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SYNTHESIS OF NEW 8-PHENYL[1,2]DITHIOLO[1,5-b]NAPHTHO[2,1-d]-[1,2]DITHIOLE-10-S^{IV}, 2,5-DIPHENYL-3,4-DIHYDRO-1,6,6a-TRITHIA-(6a-S^{IV})CYCLOPENTA[cd]PENTALENE AND 2,6-DIPHENYL-4,5-DIHYDRO-3H-[1,2]DITHIOLO[4,5,1-hi][1,2]BENZODITHIOLE-8-S^{IV} DERIVATIVES

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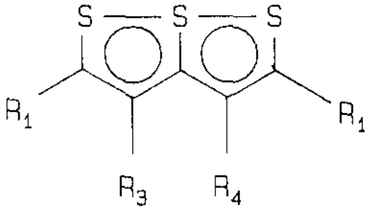
Abstract —— In order to investigate the anti-oxidant properties on lubricant oils, 5,6-dihydro-8-phenyl[1,2]dithiolo[1,5-b]naphtho[2,1-d][1,2]dithiole-10-S^{IV} and a number of phenyl substituted derivatives have been synthesized by cyclization with P_2S_5 of the corresponding 1,3,5-triketones in toluene. Moreover, some 2,5-diphenyl-3,4-dihydro-1,6,6a-trithia(6a-S^{IV})cyclopenta[cd]pentalene and 2,6-diphenyl-4,5-dihydro-3H-[1,2]dithiolo[4,5,1-hi][1,2]benzodithiole-8-S^{IV} derivatives have been synthesized by cyclization with P_2S_5 of the corresponding 2,5-dibenzoylcyclopentanone and 2,6-dibenzoylcyclohexanone derivatives in toluene.

In order to investigate their anti-oxidant properties on lubricant oils, 5,6-dihydro-8-phenyl[1,2]dithiolo[1,5-b]naphtho[2,1-d][1,2]dithiole-10-S^{IV} and a number of phenyl substituted derivatives have been synthesized by cyclization with P_2S_5 of the corresponding 1,3,5-triketones in toluene. Several compounds containing sulfur or other hetero-atoms have been employed on account of their anti-oxidant properties. They are characterized by well-defined chemical structures such as the alkylthiols, thioethers, disulfides, sulfoxides, sulfones, alkylphenol sulfides, aromatic amines, calcium, barium and aluminum dialkyl phosphates, zinc dialkyl and diaryl dithiophosphates[1] . There are also a number of other compounds whose anti-oxidant activities cannot be easily predicted on the basis of their molecular structures. An example of such compounds is given by the thiathiophthene (1) derivatives, where R_1, R_2, R_3 and R_4 may be alkyl, aryl or arylalkyl groups. Many of these derivatives have been tested successfully as anti-oxidant in the mineral oils[2]. For such substances, the mechanism of action in relation to their molecular structures and the fact that they don't show always the same effect with respect of synthetic oils[1] are still to be explained. Taking into account the utility of thiathiophthene derivatives, we have synthesized same of the latter compounds to study their anti-oxidant activities.



