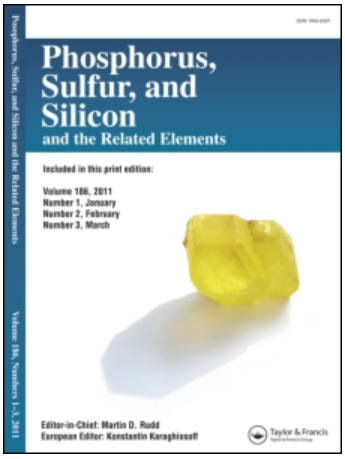


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# REACTION OF HINDERD α,β - UNSATURATED KETONES WITH 2,4-BIS(4-METHOXYPHENYL)-1,3,2,4- DITHIADIPHOSPHETANE-2,4-DISULFIDE

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# REACTION OF HINDERD α,β - UNSATURATED KETONES WITH 2,4-BIS(4-METHOXYPHENYL)-1,3,2,4-DITHIADIPHOSPHETANE-2,4-DISULFIDE

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*(Received March 27, 2000; In final form June 19, 2000)*



Six new hindered α,β-unsaturated ketones (**22c-h**) were prepared. Though the reaction of α,β-unsaturated ketones (**22a,b**) with 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide (**23**) in refluxing benzene gave the corresponding 2-arylidene-1-thiotetralone dimers (**26a,b**) and 3*H*-1,2-thiaphospholene-2-sulfides (**28a,b**), the reaction of hindered α,β-unsaturated ketones (**22d-h**) with 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide (**23**) in refluxing benzene gave only identified 3*H*-1,2-thiaphospholene-2-sulfides (**28c-g**).

*Keywords:* hindered α,β-unsaturated ketones (22c-h); 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide (23); 2-arylidene-1-thiotetralone dimers (26a,b); 3*H*-1,2-thiaphospholene-2-sulfides (28a-g)

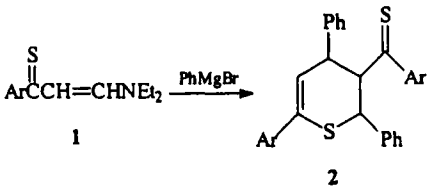
## INTRODUCTION

α,β-Unsaturated thiones are little known because of their instability in the monomeric form[1-9] and tendency to undergo [4 + 2] cycloaddition in which the thione itself may serve as a dienophile or a dien.

For example, Quiniou *et al.*[10] reported that treatment of vinylogous thioamide **1** with phenylmagnesium bromide gave 3-methoxythiobenzoyl-6-methoxyphenyl-2,4-diphenyl-3,4-dihydro-2*H*-thiopyran (**2**).

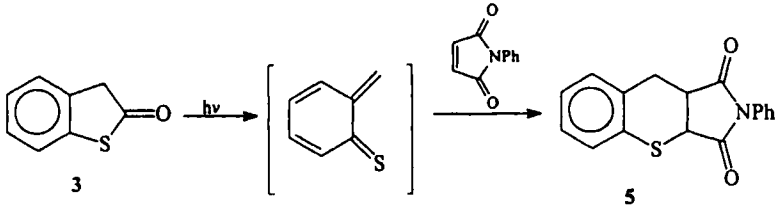
The adduct **5** has been prepared *via* the photoreaction of the thiolactone **3** in the presence of *N*-phenylmaleimide which, afforded good chemical evidence for the intermediacy of the *ortho*-quinoid thioketone **4**.[11]

* Corresponding Author.



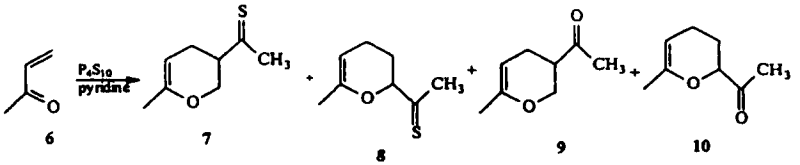
1 2

Ar = *p*-$CH_3O$-$C_6H_4$



3 4 5

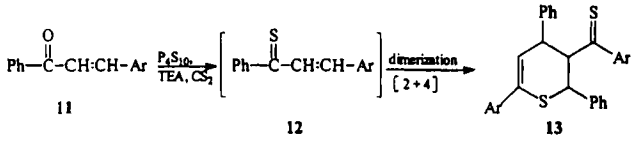
Also, Lipkowitz *et al.*[12] reported that treatment of methyl vinyl ketone (**6**) with $P_4S_{10}$ in pyridine gave four isomeric products **7, 8, 9** and **10**.

