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PHENOXATHIIN CHEMISTRY. NEW CARBONYL COMPOUNDS AND DERIVATIVES

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ABSTRACT

Starting with 2-acetylphenoxathiin , 2-ω-bromoacetylphenoxathiinyl-10,10-dioxide **2** was obtained. By means of the Kornblum reaction the corresponding glyoxal **4** was synthesized. From compound **2**, the aminothiazole **3** and the 1,4-diketone **7** were also obtained. By the reaction of 2-ω-bromoacetylphenoxathiin **8** and sodium acetylacetonate "one pot" synthesis of 1,4-diketone **9** was performed. Compound **9** was converted to pyrrolophenoxathiin **11** and 1,4-diketone **7**. Starting with the brominated derivative **8** the aminoketones **12** and **13** were obtained. The new compounds were caracterised by spectral methods (^{1}H- and ^{13}C-NMR, IR, MS).

RESUMO

O composto 2-ω-bromoacetilfenoxatiinil-10,10-dioóxido 2 foi obtido a partir de 2-acetilfenoxatiina. Usando a reação de Kornblum, o glioxal correspondente 4 foi sintetizado. A partir do composto 2 foram obtidos o aminotiazol 3 e a dicetona 7. A síntese da dicetona 9 foi obtida reagindo 2-ω-bromoacetilfenoxatiina 8 com acetilacetonato de sódio. O composto 9 foi convertido para a pirolofenoxatiina 11 e a 1,4-dicetona 7. As aminocetonas 12 e 13 foram obtidas a partir do derivado bromado 8. Os novos compostos foram caracterizados usando métodos espectroscópicos (ressonância magnética nuclear de ^{1}H e ^{13}C, infravermelho e espectrometria de massa).

KEYWORD: Phenoxathiin, 1,4-Diketones, Oximes, α-Bromoketones

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INTRODUCTION

Phenoxathiin and its derivatives have been the subject of continnous research because of their multiple uses and because of multiple theoretical problems related to the reactivity of this class of heterocyclic compounds [1-8].

This paper describes the synthesis of carbonyl derivatives based on 2-acetylphenoxathiin as shown in Schemes 1 and 2. Through the action of oxidizing agents (hydrogen peroxide in acetic acid [9], chromic acid [10,11], potassium permanganate[12] or peracetic acid [12]) on the phenoxathiin nucleus the corresponding 10-oxide or 10,10-dioxide are formed.

EXPERIMENTAL PART

Melting points were determined in an open capillary and are uncorrected . IR spectra were recorded in KBr pellet with an UV-20 apparatus. ^{1}H- and ^{13}C-NMR spectra were recorded on a Varian Gemini 300 spectrometer using $CDCl_3$, DMSO-d_6 as solvent and TMS as internal standard. MS spectra were performed on JEOL GCmate spectrometer.

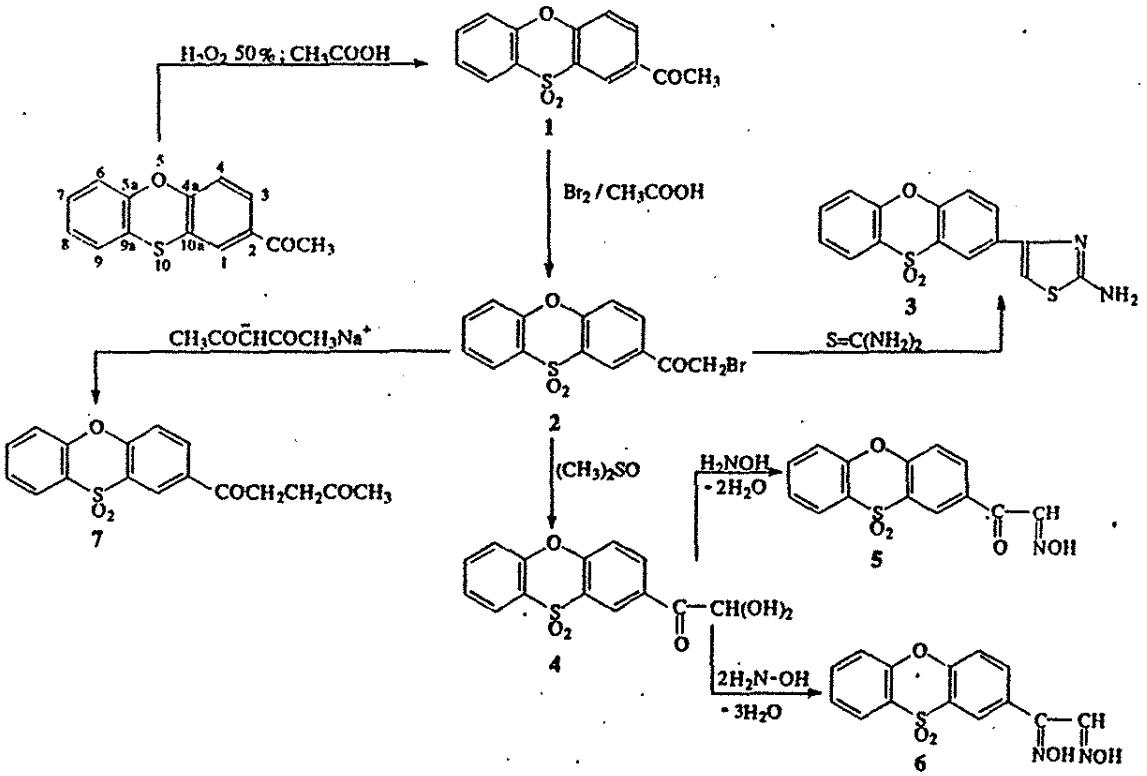
Thin layer chromatography (TLC) was performed on plates of silica gel 60-254 (Merck), unidimenssional technique. Detection of compounds was done by UV light (λ 254 nm), iodine and sulfuric acid spray.