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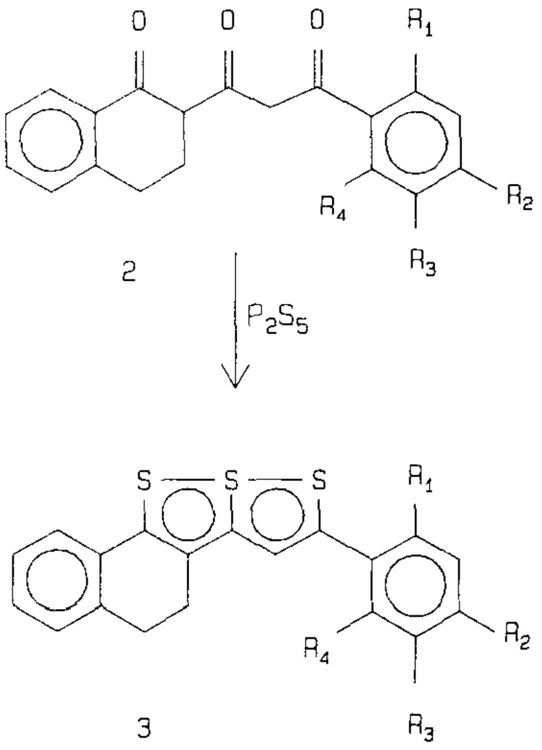
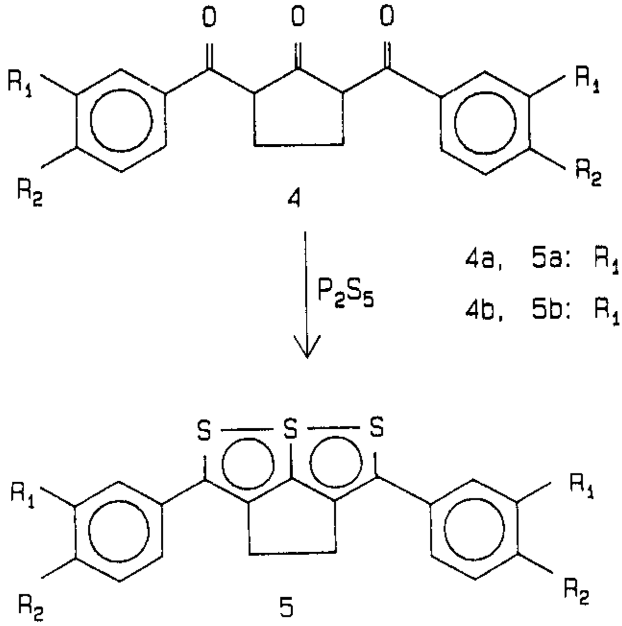
Thiathiophthenes may be obtained from α-dithiopyrones with sodium sulfide in dimethyl sulfoxide (DMSO) and subsequent oxidation by potassium ferricyanide[3]. Behringer and Grimm[4] described the formation of derivatives of 1 by reaction of thioacetic acid with 2,4-pentanedione and various α-acetylenic ketones. Other methods involved several steps[5]. An alternative route for the synthesis of thiothiophthenes is based on the reaction of P_2S_5 with carbonyl compounds[6]. In this paper we report our investigation of the cyclization into thiothiophthenes of a series of 1,3,5-triketones by P_2S_5. The triketones 2a-l were prepared by benzoylation of 2-acetyltetralone with alkyl benzoates in the presence of sodium hydride and using 1,2-dimethoxyethane as solvent[7,8]. When 2-acetyltetralone was allowed to react, under the same experimental conditions, with methyl 2,6-dichlorobenzoate, the following new compounds were obtained: 1-(2,6-dichlorophenyl)-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (2m) and 1-(2-chloro-6-methoxyphenyl)-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (2n). In order to explain the formation of 2n, it has been supposed that in the course of a Claisen-type reaction the leaving methoxyl group causes an aromatic nucleophilic substitution of a chlorine atom adjacent the ester function[8]. In the presence of other solvents such as dioxane, the reaction has always led to the same products so excluding that the methoxyl group arises from the solvent(1,2-dimethoxyethane). Furthermore, in order to synthesize other 1,3,5-triketones, 2,5-bis[4-(1,1-dimethylethyl)benzoyl]cyclopentanone (4a), 2,5-bis(3,4-dimethoxybenzoyl)cyclopentanone (4b) and 2,6-bis-[4-(1,1-dimethylethyl)benzoyl]cyclohexanone (6), were prepared as usual by benzoylation of cyclopentanone or cyclohexanone. The structures of all the triketones obtained have been supported by spectroscopic evidence. The nmr spectra showed signals characteristic of the keto-enolic structures. At this point, all the triketones obtained were easily transformed, in one step, into the corresponding thiathiophthenes.