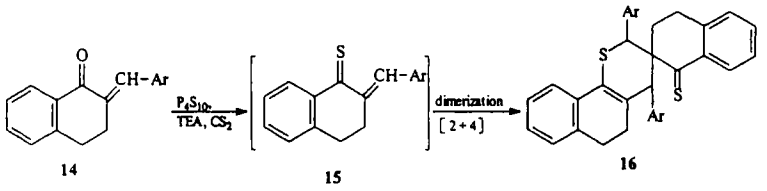


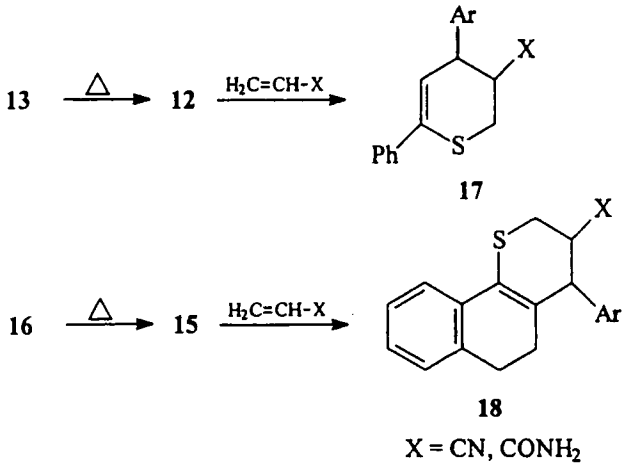
6 7 8 9 10

In 1978, Karakasa and Motoki[13] reported the preparation of thiochalcone **13a**, 4'-methoxythiochalcone **13b**, 2-benzylidene-1-thiotetralone **16a**, 2-(*p*-methoxybenzylidene)-1-thiotetralone **16b** and 2-(*p*-chlorobenzylidene)-1-thiotetralone **16c** dimers *via* the reaction of the corresponding α,β-unsaturated ketones **11** and **14** with $P_4S_{10}$. When these dimers **13** and **16** were heated in the presence of acrylonitrile or acrylamide, 3,4-dihydro-2*H*-thiopyran **17** or 5,6-dihydrobenzo[*h*]thiochroman **18** derivatives were obtained.

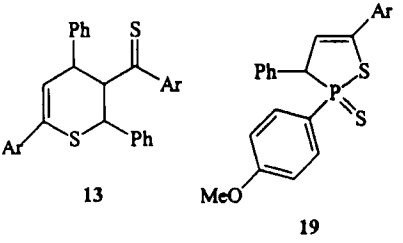
In 1982, Motoki *et al.*[14] reported the reaction of chalcones (Ar = Ph, *p*-$CH_3OC_6H_4$and *p*-$ClC_6H_4$) and 2-benzylidene-1-tetralone with 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide in refulxing benzene gave the corresponding thiochalcone dimers **13** and 2-benzylidene-1-thiotetralone dimer **16**, respectively. Whereas, the reac-





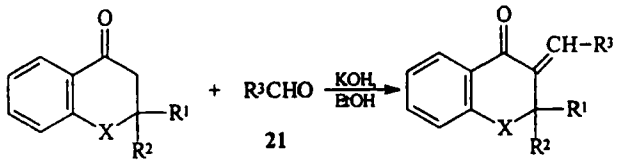


tion in refluxing xylene gave 2-(4-methoxyphenyl)-3,5-diaryl-3*H*-1,2-thiaphospholene-2-sulfides **19**.



## RESULTS AND DISCUSSION

In the present work six new hindered α,β-unsaturated ketone derivatives (**22c-h**) were prepared in moderate yields *via* the reaction of ketones (**20**) with aldehydes (**21**) in refluxing alcoholic KOH[17,18] as shown in eq. 1.