2-Acetylphenoxathiin-10,10-dioxide **1** and 2-ω-bromoacetylphenoxathiin **8** were obtained according to references [18] and [19] respectively.

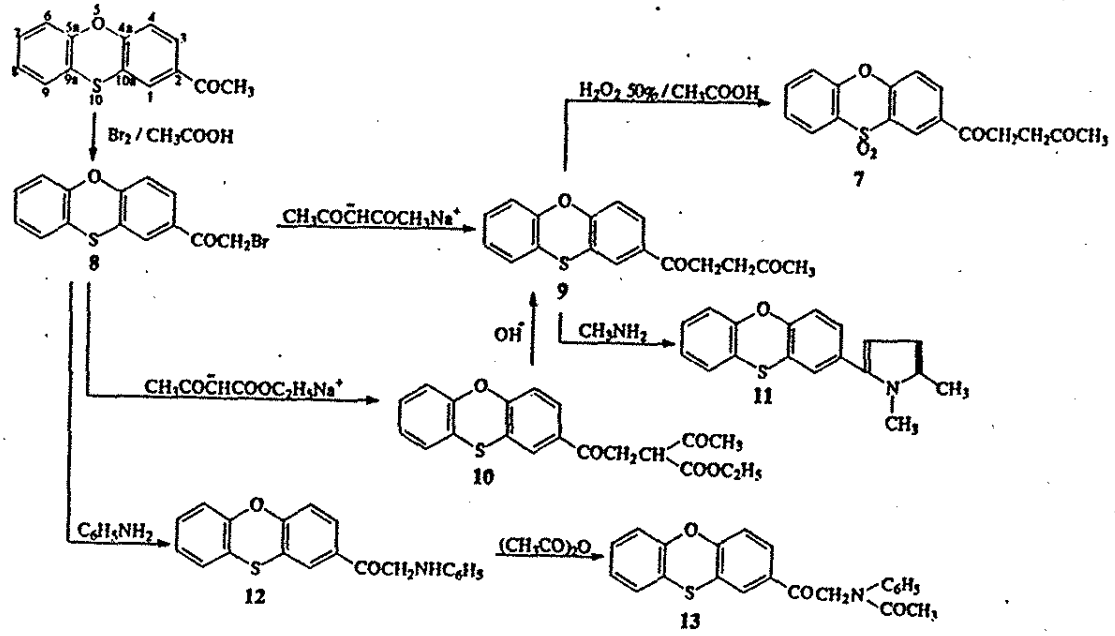
2-ω-Bromoacetylphenoxathiinyl -10,10-dioxide (**2**):

To a heated solution (40-50°) of 10 g (0.036 mole) 2-acetylphenoxathiin-10,10-dioxide in 160 mL glacial acetic acid, 1.9 mL(5.89g; 0.037 mole) bromine in 50 mL glacial acetic acid was added. The solid was filtered after 24 hours, washed with water and dried to give the compound **2** (10.3 g, 79.9%) with m.p. 198-199°. TLC: Rf 0.72 (chloroform : methanol-