2a, 3a: R_1, R_2, R_3, R_4 = H
2b, 3b: R_1 = OCH_3; R_2, R_3, R_4 = H
2c, 3c: R_1 = OCH_2CH_3; R_2, R_3, R_4 = H
2d, 3d: R_1 = $OCH_2CH_2CH_3$; R_2, R_3, R_4 = H
2e, 3e: R_1 = Cl; R_2, R_3, R_4 = H
2f, 3f: R_2 = OCH_3; R_1, R_3, R_4 = H
2g, 3g: R_2 = $C(CH_3)_3$; R_1, R_3, R_4 = H
2h, 3h: R_2 = Cl; R_1, R_3, R_4 = H
2i, 3i: R_1, R_3 = Cl; R_2, R_4 = H
2j, 3j: R_1 = OCH_3; R_3 = Cl; R_2, R_4 = H
2k, 3k: R_1 = OCH_2CH_3; R_3 = Cl; R_2, R_4 = H
2l, 3l: R_1 = $OCH_2CH_2CH_3$; R_3 = Cl; R_2, R_4 = H
2m, 3m: R_1, R_4 = Cl; R_2, R_3 = H
2n, 3n: R_1 = Cl; R_4 = OCH_3; R_2, R_3 = H



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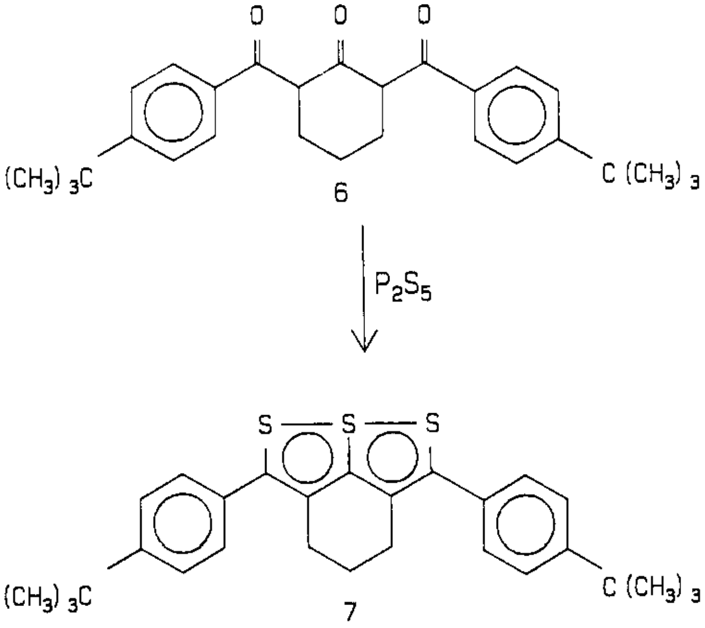
4a, 5a: R_1 = H; R_2 = $C(CH_3)_3$

4b, 5b: R_1, R_2 = OCH_3



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The cyclization of 1,3,5-triketones was carried out by treating a refluxing solution of triketones in toluene with P_2S_5. The compounds were isolated by treatment with ethanol (in which they are little soluble) of the solid material obtained after evaporation of toluene solution previously washed with KOH aqueous and successively with water until neutral. All the compounds gave satisfactory elemental analyses; ir, nmr and mass spectra were in agreement with the structures reported.

EXPERIMENTAL

Melting points were determined on Büchi 510 apparatus and are uncorrected. Ir spectra have been recorded in nujol with a Perkin-Elmer 137 ir spectrophotometer. Nmr spectra have been obtained with a Varian EM-360 at 60 MHz with tetramethylsilane as internal standard. Mass spectra were recorded on a Jeol JMS-10SG-2 mass spectrometer. Elemental analyses were carried out by the Kurt Eder service (Geneve,Suisse).

Synthesis of the 1,3,5-Triketones. General Procedure

A suspension of sodium hydride (dispersion 55-60% in oil) 10.5 g (0.25 mole) in 100 ml of 1,2-dimethoxyethane was added dropwise to a stirred solution of carbonylic compound (2-acetyltetralone, cyclopentanone or cyclohexanone) (0.05 mole) and benzoic ester derivative (0.075 mole for 2-acetyltetralone and 0.15 mole for cyclopentanone or cyclohexanone) in 100 ml of 1,2-dimethoxyethane. The mixture with 2-acetyltetralone was refluxed for 6 h, the mixture with cyclopentanone or cyclohexanone for 2 h. Most of the solvent was then removed under reduced pressure and the pasty residue was cooled to 0 °C in an ice-water bath. Diethyl ether (150 ml) was added. After stirring the mixture for a few min, 100 ml of cold water was added dropwise until the excess sodium hydride was destroyed. The two layers were separated. The ethereal layer was extracted twice with 100 ml of cold 1% aqueous sodium hydroxide. Then 200 g of crushed ice and successively 50 ml of 12 N hydrochloric acid were added at the aqueous extracts combined. The mixture was stirred for 20 min. After filtration, the resinous product obtained was dissolved in chloroform and then washed with water until neutral. After drying (anhydrous sodium sulfate), the solvent was evaporated in vacuo and the residue treated with ethanol to yield a crude product.