(1)

**20**

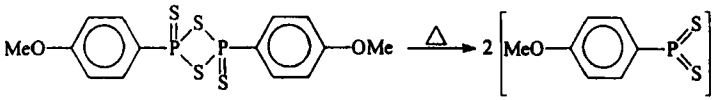
**a**; $R^1 = R^2 = H$, X = $CH_2$
**b**; $R^1$ = Et, $R^2$ = Me, X = $CH_2$
**c**; $R^1 = R^2$ = Me, X = O
**d**; $R^1 + R^2 = -(CH_2)_5-$, X = O

**22**

**a**; $R^1 = R^2 = H$, $R^3$ = furanyl, X = $CH_2$
**b**; $R^1 = R^2 = H$, $R^3$ = thienyl, X = $CH_2$
**c**; $R^1$ = Et, $R^2$ = Me, $R^3$ = furanyl, X = $CH_2$
**d**; $R^1$ = Et, $R^2$ = Me, $R^3$ = thienyl, X = $CH_2$
**e**; $R^1 = R^2$ = Me, $R^3$ = furanyl, X = O
**f**; $R^1 = R^2$ = Me, $R^3$ = thienyl, X = O
**g**; $R^1 + R^2 = -(CH_2)_5-$, $R^3$ = furanyl, X = O
**h**; $R^1 + R^2 = -(CH_2)_5-$, $R^3$ = thienyl, X = O

The structures of (**22**) were supported by analytical and spectral data. The IR spectrum of (**22c**) shows strong band at 1965 $cm^{-1}$. The $^1H$ NMR spectrum of (**22c**) shows signals at 0.95 (3H, t, 3-$CH_3CH_2$), 1.04 (3H, s, 3-$CH_3$), 1.43 (2H, q, 3-$CH_3CH_2$), 2.75 (1H, d, 4-$CH_aH_b$, $J_{HH}$ = 20 Hz), 2.91 (1H, d, 4-$CH_aH_b$, $J_{HH}$ = 20 Hz), 5.55 (1H, s, CH), 6.75–7.75 (7H, m, Ar-H). the mass spectrum of (**22c**) yielded a prominent ion peak $M^+$ at 266 (15 %) which supports structure (**22c**). There are a large number of papers dealing with the use of the efficient Lawesson's reagent.[15]

Accordingly, the reaction of **23** with α,β-unsaturated ketone derivatives (**22a-h**) in refluxing benzene according to eqns. 2–5.

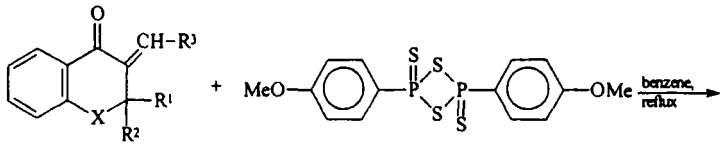



(2)

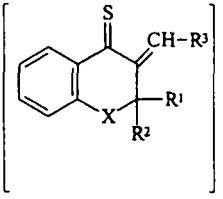
**23** **24**

In case of **22a,b** the straightforward thionation of **22**'s carbonyl group to yield the thione monomer (**25**) which immediately suffered cyclized with

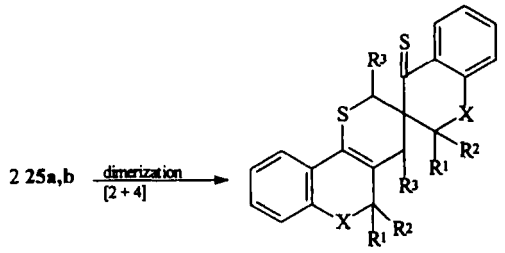
another thione monomer [2 + 4] to yield the corresponding the thione dimers (**26a,b**) eqns. (3,4). In a competing reaction, 1,4-dipolar addition between the LR monomer (**24**) and **25** led to the unstable adduct **27** which, lose sulfur to give thiaphospholenes **28a,b** eqn. (5). But in case of hindered α,β-unsaturated ketone derivatives (**22d-h**) only identified one product thiaphospholenes **28c-h** could be isolated.