SCHEME 1



SCHEME 2



4.5 : 0.5- v/v ; Detection iodine vapors); IR(cm^{-1}): 1700(νCO); 1285, 1140, 560(SO_2); 1210(νC-O-C); 860(γ2CH); 755(γ4CH) (phenoxathiin nucleus). ^{1}H-NMR(DMSO-d_6, δppm): 8.61(s, 1H, H-1); 8.35(d, 1H, H-3); 8.11(d,1H, H-9) ; 7.85(t, 1H, H-7); 7.74(d, 1H, H-4); 7.63(d, 1H, H-6); 7.58(t, 1H, H-8) 5.05(s, 2H, CH_2); ^{13}C-NMR(DMSO-$_6$; δppm): 189.58(CO); 154.02(C-4a); 150.50(C-5a); 135.45(C-3); 134.80(C-7); 130.96(C-2); 126.25(C-1); 124.72(C-8); 124.72(C-10a); 124.34(C-9a); 123.14(C-9); 120.16(C-4); 119.35(C-6); 33.9(CH_2).

Anal. Calcd. for $C_{14}H_9BrO_4S$: S, 9.12; Found: S, 9.26.

4-(2-Phenoxathiinyl-10,10-dioxide)-2-aminothiazole (**3**):

A mixture of 0.5 g (0.0014 mole) 2-ω- bromoacetylphenoxathiin-10,10-dioxide, 0.15 g (0.0019 mole) thiourea and 30 mL anhydrous isopropanol was refluxed on a water bath during an hour. The resulting precipitate was filtered and suspended in 8 mL of water. A solution of 8% sodium hydroxide was added up to pH 9-10. The solid was filtered off and dried giving 0.35 g (76%) of **3** with m.p. 294-296°. TLC: Rf 0.09 (petroleum ether : ethyl ether : dichloromethane : ethyl acetate - 7.5 : 1 : 2 : 1 - v/v/v/v. Detection: iodine vapors). IR (cm^{-1}): 3425, 3375, 3280 (νNH$_2$); 1623, 1470, 1430 (thiazole nucleus); 1280, 1150, 560(SO_2); 1230(νC-O-C); 832(γ2CH); 748(γ4CH) (phenoxathiin nucleus); ^{1}H-NMR(DMSO-d_6; δppm):8.41(d, 1H, H-1); 8.20(dd, 1H, H-3); 8.08(d, 1H, H-9); 7.82(t, 1H, H-7); 7.60(d, 1H, H-4); 7.59(d, 1H, H-6); 7.54(t, 1H, H-8); 7.28(s, 1H, CH-thiazole); 7.20(s, 2H, NH_2); ^{13}C-NMR(DMSO-d_6; δppm): 168.61(thiazole C-2); 150.81(C-5a); 149.57(C-4a); 147.00(thiazole C-4); 135.06(C-2); 132.18(C-7); 131.50(C-3); 125.58(C-8); 124.43(C-1); 124.19(C-10a); 123.04(C-9a); 119.47(C-9); 119.13(C-6); 119.13(C-4); 103.28(thiazole C-5); MS: m/z 330 (M^+, 100%).

Anal. Calcd. for $C_{15}H_{10}N_2S_2O_3$: S, 19.41; Found: S,19.75.

2-(2-Phenoxathiinyl-10,10-dioxide)-glyoxal hydrate (**4**):

A solution of 5 g (0.014 mole) 2-ω- bromoacetylphenoxathiin-10,10-dioxide in 30 mL dimethyl sulfoxide was obtained by heating to 50°. The mixture was maintained for 48 hours at room temperature, then was poured in water. The resulting solid was filtered. The yield was 4.3 g (99.9%) of compound **4**.