1-(2,6-Dichlorophenyl)-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (2m) and 1-(2-chloro-6-methoxyphenyl)-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (2n).

The crude product obtained from the reaction of 2-acetyltetralone with methyl 2,6-dichlorobenzoate was chromatographed over a column of silica gel (cyclohexane/ethyl acetate 95:5) to give 2m and 2n.

Compound 2m had mp 139-140 °C (from ethanol, yield 20%); ir (nujol): 1580-1605 cm^{-1}; ^{1}H-nmr ($CDCl_3$): δ 2.10-3.10 (m,4H,C^3-H and C^4-H); 6.90-8.00 (m,7H,aromatic H); 4.05, 5.75, 15.00 and 16.15 (4s,3H,C^2-H and CO-CH_2-CO, keto-enolic structure); ms:m/z 360 (M^+). Anal.Calcd for $C_{19}H_{14}Cl_2O_3$: C, 63.15; H, 3.87; Cl, 19.66. Found: C, 63.02; H, 4.24; Cl, 19.31.

Compound 2n had mp 102-103 °C (from ethanol, yield 43%); ir (nujol): 1580-1605 cm^{-1}; ^{1}H-nmr ($CDCl_3$): δ 2.30-3.10 (m,4H,C^3-H and C^4-H); 3.80 (s,3H,OCH_3); 6.70-8.00 (m,7H,aromatic H); 4.05, 5.80, 15.10 and 16.30 (4s,3H,C^2-H and CO-CH_2-CO, keto-enolic structure); ms:m/z 356 (M^+). Anal.Calcd for $C_{20}H_{17}ClO_4$: C, 67.32; H, 4.80; Cl, 9.94. Found: C, 67.31; H, 4.98; Cl, 10.31.

2,5-Bis[4-(1,1-dimethylethyl)benzoyl]cyclopentanone (4a).

This compound was obtained in 69% yield from reaction of cyclopentanone with methyl 4-tert-butylbenzoate, mp 160-161 °C (ethanol); ir (nujol): 1590 cm^{-1}; ^{1}H-nmr ($CDCl_3$): δ 1.30 [s,18H,$C(CH_3)_3$]; 2.20-3.20 (m,4H,C^3-H and C^4-H); 7.10-8.20 (m,8H,aromatic H); 4.50, 13.60 and 14.10 (2H,C^2-H and C^5-H keto-enolic structure); ms:m/z 404 (M^+). Anal.Calcd for $C_{27}H_{32}O_3$: C, 80.16; H, 7.97. Found: C, 80.23; H, 8.02.

2,5-Bis(3,4-dimethoxybenzoyl)cyclopentanone (4b).

This compound was obtained in 72% yield from reaction of cyclopentanone with methyl 3,4-dimethoxybenzoate, mp 155-156 °C (ethanol); ir (nujol): 1595-1625 cm^{-1}; ^{1}H-nmr ($CDCl_3$): δ 2.20-3.20 (m,4H,C^3-H and C^4-H); 3.90 (s,12H,OCH_3); 6.70-7.80 (m,6H,aromatic H); 4.50 and 14.70 (2H,C^2-H and C^5-H keto-enolic structure); ms:m/z 412 (M^+). Anal.Calcd for $C_{23}H_{24}O_7$: C, 66.98; H, 5.87. Found: C, 66.99; H, 5.93.

2,6-*Bis*[4-(1,1-dimethylethyl)benzoyl]cyclohexanone (6).

This compound was obtained in 80% yield from reaction of cyclopentanone with methyl 4-*tert*-butylbenzoate, mp 163-164 °C (ethanol); ir (nujol): 1575-1605 cm^{-1}; ^1H-nmr ($CDCl_3$): δ 1.30 [s,18H,$C(CH_3)_3$]; 1.80-2.70 (m,6H,C^3-H, C^4-H and C^5-H); 7.05-8.00 (m,8H,aromatic H); 4.45, 15.55 and 16.55 (2H,C^2-H and C^6-H, keto-enolic structure); ms:m/z 418 (M^+). *Anal*.Calcd for $C_{28}H_{34}O_3$: C, 80.34; H, 8.19. Found: C, 80.36; H, 8.18.