**22** **23**




**25** (3)

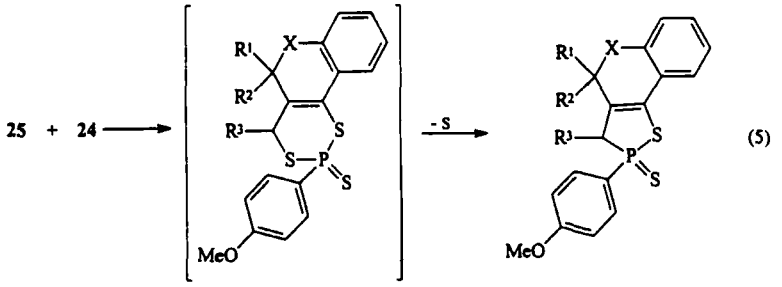



**26** (4)

**a**; $R^1 = R^2 = H$; $R^3$ = furanyl, X = $CH_2$
**b**; $R^1 = R^2 = H$; $R^3$ = thienyl, X = $CH_2$

The structures of **26a,b** were confirmed by analytical and spectral data. The $^1H$ NMR spectrum of **26a** showed singlets at 3.65 and 5.62 ppm; these were assigned to the 4-CH and 2-CH in the 3,4-dihydro-2*H*-thiopyran ring. The MS spectrum of **26a** yielded $M^+$ at 480 (10%).

Also, the structures of **28a-g** were confirmed by analytical and spectral data. Namely, the $^1H$ NMR spectrum of **28a** showed the signal at 5.39 (d,




(5)

27

28

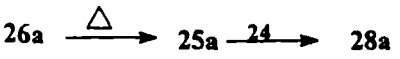
a; $R^1 = R^2 = H$, $R^3$ = furanyl, X = $CH_2$
b; $R^1 = R^2 = H$, $R^3$ = thienyl, X = $CH_2$
c; $R^1$ = Et, $R^2$ = Me, $R^3$ = thienyl, X = CH
d; $R^1 = R^2$ = Me, $R^3$ = furanyl, X = O
e; $R^1 = R^2$ = Me, $R^3$ = thienyl, X = O
f; $R^1 + R^2 = -(CH_2)_5-$, $R^3$ = furanyl, X = O
g; $R^1 + R^2 = -(CH_2)_5-$, $R^3$ = thienyl, X = O



$J_{PH}$ = 15 Hz, 1H, H-3). The mass spectra of **26** and **28** showed evidence for the retro Diels-Alder reaction intense ions for α,β-unsaturated thiones, and the characteristic peak recognized by the assumption that α,β-unsaturated thione ion loses a hydrogen to give the stable thiopyrrylium ion[13,14] as shown in scheme 1.

Moreover, the $^{31}P$ NMR spectra of **28b** and **28c** showed the presence of one kind of phosphorus atom (85% $H_3PO_4$, DMSO; δ 88.96).

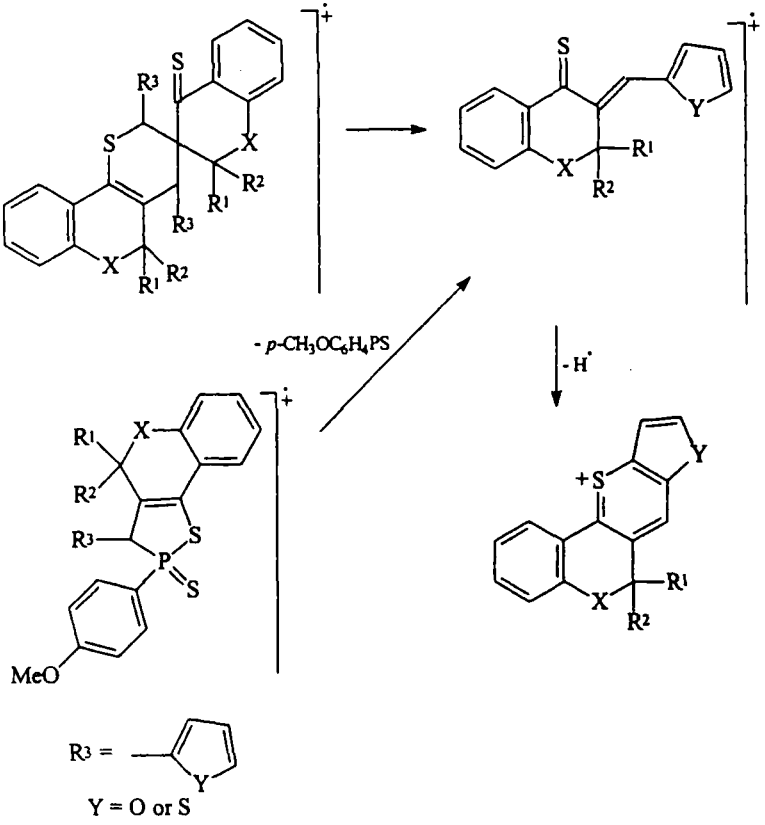
In additional experiment, **26a** was heated with **23** under reflux xylene for 1h. gave the thiaphospholene **28a**, which identified by the m.p. and TLC. eqn. (6).




