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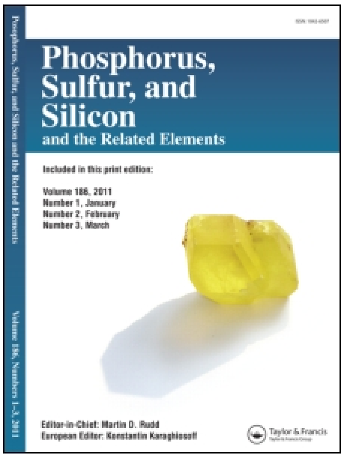

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# ORGANOPHOSPHORUS COMPOUNDS ACTION OF 2,4-BIS-(4-METHOXYPHENYL)-1,3,2,4-DITHIAPHOSPHETANE-2,4-DISULFIDE (LAWESSON REAGENT) AND 2,4-BIS-(PHENYLTHIO)-1,3-DITHIA-2,4-DIPHOSPHETANE-2,4-DISULFIDE (JAPANESE REAGENT) ON FLAVONE, α-NAPHTHOFLAVONE AND β-NAPHTHOFLAVONE

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# ORGANOPHOSPHORUS COMPOUNDS ACTION OF 2,4-BIS-(4-METHOXYPHENYL)-1,3,2,4-DITHIAPHOSPHETANE-2,4-DISULFIDE (LAWESSON REAGENT) AND 2,4-BIS-(PHENYLTHIO)-1,3-DITHIA-2,4-DIPHOSPHETANE-2,4-DISULFIDE (JAPANESE REAGENT) ON FLAVONE, α-NAPHTHOFLAVONE AND β-NAPHTHOFLAVONE

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*(Received June 24, 1991; in final form July 26, 1991)*

Japanese reagent JR, **1b** converts 2-phenyl-(5,6-benz)-γ-pyrone (flavone, **2a**) into 2-phenyl-5,6-benzpyrane-4-thione **2b**. Lawesson reagent LR, **1a** converts 2-phenyl-7,8-benzo-1,4-chromone (α-naphthoflavone, **3a**) and 2-phenyl-5,6-benzo-1,4-chromone (β-naphthoflavone **4a**) into their corresponding thioketones **3b** and **4b** respectively. Thiation of **3a** and **4a** with Lawesson reagent, **1a** can be induced photochemically to give **3b** and **4b**. Thiation of α-naphthoflavone **3a** and β-naphthoflavone **4a** with Japanese reagent JR, **1b** is accompanied with ring opening at the heterocyclic oxygen atom of the γ-pyrone ring to yield products **5** and **6** respectively. The given structures were based upon analytical, chemical and spectroscopic results.

*Key words:* Lawesson reagent; Japanese reagent; thiation; γ-pyrones.

## INTRODUCTION

Powerful O/S exchange reagents are of current interest. Among these reagents which are readily available and appreciable under mild reaction conditions are hydrogen sulfide,[1] thiophosphoryl bromide,[2] phosphorus pentasulfide,[3] Lawesson's reagent,[4] 2,4-bis-[4-phenoxyphenyl]-1,3-dithia-2,4-diphosphetane-2,4-disulfide[5] and recently 2,4-bis-[phenylthio]-1,3-dithia-2,4-diphosphetane-2,4-disulfide, Japanese reagent.[6]

In contribution to our growing interest in studying the behaviour of flavone towards 2,4-bis-(4-methoxyphenyl)-1,3,2,4-dithiaphosphetane-2,4-disulfide[7] (Lawesson reagent LR, **1a**), we report here the action of 2,4-bis(phenylthio)-1,3-dithia-2,4-diphosphetane-2,4-disulfide (Japanese reagent JR, **1b**) on flavone. The work was extended to study the effect of LR, **1a** and JR, **1b**, on 7,8-benzoflavone (α-naphthoflavone **3a**) and 5,6-benzoflavone (β-naphthoflavone **4a**).