Crystals with m.p. 128.5-129.5° were formed by recrystallization from an ethanol-water mixture (1:3 -v/v). TLC: Rf 0.74 (chloroform : methanol-4.5 : 0.5 - v/v; Detection: iodine vapors). IR(cm^{-1}): 3400(νOH); 1700(νCO); 1300, 1160, 555(SO_2); 1275(νC-O-C); 815(γ2CH); 755(γ4CH) (phenoxathiin nucleus)). ^{1}H-NMR(DMSO-d_6, δppm): 8.72(s, 1H, H-1); 8.38(d, 1H, H-3); 8.09(d, 1H, H-9); 7.83(t, 1H, H-7); 7.71(d, 1H, H-4); 7.63(d, 1H, H-6); 7.57(t, 1H, H-8); 7.40 (d, 2H, OH); 5.48 (t, 1H, CH); ^{13}C-NMR (DMSO-d_6, δppm): 192.15(CO); 154.00(C-4a); 150.76(C-5a); 135.51(C-7); 135.51(C-3); 130.30(C-2); 126.30(C-8); 125.51(C-1); 124.56(C-10a); 124.52(C-9a); 123.24(C-9); 119.91(C-4); 119.46(C-6); 96.15 ($CH(OH)_2$).

Anal. Calcd. for $C_{14}H_{10}O_6S$: S, 10.46; Found: S, 10.58

2-(2-Phenoxathiinyl-10,10-dioxide)glyoxal monoxime (**5**):

To 1.1 g (0.0036 mole) of 2-(2-phenoxathiinyl-10,10-dioxide)glyoxal hydrate, 0.25 g (0.0036 mole) hydroxylamine hydrochloride, 6 mL pyridine and 6 mL methanol were added. The mixture was maintained at room temperature for 24 hours and then was poured in ice-water. The precipitate was removed by filtration, washed by water and dried. The yield of product **5** was 0.9 g (82.6 %) with m.p. 165-166°. After four recrystallization from ethanol m.p.186-187° (des.). TLC: Rf 0.69 (chloroform : methanol - 4.5 : 0.5 - v/v; Detection: iodine vapors); IR(cm^{-1}): 1640(νCO); 1230(νC-O-C); 1290, 1155, 515(SO_2); 860(γ2CH); 755(γ4CH) (phenoxathiin nucleus). ^{1}H-NMR(DMSO-d_6; δppm): 8.70(d, 1H, H-1); 8.32(dd, 1H, H-3); 8.09(dd, 1H, H-9); 8.00(s, 1H, CH); 7.85(m, 1H, H-7); 7.71(d, 1H, H-4); 7.62(dd, 1H, H-6); 7.60(m, 1H, H-8); ^{13}C-NMR(DMSO-d_6; δppm): 186.10(CO); 153.53(C-4a); 150.45(C-5a); 148.19(CH=NOH); 135.50(C-3); 135.33(C-7); 132.50(C-2); 126.11(C-8); 125.61(C-1); 124.20(C-10a); 124.06(C-9a); 123.05(C-9); 119.64(C-4); 119.28(C-6).

Anal. Calcd. for $C_{14}H_9O_5NS$: S, 10.57 ; Found: S, 10.61

2-(2-Phenoxathiinyl-10,10-dioxide)glyoxal dioxime (**6**):

To 1.1 g (0.0036 mole) of 2-(2-phenoxathiinyl-10,10-dioxide)glyoxal hydrate were added 0.7 g (0.01 mole) hydroxylamine hydrochloride, 14 mL pyridine and 14 mL methanol. The mixture was refluxed for 2 hours, then cooled off and poured in water. The resulting solid was filtered after 24

hours. After drying 0.91g (79.6%) of compound **5** was obtained, m.p. 204-205°.

Recrystallization from a mixture of ethanol and water (1 : 3 - v/v) gave the compound **6**. m.p. 209-210°. TLC: Rf 0.54 (chloroform : methanol - 4.5 : 0.5 - v/v; Detection: iodine vapors); IR(cm^{-1}): 1590(νC=NOH); 1225(νC-O-C); 1280,1155,520(SO_2); 870(γ2CH); 720(γ4CH) (phenoxathiin nucleus); ^{1}H-NMR(DMSO-d_6; δppm): 11.99 and 11.98 (s, 2H, NOH); 8.25(d, 1H, H-1); 8.09(dd, 1H, H-9); 8.04(dd, 1H, H-3); 7.94(s, 1H, CH); 7.86(m, 1H, H-7); 7.66(d, 1H, H-4); 7.64 (dd, 1H, H-6); 7.56(m, 1H, H-8); ^{13}C-NMR (DMSO-d_6; δppm): 150.77(C-4a); 150.65(C-5a); 148.60 (C=NOH); 147.42 (CH=NOH); 135.21(C-7); 136.00(C-3); 131.10(C-2); 125.79(C-8); 124.36(C-9a); 123.99(C-10a); 123.60(C-1); 123.04(C-9); 119.20(C-6); 118.64(C-4). MS: m/z 318(M^+, 25%).