(6)

## EXPERIMENTAL

$^1H$ NMR spectra were taken for samples in $CDCl_3$ (unless otherwise mentioned) with TMS as an internal standard with a Jeol Ex-270 NMR spec-




SCHEME 1

trometer. $^{31}P$ NMR spectra were taken for samples in DMSO with $H_3PO_4$ (85%) as an internal standard with a Varian Mercury 300 MHz spectrometer. EI (70 ev) mass spectra were recorded on an EI+QIMSLMR UPLR apparatus. IR spectra were obtained with a Perkin-Elmer 1650 instrument for neat samples (for liquids) or KBr wafers (for solid). Microanalyses were performed by the Central Services Laboratory, National Research Centre. The known compounds **20b**,[19] **20c**,[20] **20d**,[20] **22a**[21] and **22b**[21] were prepared according to litrature procedures.

## Preparation of α,β-unsaturated ketone derivatives 22c-h

A general procedure for the synthesis of chalcones was follwed.[22] A solution of 0.01 mol of aldehyde in 8 ml of ethanol was added to a well-stirred solution of 0.4 g of sodium hydroxide in 10 ml ethanol. To this suspension was added 0.01 mol of **20** the resulting solution was refluxed with stirring for 6h. The solvent was evaporated. 10 ml $CHCl_3$and 20 ml water were added, the organic layer was separated, dried over $CaCl_2$, evaporated under vacuum and the oily residue was chromatographed on silica gel (Fluka 60, particle size 0.06–0.20 mm, ether-hexane 1:50) to give **22**.

### *3-Ethyl-1,2,3,4-tettrahydro-2-(furanylmethylene)-3-methylnaphthalen-1-one (22c)*

From **20b**. Yellow oil, yield 50%. IR (neat): $\nu_{C=O}$ = 1659 $cm^{-1}$. $^1H$ NMR: δ = 0.95 (3H, t, 3-C$H_3$$CH_2$), 1.04 (3H, s, 3-$CH_3$), 1.43 (2H, q, 3-$CH_3$C$H_2$), 2.75 (1H, d, 4-C$H_a$$H_b$, $J_{HH}$ = 20 Hz), 2.91 (1H, d, 4-$CH_a$$H_b$, $J_{HH}$ = 20 Hz), 5.55 (1H, s, CH), 6.75–7.75 (7H, m, Ar-H). MS (EI): m/z (%) 266 (M, 15), 237 (M – $C_2H_5$, 20), 188 (M – $C_5H_2O$, 56), 181 (84), 165 (48), 159 (40), 131 (42), 118 (100), 91 (54). Anal. Calcd for $C_{18}H_{18}O_2$ (266.32): C, 81.17; H, 6.81%. Found: C, 81.02; H, 6.75.

### *3-Ethyl-1,2,3,4-tettrahydro-2-(thienylmethylene)-3-methylnaphthalen-1-one (22d)*

From **20b**. Yellow oil, yield 55%. IR (neat): $\nu_{C=O}$ = 1668 $cm^{-1}$. $^1H$ NMR: δ = 0.90 (3H, t, 3-C$H_3$$CH_2$), 1.00 (3H, s, 3-$CH_3$), 1.39 (2H, q, 3-$CH_3$C$H_2$), 2.79 (1H, d, 4-C$H_a$$H_b$, $J_{HH}$ = 20 Hz), 2.89 (1H, d, 4-$CH_a$$H_b$, $J_{HH}$ = 20 Hz), 5.57 (1H, s, CH), 7.10–8.01 (7H, m, Ar-H). MS (EI): m/z (%) 282 (M, 45), 253 (M – $C_2H_5$, 100), 235 (20), 188 (15), 118 (20), 90 (10). Anal. Calcd for $C_{18}H_{18}OS$ (282.38): C, 76.55; H, 6.42; S, 11.35%. Found: C, 76.39; H, 6.29; S, 11.09.