## RESULTS AND DISCUSSION

We have found that, when a mixture of α-naphthoflavone **3a** and LR, **1a**, was refluxed in dry toluene for 6 hr, an orange red crystalline material was formed

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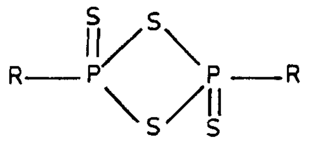
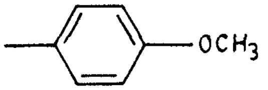
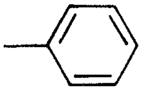


1a, R =

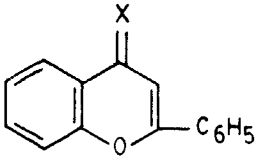


b, R = S

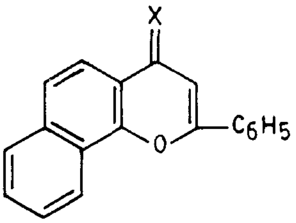


(85%) whose physical and spectroscopic characteristics exactly matched those of α-naphtho-4-thioflavone[8] **3b**.

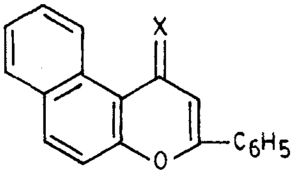
Similarly, β-naphthoflavone **4a** and LR, **1a** produced β-naphtho-4-thioflavone[9] in ca 90% yield.



2a, X = O
b, X = S



3a, X = O
b, X = S



4a, X = O
b, X = S

It has been found that, when a mixture of **3a** and LR, **1a**, in dry benzene was exposed to sunlight for 30 days (Schlenk tube), or irradiated with a Hg-high pressure lamp, thione **3b** was formed in 70% yield.

Similarly, β-naphthoflavone **4a** and LR, **1a** produced β-naphtho-4-thioflavone **4b** in 68% yield when exposed to solar radiations (Schlenk tube) or irradiated with a Hg high pressure lamp.

The identity of **2b, 3b** and **4b** was established by comparison of their physical and spectroscopic characteristics (IR, PMR and mixed m.p.) with those of an authentic specimen prepared by the action of phosphorus pentasulfide on **2a, 3a** and **4a**.

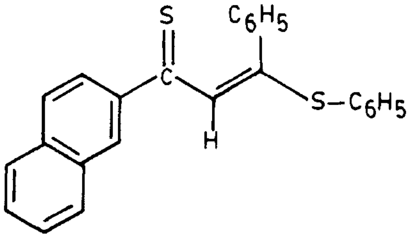
The action of JR, **1b** on flavone **2a**, α-naphthoflavone **3a** and β-naphthoflavone **4a** is sometimes different from that of LR, **1a**.

It has been found that when a mixture of flavone **2a** and JR, **1b**, was stirred in dry toluene at room temperature for 3 hr, a deep red crystalline solid was formed which was identified to be thioflavone.[10]

We have found that when a mixture of α-naphthoflavone **3a** and JR, **1b**, was stirred in dry toluene for 3 hr at room temperature or refluxed for 15 min in the same solvent a brown crystalline substance was formed that contained sulfur in its elemental analysis and didn't contain phosphorus. It was assigned structure **5** based on spectral data (cf. experimental).

Similarly, β-naphthoflavone **4a** and JR, **1b**, yielded a product to which structure **6** was assigned for the following reasons: (a) Its elemental analysis and molecular weight determination corresponded to $C_{25}H_{18}S_2$ (m/z, 382). (b) Its IR spectrum lacked the C=O group absorption band which is recorded in the spectrum of naphthoflavone. The spectrum however, showed strong absorption bands in the region 1600–1500 $cm^{-1}$ due to the aromatic stretching vibrations. Also, a strong band at 1190 $cm^{-1}$ due to C=S was present. (c) The PMR spectrum of **6** showed a singlet at 6.9 ppm (1H, methylene proton, s). The aromatic protons (17H) gave a multiplet in the δ 7.3–8.7 ppm region. (d) The mass spectra showed a molecular ion peak at m/z 382; $M^+$, 10%.

