was extracted with chloroform (100 ml), filtered and the filtrate was concentrated. The residue was chromatographed on silica gel column (200 g) in chloroform-methanol (9:1) to afford 600 mg (85 %) of viscous oil (**6)**.

IR (KBr): 1661, 1512, 1505, 1202, 1184, 1163, 955, 768. ^{1}H NMR ($CDCl_3$): 1.8–2.1(m, 4H), 2.86–3.2(m, 4H), 5.18 (s, 1H), 6.76–7.36 (q, 4H). ^{13}C NMR ($CDCl_3$): 24.5, 31.6, 50.3, 115.4, 128.6, 132.7, 155.4. ^{31}P NMR ($CDCl_3$): 8.64 (s). Anal. Calcd for $C_{60}H_{66}O_6P_3N_3S_{12}$: C, 51.38 H, 4.71 N, 2.99 Found : C, 51.00 H, 4.25 N, 3.17.

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Sample Availability: Samples available from the author.