### *2,2-Dimethyl-3-(furanylmethylene)chroman-4-one (22e)*

From **20c**. Yellow oil, yield 40%. IR (neat): $\nu_{C=O}$ = 1655 $cm^{-1}$. $^1H$ NMR: δ = 1.85 (6H, s, 2 $CH_3$), 5.55 (H, s, CH), 7.01–7.95 (7H, m, Ar-H). MS (EI): m/z (%) 254 (M, 40), 239 (M – $CH_3$, 100), 211 (8), 197 (5), 165 (48), 120 (21), 91 (15). Anal. Calcd for $C_{16}H_{14}O_3$ (254.27): C, 75.57; H, 5.54%. Found: C, 75.32; H, 5.44.

*2,2-Dimethyl-3-(thienylmethylene)chroman-4-one (22f)*

From **20c**. Orang crystals, m.p. 96–98 °C, yield 40%. IR (KBr): $\nu_{C=O}$= 1654 $cm^{-1}$. $^1H$ NMR: δ = 2.10 (6H, s, 2 $CH_3$), 5.55 (H, s, CH), 6.71–7.85 (7H, m, Ar-H). MS (EI): m/z (%) 270 (M, 20), 255 (M – $CH_3$, 18), 215 (20), 194 (52), 179 (80), 165 (96), 152 (36), 129 (28), 121 (56), 105 (100), 91 (44). Anal. Calcd for $C_{16}H_{14}O_2S$ (270.33): C, 71.08; H, 5.21; S, 11.85%. Found: C, 71.01; H, 5.15; S, 11.70.

*2-Spirocyclohexyl-3-(furanylmethylene)chroman-4-one (22g)*

From **20d** Yellow oil, yield 50%. IR (neat): $\nu_{C=O}$ = 1653 $cm^{-1}$. $^1H$ NMR: δ = 1.45–1.89 (10H, m, 5 $CH_2$), 5.56 (H, s, CH), 6.75–7.75 (7H, m, Ar-H). MS (EI): m/z (%) 294 (M, 100), 265 (M – $C_2H_5$, 12), 251 (M – $C_3H_7$, 16), 213 (M – $C_4H_5O$, 24), 173 (12), 120 (80), 91 (15). Anal. Calcd for $C_{19}H_{18}O_3$ (294.33): C, 77.52; H, 6.16%. Found: C, 77.31; H, 5.91.

*2-Spirocyclohexyl-3-(thienylmethylene)chroman-4-one (22h)*

From **20d** Yellow crystals, m.p. 131–133 °C, yield 50%. IR (KBr): $\nu_{C=O}$ = 1658 $cm^{-1}$. $^1H$ NMR: δ = 1.55–1.89 (10H, m, 5 $CH_2$), 5.55 (H, s, CH), 6.75–7.65 (7H, m, Ar-H). MS (EI): m/z (%) 310 (M, 100), 268 (M – $C_3H_6$, 12), 226 (M – $C_4H_3$, 12), 184 (12), 147 (12), 121 (56), 91 (15). Anal. Calcd for $C_{19}H_{18}O_2S$ (310.39): C, 73.51; H, 5.84; S, 10.32%. Found: C, 73.41; H, 5.75; S, 10.11.



## Reaction of 22 with Lawesson's reagent

The following reactions were carried out according to a literature procedure.[14] A mixture of **22** (2 mmol) and **23** (1.2 mmol) in benzene (10 ml) was refluxed for 30 min. After cooling, the reaction mixture was filtered off and the filtrate was evaporated. The residue was chromatographed on silica gel (Fluka 60, particle size 0.06–0.20 mm) using ether-hexane 1:10 as an eluent. The solvent was evaporated and the residue was recrystallized from ethanol to give:

*2,4-Difuranyl-1',2',3',4'-tetrahydrospironaphthalene-2',3-{3,4-dihydronaphthalen[1,2-b]-2,4-dihydrothiopyran}-1'-thione (26a)*

From **22a**. Dark green crystals, m.p. 122–25 °C, yield 40%. $^1H$ NMR: δ = 2.15–3.25 (8H, m, 2 $CH_2CH_2$), 3.65 (1H, s, 4-CH), 5.62 (1H, s, 2-CH), 6.65–7.75 (14H, m, Ar-H). MS (EI): m/z (%) 480 (M, 10), 462 (15), 368

(28), 340 (16), 272 (52), 240 (100), 208 (24), 178 (52), 165 (48), 128 (56), 115 (60). Anal. Calcd for $C_{30}H_{24}O_2S_2$(480.61): C, 77.96; H, 5.03; S, 13.34. Found C, 77.81; H, 4.95; S, 13.25.