Synthesis of Thiathiophthenes. General Procedure.

P_2S_5 (6g, 0.03 mole) was added slowly to a solution of 1,3,5 triketone (0.01 mole) in toluene (300ml). The resulting suspension was refluxed for 2 h. After cooling the reaction mixture was filtered. The filtrate was treated with 100 ml of 3% aqueous potassium hydroxide and with water (3x100ml) until neutral and evaporated under reduced pressure. The residue was treated with warm ethanol (10ml) and filtered off to yield a crude product.

5,6-Dihydro-8-phenyl[1,2]dithiolo[1,5-*b*]naphtho[2,1-*d*][1,2]-dithiole-10-S^{IV} (3a)

This compound was obtained in 44% yield from reaction of 1-phenyl-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (2a) with P_2S_5; mp 151-152 °C (chloroform-ethanol); ^1H-nmr ($CDCl_3$): δ 3.00-3.40 (m,4H,CH_2-CH_2); 7.30-8.10 (m,9H,aromatic H); 8.25 (s,1H,C^7-H); ms:m/z 338 (M^+). *Anal*.Calcd for $C_{19}H_{14}S_3$: C, 67.41; H, 4.17; S, 28.41. Found: C, 67.21; H, 4.36; S, 28.17.

5,6-Dihydro-8-(2-methoxyphenyl)[1,2]dithiolo[1,5-*b*]naphtho[2,1-*d*][1,2]dithiole-10-S^{IV} (3b).

This compound was obtained in 58% yield from reaction of 1-(2-methoxyphenyl)-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (2b) with P_2S_5; mp 192-193 °C (chloroform-ethanol); ^1H-nmr ($CDCl_3$): δ 2.90-3.20 (m,4H,CH_2-CH_2); 3.80 (s,3H,OCH_3); 6.80-7.35 and 7.40-8.00 (2m,8H,aromatic H); 8.30 (s,1H,C^7-H); ms:m/z 368 (M^+). *Anal*.Calcd for $C_{20}H_{16}OS_3$: C, 65.18; H, 4.38; S, 26.10. Found: C, 65.00; H, 4.51; S, 26.09.

5,6-Dihydro-8-(2-ethoxyphenyl)[1,2]dithiolo[1,5-*b*]naphtho[2,1-*d*][1,2]dithiole-10-S^{IV} (3c).

This compound was obtained in 59 % yield from reaction of 1-(2-ethoxyphenyl)-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (2c) with P_2S_5; mp 157-158 °C (chloroform-ethanol); ^{1}H-nmr ($CDCl_3$): δ 1.45 (t,J=6 Hz,3H,OCH_2-$\underline{CH}_3$); 2.90-3.20 (m,4H,CH_2-CH_2); 4.10 (q,J=6Hz,2H,O$\underline{CH}_2$-CH_3); 6.75-7.40 and 7.60-7.90 (2m,8H,aromatic H); 8.45 (s,1H,C^7H); ms:m/z 382 (M^+). *Anal.*Calcd for $C_{21}H_{18}OS_3$: C, 65.91; H, 4.74; S, 25.16. Found: C, 66.11; H, 4.93; S, 25.30.

5,6-Dihydro-8-(2-propoxyphenyl)[1,2]dithiolo[1,5-b]naphtho[2,1-d][1,2]dithiole-10-S^{IV} (3d).

This compound was obtained in 43 % yield from reaction of 1-(2-propoxyphenyl)-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (2d) with P_2S_5; mp 153-154 °C (chloroform-ethanol); ^{1}H-nmr ($CDCl_3$): δ1.05 (t,J=6 Hz,3H, OCH_2-CH_2-$\underline{CH}_3$); 1.75 (sext,J=6Hz,2H,OCH_2-$\underline{CH}_2$-CH_3); 2.90-3.25 (m,4H,CH_2-CH_2); 4.00 (t,J=6Hz,2H,O$\underline{CH}_2$-CH_2-CH_3); 6.75-7.49 and 7.45-8.00 (2m,8H,aromatic H); 8.45 (s,1H,C^7-H); ms:m/z 396 (M^+). *Anal.*Calcd for $C_{22}H_{20}OS_3$: C, 66.63; H, 5.08; S, 24.25. Found: C, 66.83; H, 5.23; S, 24.28.