Anal. Calcd. for $C_{14}H_{10}N_2O_5S$: S, 10.07 ; Found: S, 10.12.

2-[2-(Phenoxathiinyl-10,10-dioxide)carbonyl]ethyl methyl ketone (7):

A. A mixture of 0.97g (0.0027 mole) 2-ω-bromoacetylphenoxathiin-10,10-dioxide, 0.86g (0.007 mole) sodium acetylacetonate and 10 mL anhydrous ethanol was lightly heated during 15 minutes, then poured in water(Note 1). The precipitate was filtered and 0.6 g (66.7%) of compound **7** were obtained. m.p. 145-146°.

Note 1: Any increased of reaction time and strong heating may result in a decrease of the reaction yield.

B. To 0.6 g (0.002 mole) of compound **9** dissolved in 5 mL glacial acetic acid, 1 mL of 50% hydrogen peroxide were added, upon heating, then after 30 minutes another 1 mL 50% hydrogen peroxide was added. The mixture was refluxed for 90 minutes, then was cooled and the precipitate was filtered off. The yield of compound **7** was 0.45 g (68.2%) with m.p. 144-146° (Note 1).

Note 1: If water was added to the filtrate 0.1 g further product was obtained.

2-[2'-(Phenoxathiinyl-10,10-dioxide)carbonyl]ethyl methyl ketone recrystallized from methanol lead to crystals with m.p. 146-147°.TLC: Rf 0.17 (benzene : ethylacetate - 9 : 1 - v/v); IR(cm^{-1}): 1715(νCOCH$_3$); 1685(νCO); 1300, 1150, 565(SO_2); 1275(νC-O-C); 840(γ2CH); 765(γ4CH) (phenoxathiin nucleus).

Anal. Calcd. for $C_{17}H_{14}O_5S$: S, 9.70; Found: S, 9.48.

2-(2-Phenoxathiinylcarbonyl)ethyl methyl ketone (**9**):

A. A mixture of 3.49 g (0.011 mole) 2-ω- bromoacetylphenoxathiin, 3.46 g (0.028 mole) sodium acetylacetonate (Note 1) and 20 mL anhydrous ethanol were refluxed for 30 minutes, then cooled off. The solid was filtered and 3.18 g (98.15%) of product **9** with m.p. 121-122° were obtained.

Note 1: Sodium acetylacetonate was obtained according to reference [16].

B. To 0.55 g (0.0015 mole) of product **10,** 2.5 mL 4% sodium hydroxide was added. The mixture was boiled for 50 minutes. After cooling for 30 minutes at room temperature the solid was filtered and washed with 0.5 mL 12N sulfuric acid. The yield of diketone **9** was 0.14 g (31.8%).

2-(2-Phenoxathiinylcarbonyl)ethyl methyl ketone recrystallized from acetone had the m.p. 126-127°. TLC: Rf 0.33 (Benzene : ethyl acetate - 9:1 - v/v; Detection:sulfuric acid spray - red-violet spot); IR(cm^{-1}):1701(νCOCH$_3$); 1680(νCO); 1270(νC-O-C); 820(γ2CH); 750(γ4CH) (phenoxathiin nucleus); ^{1}H-NMR(DMSO-d_6; δppm): 7.81(d, 1H, H-1); 7.78(dd, 1H, H-3); 7.20-7.26(m, 2H, H-7 and H-9); 7.15(d, 1H, H-4); 7.08-7.13(m, 2H, H-6 and H-8); 3.14 and 2.76(-CH_2-); 2.13(CH_3); ^{13}C-NMR(DMSO-d_6, δppm): 207.02($COCH_3$); 196.65(CO); 154.49(C-4a); 150.32(C-5a); 133.34(C-2); 128.48(C-1); 128.41(C-3); 127.01(C-9); 126.90(C-7); 125.53(C-8); 119.49(C-10a); 118.12(C-9a): 117.77(C-4); 117.70(C-6); 36.6 and 32.01(-CH_2-); 29.65(CH_3); MS: m/z 298 (M^+, 60%).

Anal. Calcd. for $C_{17}H_{14}O_3S$: S, 10.74; Found: S,10.51.