***2-(4-Methoxyphenyl)-3-furnyl-4,5-dihydronaphthalene[1,2-e]-3H-1,2-thiaphospholene-2-sulfide (28a)***

From **22a**. Colorless crystals, m.p. 101–3 °C, yield 30%. $^1$H NMR: δ = 2.22–2.58 (4H, m, $CH_2CH_2$), 3.80 (3H, s, $OCH_3$), 5.39 (H, d, 3-CH, $J_{PH}$ = 15Hz), 6.65–7.65 (11H, m, Ar-H). MS (EI): m/z (%) 410 (M, 80), 377 (100), 240 (M – *p*-$MeOC_6H_4PS$, 20), 239 (12), 178 (18), 155 (15). Anal. Calcd for $C_{22}H_{19}O_2PS_2$ (410.46): C, 64.37; H, 4.66; P, 7.54; S, 15.62. Found C, 64.27; H, 4.58; P, 7.35; S, 15.51.

***2,4-Dithienyl-1`,2`,3`,4`-tetrahydrospironaphthalene-2`,3-{3,4-dihydronaphthalen[1,2-b]-2,4-dihydrothiopyran}-1`-thione (26b)***

From **22b**. Dark green crystals, m.p. 130–33 °C, yield 45%. $^1$H NMR: δ = 2.20–3.35 (8H, m, 2 $CH_2CH_2$), 3.65 (1H, s, 4-CH), 5.62 (1H, s, 2-CH), 6.75–7.85 (14H, m, Ar-H). MS (EI): m/z (%) 512 (M, 3), 447 (4), 288 (24), 255 (100), 221 (56), 208 (20), 171 (16), 128 (48), 115 (32). Anal. Calcd for $C_{30}H_{24}S_4$ (512.75): C, 70.26; H, 4.71; S, 25.01. Found C, 70.15; H, 4.69; S, 24.85.

***2-(4-Methoxyphenyl)-3-thienyl-4,5-dihydronaphthalene[1,2-e]-3H-1,2-thiaphospholene-2-sulfide (28b)***

From **22b**. Colorless crystals, m.p. 152–55 °C, yield 30%. $^1$H NMR: δ = 2.25–2.58 (4H, m, $CH_2CH_2$), 3.78 (3H, s, $OCH_3$), 5.39 (H, d, 3-CH, $J_{PH}$ = 15Hz), 6.68–7.70 (11H, m, Ar-H). $^{31}$P NMR (DMSO): 88.96. MS (EI): m/z (%) 426 (M, 20), 425 (M – H, 72), 392 (100), 255 (M – *p*-$MeOC_6H_4PS$, 76), 220 (36), 188 (12). Anal. Calcd for $C_{22}H_{19}OPS_3$ (426.53): C, 61.94; H, 4.48; P, 7.26; S, 22.55. Found C, 61.75; H, 4.39; P, 7.06; S, 22.11.

***4-Ethyl-2-(4-methoxyphenyl)-4-methyl-3-thienyl-4,5-dihydronaphthalene [1,2-e]-3H-1,2-thiaphospholene-2-sulfide (28c)***

From **22c**. Colorless crystals, m.p. 142–45 °C, yield 20%. $^1$H NMR: δ = 0.95 (3H, t, 4-C$H_3$$CH_2$), 1.10 (3H, s, 4-$CH_3$), 1.40 (2H, q, 4-$CH_3$C$H_2$), 2.77 (H, d, 5-C$H_a$$H_b$, $J_{HH}$= 20 Hz), 2.90 (H, d, 5-$CH_a$$H_b$,

$J_{HH}$ = 20 Hz), 3.85 (3H, s, OMe), 5.40 (H, d, 3-CH, $J_{PH}$ = 15 Hz), 6.70–7.85 (11H, m, Ar-H). $^{31}$P NMR (DMSO): = 88.95. MS (EI): m/z (%) 468 (M, 5), 435 (100), 298 (M – *p*-$MeOC_6H_4PS$, 70), 262 (20), 188 (10). Anal. Calcd for $C_{25}H_{25}OPS_3$(468.61): C, 64.07; H, 5.57; P, 6.60; S, 20.52%. Found: C, 63.91; H, 5.29; P, 6.58; S, 20.31.