8-(2-Chlorophenyl)-5,6-dihydro-[1,2]dithiolo[1,5-b]naphtho[2,1-d][1,2]dithiole-10-S^{IV} (3e).

This compound was obtained in 32 % yield from reaction of 1-(2-chlorophenyl)-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (2e) with P_2S_5; mp 188-189 °C (chloroform-ethanol); ^{1}H-nmr ($CDCl_3$): δ 3.05-3.35 (m,4H,CH_2-CH_2) 7.20-7.70 (m,8H,aromatic H); 8.15 (s,1H,C^7-H); ms:m/z 372 (M^+). *Anal.* Calcd for $C_{19}H_{13}ClS_3$: C, 61.18; H, 3.51; Cl, 9.52; S, 25.73. Found: C, 60.99; H, 3.68; Cl, 9.78; S, 25.51.

5,6-Dihydro-8-(4-methoxyphenyl)[1,2]dithiolo[1,5-b]naphtho[2,1-d][1,2]dithiole-10-S^{IV} (3f).

This compound was obtained in 37% yield from reaction of 1-(4-methoxyphenyl)-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (2f) with P_2S_5; mp 139-140 °C (chloroform-ethanol); ^{1}H-nmr ($CDCl_3$): δ3.00-3.30 (m,4H, CH_2-CH_2); 3.90 (s,3H,OCH_3); 7.00 and 7.90 (2d,J=9Hz,4H,aromatic H); 7.25-7.60 and 7.75-8.05 (2m,4H,aromatic H); 8.20 (s,1H,C^7-H); ms:m/z 368 (M^+). *Anal.*Calcd. for $C_{20}H_{16}OS_3$: C, 65.18; H,4.38; S, 26.10. Found: C, 65.42; H, 4.58; S, 26.04.

8-[4-(1,1-Dimethylethyl)phenyl]-5,6-dihydro-[1,2]dithiolo(1,5-*b*)naphtho[2,1-*d*]-[1,2]-dithiole-10-S^{IV} (3g).

This compound was obtained in 44% yield from reaction of 1-[4-(1,1-dimethylethyl)phenyl]-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (*2g*) with P_2S_5; mp 163-164 °C (chloroform-ethanol); ^{1}H-nmr ($CDCl_3$): δ 1.30 (s,9H,$C(CH_3)_3$; 3.00-3.30 (m,4H,CH_2-CH_2); 7.10-7.55 and 7.65-7.90 (2m,4H,aromatic H); 7.35 and 7.75 (2d,J=9Hz,4H,aromatic H); 8.10 (s,1H,C^7-H); ms:m/z 394 (M^+). *Anal*.Calcd for $C_{23}H_{22}S_3$: C, 70.00; H, 5.62; S, 24.37. Found: C, 70.18; H, 5.80; S, 24.29.

8-(4-Chlorophenyl)-5,6-dihydro-[1,2]dithiolo[1,5-*b*]naphtho[2,1-*d*][1,2]dithiole-10-S^{IV} (3h).

This compound was obtained in 45% yield from reaction of 1-(4-chlorophenyl)-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (*2h*) with P_2S_5; mp 175-176 °C (chloroform-ethanol); ^{1}H-nmr ($CDCl_3$): δ 3.00-3.40 (m,4H, CH_2-CH_2); 7.30-7.70 and 7.80-8.10 (2m,4H,aromatic H); 7.55 and 7.95 (2d,J=9Hz,4H, aromatic H); 8.30 (s,1H,C^7-H); ms:m/z 372 (M^+). *Anal*.Calcd for $C_{19}H_{13}ClS_3$: C, 61.19; H,3.51; Cl, 9.51; S, 25.79. Found: C, 60.93; H, 3.79; Cl, 9.42; S, 25.48.

8-(2,5-Dichlorophenyl)-5,6-dihydro-[1,2]dithiolo[1,5-*b*]naphtho[2,1-*d*][1,2]dithiole-10-S^{IV} (3i).