2-(2-Phenoxathiinylcarbonyl)-1-(ethoxycarbonyl)ethyl methyl ketone (**10**):

A mixture consisting of 1.16 g (0.0036 mole) 2-ω- bromoacetyl-phenoxathiin, 1.44 g sodium ethylacetoacetate (Note 1) was lightly heated up to dissolving and further heated for another 5 minutes. A white precipitate was formed which was filtered and the solution was thoroughly cooled. The resulting precipitate was filtered and 0.87 g (65.1%) of compound **9** were obtained with m.p. 88-93° (Note 1).

Note 1 : The sodium ethylacetoacetate was obtained according to reference [20].

Compound **10** recrystallized from anhydrous ethanol has the m.p. 93-94°. TLC: Rf 0.15 (benzene : ethyl acetate - 9 : 1 - v/v; Detection: sulfuric acid spray - blue spot); IR(cm^{-1}): 1735($\nu COOC_2H_5$); 1710($\nu COCH_3$); 1670(νCO); 1275($\nu C\text{-}O\text{-}C$); 815($\gamma 2CH$); 752($\gamma 4CH$) (phenoxathiin nucleus); ^{1}H-NMR (DMSO-d_6; δppm): 7.9(s, 1H, H-1); 7.73(d, 1H, H-3); 7.1-6.96(m, 5H, H-4 - H-9); 4.23(q, 2H, CH_2); 4.11(t, 1H, CH); 3.43(d, 2H, CH_2); 2.36(s, 3H, CH_3); 1.3(t, 3H, CH_3);

Anal. Calcd. for $C_{20}H_{18}O_5S$: S,8.65; Found: S, 8.82.

1,5-Dimethyl-2-(2-phenoxathiinyl)-pyrrole (**11**):

A mixture consisting of 0.75 g (0.0025 mole) diketone **9** and 4 mL ethanol was lightly heated until clearing of the solution after which 4 mL of 30% methylamine and 4 mL ethanol were added. The mixture was heated during 30 minutes at 75-80°, then kept at room temperature for 12 hours. The resulting solid was filtered and 0.72 g (97.3%) of compound **11** with m.p. 113-114° was obtained. The product recrystallized from ethanol has a m.p. 116-117°. TLC: Rf 0.70 (benzene : ethylacetate -9 : 1 -v/v); IR(cm^{-1}): 3450 (νNH_2); 1220($\nu C\text{-}O\text{-}C$); 830($\gamma 2CH$); 755($\gamma 4CH$) (phenoxathiin nucleus); MS: m/z 293(M^+, 100%).

Anal. Calcd. for $C_{18}H_{15}NOS$: S, 10.92; Found: S, 10.76.

2-ω- Anilinoacetylphenoxathiin (**12**):

To 1.62 g (0.005 mole) of 2-ω-bromoacetylphenoxathiin and 10 mL anhydrous ethanol, 1mL (1.07 g; 0.01 mole) of aniline was added. The mixture was stirred at room temperature for 24 hours, then refluxed for 15 minutes. After cooling the mixture was poured in water. The solid was filtered and 1.6 g (95.24%) of compound **12** with m.p. 165-170° was obtained.

The product recrystallised from ethanol led to crystals with m.p. 174-175°. TLC: Rf 0.60(benzene : ethyl acetate - 9 : 1 - v/v; Detection: sulfuric acid spray - violet spot); IR(cm^{-1}): 3380(νNH_2); 1680(νCO); 1270($\nu C\text{-}O\text{-}C$); 820($\gamma 2CH$); 749($\gamma 4CH$) (phenoxathiin nucleus). ^{1}H-NMR(DMSO-d_6; δppm): 7.95(s, 1H, H-1); 7.88(d, 1H, H-3); 7.27-7.18(m, 3H, H-4, H-7 and

H-9); 7.13-7.06(m, 2H, H-6 and H-8); 7.04(t, 2H, H^{metha}-aniline); 6.66(d, 2H, H^{ortho}-aniline); 6.54(t, 1H, H^{para}-aniline); 4.60 (d, 2H, CH_2); 4.35(s, 1H, NH); ^{13}C-NMR(DMSO-d_6; δppm): 194.89(CO); 154.73(C-4a); 150.31(C-5a); 148.01 (C^1-aniline); 131.98(C-2); 128.77(C^{metha}-aniline); 128.53(C-1); 128.44(C-3); 127.05(C-9); 127.02(C-7); 125.59(C-8); 119.60(C-10a); 118.08(C-9a); 117.81(C-6); 117.81(C-4); 116.16(C^{para}-aniline); 112.47(C^{ortho}-aniline); 49.76(CH_2); MS: m/z 333(M^+, 40%).