### *4,4-Dimethyl-2(4-methoxyphenyl)-3-furanyl-4H-chromeno[3,4-e]-3H-1,2-thiaphospholene-2-sulfide (28d)*

From **22e**. Colorless crystals, m.p. 79–81 °C, yield 20%. $^1$H NMR: δ = 1.80 (6H, s, 2 $CH_3$), 3.80 (3H, s, OMe), 5.35 (H, d, 3-CH, $J_{PH}$ = 15), 6.65–7.75 (11H, m, Ar-H). MS (EI): m/z (%) 440 (M, 16), 407 (20), 270 (M – *p*-$MeOC_6H_4PS$, 35), 255 (100), 239 (16), 121 (8). Anal. Calcd for $C_{23}H_{21}O_3PS_2$ (440.59): C, 62.69; H, 4.80; P, 7.02; S, 14.55%. Found: C, 62.51; H, 4.79; P, 6.85; S, 14.25.

### *4,4-Dimethyl-2(4-methoxyphenyl)-3-thienyl-4H-chromeno[3,4-e]-3H-1,2-thiaphospholene-2-sulfide (28e)*

From **22f**. Colorless crystals, m.p. 82–5 °C, yield 25%. $^1$H NMR: δ = 1.85 (6H, s, 2 $CH_3$), 3.85 (3H, s, OMe), 5.35 (1H, d, 3-CH, $J_{PH}$ = 15), 6.70–7.80 (11H, m, Ar-H). MS (EI): m/z (%) 456 (M, 4), 423 (10), 286 (M – *p*-$MeOC_6H_4PS$, 20), 284 (40), 201 (40), 139 (100). Anal. Calcd for $C_{23}H_{21}O_2PS_3$ (456.56): C, 60.50; H, 4.63; P, 6.78; S, 21.06%. Found: C, 60.35; H, 4.42; P, 6.55; S, 20.82.

### *2-(4-Methoxyphenyl)-3-furanyl spirocyclohexyl-1`,4–4H-chromeno[3,4-e]-3H-1,2-thiaphospholene-2-sulfide (28f)*

From **22g**. Colorless crystals, m.p. 168–171 °C, yield 25%. $^1$H NMR: δ = 0.95–1.90 (10H, m, 5 $CH_2$), 3.81 (3H, s, OMe), 5.30 (1H, d, 3-CH, $J_{PH}$ = 15), 6.80–7.65 (11H, m, Ar-H). MS (EI): m/z (%) 480 (M, 20), 447 (35), 310 (M - *p*-$MeOC_6H_4PS$, 50), 267 (100), 253 (24), 239 (20), 171 (16), 139 (15). Anal. Calcd for $C_{26}H_{25}O_3PS_2$ (480.55): C, 64.97; H, 5.24; P, 6.44; S, 13.34%. Found: C, 64.81; H, 5.18; P, 6.19; S, 13.09.

### *2-(4-Methoxyphenyl)-3-thienyl spirocyclohexyl-1`,4–4H-chromeno[3,4-e]-3H-1,2-thiaphospholene-2-sulfide (28g)*

From **22h**. Colorless crystals, m.p. 142–45 °C, yield 25%. $^1$H NMR: δ = 0.95–1.95 (10H, m, 5 $CH_2$), 3.80 (3H, s, OMe), 5.35 (1H, d, 3-CH,

$J_{PH}$ = 15), 6.80–7.65 (11H, m, Ar-H). MS (EI): m/z (%) 496 (M, 10), 463 (35), 399 (100), 326 (M – *p*-$MeOC_6H_4PS$, 24), 291 (28), 241 (24), 139 (36). Anal. Calcd for $C_{26}H_{25}O_2PS_3$ (496.62): C, 62.87; H, 5.07; P, 6.23; S, 19.36%. Found: C, 62.71; H, 4.91; P, 6.01; S, 19.11.

## Reaction of 26a with Lawesson's reagent

A mixture of **26a** (0.05 gm, 0.1 mmol) and **23** (0.025 gm, 0.06 mmol) in xylene (10 ml) was refluxed for 1h. After cooling, the reaction mixture was filtered off and the filtrate was evaporated. The residue was chromatographed on silica gel (Fluka 60, particle size 0.06–0.20mm, ether-hexane 1:10). The solvent was evaporated to give **28a** 0.01 gm (30%), m.p. 101–103 °C.



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