A mechanism accounting for the formation of structure **5** (or **6**) depends on[6] initial thiation of naphthoflavone followed by opening of the γ-pyrone ring.



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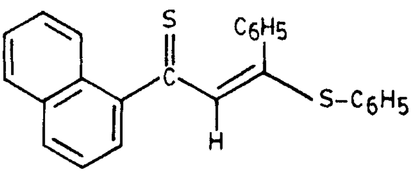

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## CONCLUSION

The action of LR, **1a**, is an effective thiating agent for flavone and its derivatives.

The action of JR, **1b**, on flavone is quite different from that of naphthoflavone. Its action on flavone, is that of an effective thiating agent for carbonyl-oxygen. The action of JR, **1b** on naphthoflavone is a thiation for the carbonyl-oxygen atom of the γ-pyrane ring **3a** and **4a** together with ring rupture at its heterocyclic oxygen atome.

## EXPERIMENTAL

All melting points were uncorrected. Benzene (thiophene free), toluene and petroleum ether were dried over sodium. The IR spectra (run in KBr and expressed in $cm^{-1}$) were recorded with a Beckmann 4220 Infracord. The $^1$H-NMR spectra were measured (in $CDCl_3$ or DMSO-$d_6$ and expressed in the δ-scale, ppm) at 60 MHz or 90 MHz on a Varian instrument using TMS as an internal standard. The mass spectra were performed at 70 eV using a Varian MAT 112 Mass Spectrometer.

Lawesson reagent **1a**[11] and Japanese reagent **1b**[6] were prepared according to an established procedure and twice crystallized before use.

Silica gel (kieselgel 60, particle size 0.2–0.5 mm, E. Merck, Darmstadt) was used for column chromatography. A pyrex glass column was used, 60 cm long and 2 cm diameter.

*The reaction of 2,4-bis (4-methoxyphenyl)-1,3,2,4-dithiaphosphetane-2,4-disulfide (LR,* **1a**) *with 7,8-benzoflavone (α-naphthoflavone,* **3a**) *and 5,6-benzoflavone (β-naphthoflavone,* **4a**). *General proce-*

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*dure.* A mixture of 0.005 mol of the γ-pyrone derivative (**3a** or **4a**) and 0.0025 mol of LR, **1a**, was heated in 25 ml dry toluene under reflux with stirring for about 6 hr until no more of the starting material could be detected (TLC). After cooling to room temperature, the reaction mixture was evaporated till dryness, in vacuo, in the presence of 5 g of silica gel. This mixture was introduced into a column charged with silica gel and packed with the appropriate eluent stated below. The following thioketones were isolated and identified.

I) 2-phenyl-7,8-benzo-4-thiochromone (α-naphtho-thioflavone, **3b**) ($C_{19}H_{15}OS$).
m.p. 171-2° [Reported[8]: 170°C] yield 85%.
Eluent used (benzene—pet. ether, 3:7, v/v).

II) 2-phenyl-5,6-benzo-4-thiochromone (β-naphtho-thioflavone, **4b**) ($C_{19}H_{12}OS$).
m.p. 149° [Reported[9]: 148°C] yield 90%.
Eluent used (benzene—pet. ether, 4:6, v/v).

*Action of phosphorus pentasulfide* $(P_2S_5)_x$ *on* **2a, 3a** *and* **4a.** A mixture of 0.005 mol of γ-pyrone derivative **2a, 3a** or **4a** and 0.005 mol of $(P_2S_5)_x$ was heated in 25 ml dry toluene under reflux with stirring for about 12 hr. After evaporation of the solvent, the solid material was recrystallized from ethyl alcohol to give **2b, 3b** and **4b** at yields 40%, 50% and 45% respectively.