Anal. Calcd. for $C_{20}H_{15}O_2SN$: S, 9.61; Found: S, 9.40.

2-(ω-N-Acetylanilino)acetylphenoxathiin (**13**):

A mixture of 0.7 g (0.002 mole) of compound **12** and 10 mL acetic anhydride was heated for 4 hours, then maintained at room temperature for 24 hours. The reaction mixture was poured in water and the solid was filtered off and washed with water. The yield was 0.65 g (82.5%) of compound **13**. After recrystallization from acetic acid crystals with m.p. 182-183° were obtained. TLC: Rf 0.15 (benzene : ethyl acetate - 9:1 - v/v ; Detection: sulfuric acid spray - green spot) IR(cm^{-1}): 1690(νCOCH$_3$); 1650(νCO); 1270(νC-O-C); 830(γ2CH); 760(γ4CH) (phenoxathiin nucleus). ^{1}H-NMR(DMSO-d_6; δppm): 7.9(s, 1H, H-1); 7.76(d, 1H, H-3); 7.1-6.96(m, 5H, H-4 - H-9); 7.20-7.00(m, 5H, aniline); 5.08(s, 2H, CH_2); 2.00(s, 1H, CH_3).

Anal. Calcd. for $C_{22}H_{17}NO_2S$: S, 8.91; Found: S, 8.72.

RESULTS AND DISCUSSION

By oxidizing reaction with hydrogen peroxide in acetic acid on 2-acetylphenoxathiin, the corresponding 10,10-dioxide product **1** is obtained (see Scheme 1).

By bromination of compound **1** in acetic acid, 2-ω-bromoacetylphenoxathiin-10,10-dioxide, **2,** is formed.

The brominated derivative is the starting material in the synthesis of compound **3** (through its reaction with thiourea) and upon the Kornblum oxidizing reaction with dimethyl sulfoxide to dicarbonylic compound **4** is obtained which has been characterized by oximes **5** and **6**.

2-ω-Bromoacetylphenoxathiin-10,10-dioxide has been used for the synthesis of a substituted 1,4-diketone **7** (Scheme 1).

The same compound has been also obtained from 2-ω-bromoacetylphenoxathiin **8** (Scheme 2).

The reaction occurs in two steps. The diketone **9** is initially obtained which, oxidized with 50% hydrogen peroxide, turns into compound **7** . The literature described the use of acetylacetone in a two steps synthesis of the $R\text{-}CH_2CH_2COCH_3$ type ketone through an alkylation - splitting method [14,15]. Product **9** has been directly synthesized with sodium acetylacetonate in ethanol medium according to reference [16] applied to phenetyl ketones. This derivative oxidized with hydrogen peroxide turns into compound **7**. Another way for obtaining compound **9** is the reaction between 2-ω-bromoacetylphenoxathiin with sodium ethylacetoacetate when compound **10** is formed . The latter in an alkaline medium turns in substituted 1,4 diketone **9**. The synthesis of derivative **9** has been performe because of the well-known importance of 1,4-diketones which are often used as intermediates for the preparation of heterocycles. Thus, the synthesis of a derivative with a pyrrolic nucleus was performed by the action of methylamine on 1,4-diketonic compound **9** according to the Paal-Knorr reaction [17] resulting in substance **11**.

Substance **12** was obtained from 2-ω-bromoacetylphenoxathiin with aniline in alcohol medium. This compound by treating with acetic anhydride turns into the corresponding acetyl derivative **13**.

The synthesized products were characterized by mass spectrometry, IR and NMR spectra, while purity was confirmed by TLC. The main absorption bands and chemical shifts for the synthesized compounds, as well as the Rf values are presented in the experimental section of the paper.

CONCLUSIONS

Ten new compounds of the phenoxathiin class were synthesized and characterised by chemical and physico-chemical methods.

The "one pot" synthesis of the 1,4-diketones **7** and **9** from the corresponding ω-bromoketones and sodium acetoacetonate was described.

By the Kornblum reaction the glyoxal **4** was synthesized and from this compound the mono- and dioximes **5** and **6** were obtained.

Using methylamine, compound **9** and the Paal-Knorr reaction, the pyrrolophenoxathiin **11** was synthesized.

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