This compound was obtained in 32 % yield from reaction of 1-(2,5-dichlorophenyl)-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (*2i*) with P_2S_5; mp 131-132 °C (chloroform-ethanol); ^{1}H-nmr ($CDCl_3$): δ 2.95-3.20 (m,4H, CH_2-CH_2); 7.15-7.40 and 7.45-7.55 (2m,7H,aromatic H); 8.00 (s,1H,C^7-H); ms:m/z 406 (M^+). *Anal*. Calcd for $C_{19}H_{12}Cl_2S_3$: C, 56.01; H, 2.97; Cl, 17.41; S, 23.61. Found: C, 56.05; H, 2.99; Cl, 17.17; S, 23.69.

8-(5-Chloro-2-methoxyphenyl)-5,6-dihydro-[1,2]dithiolo[1,5-*b*]naphtho[2,1-*d*]-[1,2]dithiole-10-S^{IV} (3j).

This compound was obtained in 39 % yield from reaction of 1-(5-chloro-2-methoxyphenyl)-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (*2j*) with P_2S_5; mp 205-206 °C (chloroform-ethanol); ^{1}H-nmr ($CDCl_3$): δ 3.05-3.30 (m,4H,CH_2-CH_2); 3.95 (s,3H,OCH_3) 6.90-7.80 (m,7H,aromatic H); 8.40 (s,1H,C^7-H);

ms:m/z 402 (M$^+$). *Anal*.Calcd for $C_{20}H_{15}ClOS_3$: C, 59.61; H, 3.75; Cl, 8.80; S, 23.87. Found: C, 59.71; H, 4.00; Cl, 9.03; S, 23.86.

8-(5-Chloro-2-ethoxyphenyl)-5,6-dihydro-[1,2]dithiolo[1,5-*b*]naphtho[2,1-*d*]-[1,2]dithiole-10-S^{IV} (3k).

This compound was obtained in 41 % yield from reaction of 1-(5-chloro-2-ethoxyphenyl)-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (**2k**) with P_2S_5 ; mp 177-178 °C (chloroform-ethanol); ^{1}H-nmr ($CDCl_3$): δ 1.45 (t, J=7 Hz,3H,OCH_2-$\underline{CH_3}$); 2.95-3.25 (m,4H,CH_2-CH_2); 4.10 (q, J=7Hz,2H,$O\underline{CH_2}$-CH_3); 6.70-7.90 (m,7H,aromatic H); 8.40 (s,1H,C^7-H); ms:m/z 416 (M$^+$). *Anal*.Calcd for $C_{21}H_{17}ClOS_3$: C, 60.48; H, 4.11; Cl, 8.50; S, 23.07. Found: C, 60.52; H, 4.13; Cl, 8.44; S, 22.88.

8-(5-Chloro-2-propoxyphenyl)-5,6-dihydro-[1,2]dithiolo[1,5-*b*]naphtho[2,1-*d*]-[1,2]dithiole-10-S^{IV} (3l).

This compound was obtained in 42 % yield from reaction of 1-(5-chloro-2-propoxyphenyl)-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (**2l**) with P_2S_5 ; mp 134-135 °C (chloroform-ethanol); ^{1}H-nmr ($CDCl_3$): δ 1.05 (t, J=7 Hz,3H,OCH_2-CH_2-$\underline{CH_3}$); 1.80 (sext, J=7Hz,2H,OCH_2-$\underline{CH_2}$-CH_3); 2.80-3.30 (m,4H,CH_2-CH_2); 3.95 (t, J=7Hz,2H,$O\underline{CH_2}$-CH_2-CH_3); 6.60-7.90 (m,7H,aromatic H); 8.40 (s,1H,C^7-H); ms:m/z 430 (M$^+$). *Anal*.Calcd for $C_{22}H_{19}ClOS_3$: C, 61.28; H, 4.44; Cl, 8.23; S, 22.34. Found: C, 61.43; H, 4.53; Cl, 8.29; S, 22.38.

8-(2,6-Dichlorophenyl)-5,6-dihydro-[1,2]dithiolo[1,5-*b*]naphtho[2,1-*d*]-[1,2]dithiole-10-S^{IV} (3m).