*The reaction of 2,4-bis-(4-methoxyphenyl)-1,3,2,4-dithiaphosphetane-2,4-disulfide (LR,* **1a**) *with 7,8-benzoflavone (α-naphthoflavone,* **3a**) *and 5,6-benzoflavone (β-naphthoflavone,* **4a**) *in sunlight. General procedure.* A mixture of 0.005 mol of **3a** or **4a** and 0.0025 mol of LR, **1a**, in dry benzene was sealed under dry nitrogen gas in a Schlenk tube, then exposed to sunlight for 30 days (August). The reaction mixture was evaporated till dryness, in vacuo, in the presence of 5 g of silica gel. The mixture was column-chromatographed on silica gel using the appropriate eluent stated below.

I) The following products were isolated and identified: a) 2-phenyl-7,8-benzo-4-thiochromone **3b** (yield 70%), eluent used (benzene—pet. ether, 3:7, v/v) and b) 2-phenyl-5,6-benzo-4-thiochromone **4b** (yield 68%), eluent used (benzene—pet. ether 4:6, v/v).

*III) Photoreaction of* **3a** *(or* **4a**) *and LR,* **1a** *with a Hg-high pressure lamp in dry benzene.* A mixture of 0.005 mol of **3a** (or **4a**) and 0.0025 mol of LR, **1a**, was irradiated in a pyrex vessel ($\lambda > 313$ nm) with a Hg-high pressure lamp (Philip HPK 125 w) for 24 hr whereby substantial reaction of materials has taken place as indicated from a TLC examination of the reaction mixture. Benzene was removed and the mixture was applied to a silica gel column chromatography. α-Naphtho-thioflavone **3b** (or β-naphtho-thioflavone **4b**) was obtained and identified.

*The action of 2,4-bis-(phenylthio)-1,3-dithia-2,4-diphosphetane-2,4-disulfide JR,* **1b**, *on 2-phenyl-[5,6-benz]-γ-pyron (flavone,* **2a**), *2-phenyl-7,8-benzo-1,4-chromone (α-naphthoflavone,* **3a**) *and 2-phenyl-5,6-benzo-1,4-chromome (β-naphthoflavone,* **4a**). *General procedure.* A mixture of 0.005 mol of the γ-pyrone derivative (**2a, 3a** or **4a**) and 0.0025 mol of JR, **1b** in 25 ml dry toluene was stirred at room temperature for 3 hr, or heated under reflux with stirring for about 15 min until no more of the starting material could be detected (TLC). After cooling to room temperature, the reaction mixture was evaporated till dryness, in vacuo, in the presence of 5 g silica gel. This mixture was introduced into a column charged with silica gel and eluded with the appropriate eluent stated below. The following products were isolated and identified.

I) 2-phenyl-5,6-benzpyrane-4-thione (thioflavone, **2b**) ($C_{15}H_{10}OS$).
m.p. 89° [Reported[10]: 88°C] yield 80%.
Eluent used (benzene—light petroleum, 1:9, v/v).

II) 1-Phenyl-1-(phenylthio)-3-(2-naphthyl)-prop-1-ene-3-thione **5**.
m.p. 183°C yield 60%.
Eluent used (benzene—hexane, 4:6, v/v).
Analysis Calcd. for $C_{25}H_{18}S_2$; C, 78.53; H, 4.71; S, 16.75.
Found C, 78.39; H, 4.63; S, 16.60.
IR: Bands at 1600–1500 (C=C, aromatics) and 1192 (C=S).
$^1$H-NMR: signal at 6.8 (1H, methylene proton, s) and at 7.4–8.6 (17H, aromatic, m).
MS: m/z, 382, 15%.

III) 1-Phenyl-1-(phenylthio)-3-(1-naphthyl)-prop-1-ene-3-thione **6**.
m.p. 131°C yield 65%.
Eluent used (benzene—hexane, 3:7, v/v).
Analysis Calcd. for $C_{25}H_{18}S_2$; C, 78.53; H, 4.71; S, 16.75.
Found C, 78.42; H, 4.52; S, 16.65.

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