This compound was obtained in 22 % yield from reaction of 1-(2,6-dichlorophenyl)-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (**2m**) with P_2S_5 ; mp 187-188 °C (chloroform-ethanol); ^{1}H-nmr ($CDCl_3$) δ 2.80-3.20 (m,4H,CH_2-CH_2); 6.75 (s,1H,C^7-H); 7.10-7.45 and 7.60-7.90 (m,7H,aromatic H); ms:m/z 406 (M$^+$). *Anal*.Calcd for $C_{19}H_{12}Cl_2S_3$: C, 56.03; H, 2.97; Cl, 17.43; S, 23.57. Found: C, 55.96; H, 2.80; Cl, 17.21; S, 23.51.

8-(2-Chloro-6-methoxyphenyl)-5,6-dihydro-[1,2]dithiolo[1,5-*b*]naphtho[2,1-*d*]-[1,2]dithiole-10-S^{IV} (3n).

This compound was obtained in 38 % yield from reaction of 1-(2-chloro-6-methoxyphenyl)-3-(1,2,3,4-tetrahydro-1-oxo-2-naphthalenyl)-1,3-propanedione (**2n**) with P_2S_5 ; mp 202-203 °C (chloroform-ethanol); ^{1}H-nmr ($CDCl_3$): δ 3.00-3.30 (m,4H,CH_2-CH_2); 3.85 (s,3H,OCH_3); 6.80-7.90 (m,7H,aromatic H); 8.20 (s,1H,C^7-H); ms:m/z 402 (M^+). Anal.Calcd for $C_{20}H_{15}ClOS_3$: C, 59.61; H, 3.76; Cl, 8.82; S, 23.85. Found: C, 58.94; H, 3.75; Cl, 10.01; S, 23.51.

2,5-Bis[4-(1,1-dimethylethyl)phenyl]-3,4-dihydro-1,6,6a-trithia(6a-S^{IV})cyclopenta[cd]pentalene (5a).

This compound was obtained in 60% yield from reaction of 2,5-bis[4-(1,1-dimethylethyl)benzoyl]cyclopentanone (4a) with P_2S_5; mp 280-281 °C (chloroform-ethanol); ^{1}H-nmr ($CDCl_3$): δ 1,30 [s,18H,$C(CH_3)_3$]; 3.45 (s,4H,C^3-H and C^4-H); 7.10-7.70 (m,8H,aromatic H); ms:m/z 450 (M^+). Anal.Calcd for $C_{27}H_{30}S_3$: C, 71.95; H, 6.71; S, 21.34. Found: C, 71.93; H, 6.74; S, 21.26.

2,5-Bis(3-4-dimethoxyphenyl]-3,4-dihydro-1,6,6a-trithia(6a-S^{IV})cyclopenta[cd]-pentalene (5b).

This compound was obtained in 40% yield from reaction of 2,5-bis(3-4-dimethoxybenzoyl)cyclopentanone (4b) with P_2S_5; mp 173-174 °C (chloroform-ethanol); ^{1}H-nmr ($CDCl_3$): δ 3.90 (s,12H,OCH3); 3.50 (s,4H,C^3-H and C^4-H); 7.00-7.40 (m,6H,aromatic H); ms:m/z 458 (M^+). Anal.Calcd for $C_{23}H_{22}O_4S_3$: C, 60.26; H, 4.80; S, 20.96. Found: C, 60.01; H, 4.84; S, 21.06.

2,6-Bis[4-(1,1-dimethylethyl)phenyl]-4,5-dihydro-3H-[1,2]dithiolo[4,5,1-hi]-[1,2]benzodithiole-8-S^{IV} (7).

This compound was obtained in 58% yield from reaction of 2,6-bis[4-(1,1-dimethylethyl)benzoyl]cyclohexanone (6) with P_2S_5; mp 277-278 °C (chloroform-ethanol); ^{1}H-nmr ($CDCl_3$): δ 1,25 [s,18H,$C(CH_3)_3$]; 1.60-1.90 (m,2H,C^4-H); 2.60-3.10 (m,4H,C^3-H and C^5-H); 7.20 (s,8H,aromatic H); ms:m/z 464 (M^+). Anal.Calcd for $C_{28}H_{32}S_3$: C, 72.36; H, 6.94; S, 20.70. Found: C, 72.33; H, 6.94; S, 20.80.

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