

# THE BEHAVIOUR OF LAWESSON'S REAGENT AND DIALKYLAMINOPHOSPHINES TOWARDS DICYANOMETHYLENE DERIVATIVES OF XANTHONE AND FLUORENONE

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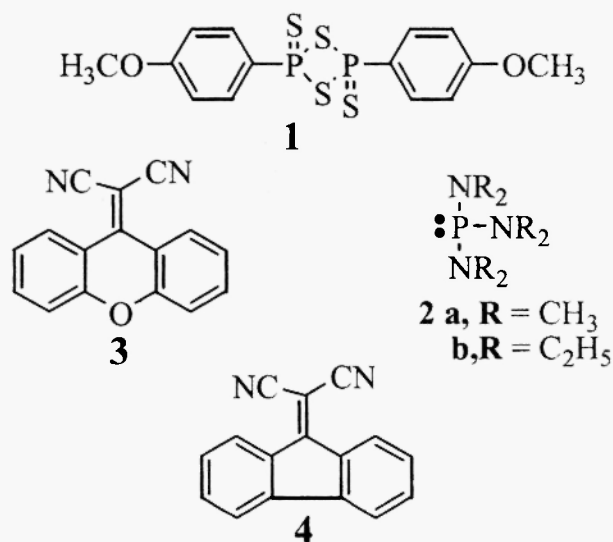
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**Abstract:** Lawesson's reagent **1** reacts with xanthen-9-ylidenemalononitrile **3** to give adducts **5a**, **6a** and **7**, respectively. In case of the reaction of fluoren-9-ylidenemalononitrile **4** with **1**, only 3-amino-2-fluoren-9-ylidene-3-thioxopropanenitrile **5b** is obtained together with trimer **7**. Whereas, trisdialkylaminophosphines **2a,b** reacts with nitrile **3** to give the dipolar adducts **8** and **9**, the corresponding dialkylaminophosphonate adducts **10a** and **10b** are obtained from the reaction of **2a,b** with nitrile **4**. Structural reasoning for the new adducts was based on compatible analytical and spectral data.

## Introduction

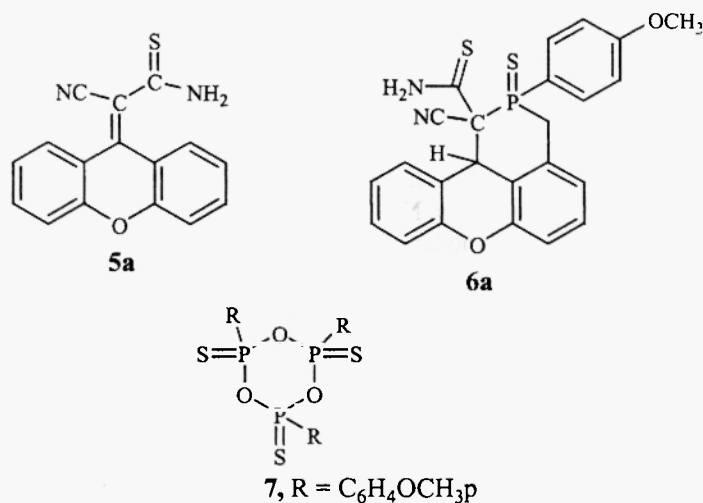
In previous publication we examined the action of 2,4-bis-(4-methoxy-phenyl)-1,3,2,4-dithiaphosphetane-2,4-disulfide (Lawesson's reagent LR) on 2-amino-1,4-naphthoquinones (**1**). Our continuous effort to look for the synthesis of new heterocyclic compounds (**2**) led us to investigate the behaviour of Lawesson's reagent **1** and dialkylaminophosphines **2** towards dicyanomethylene derivatives of xanthone **3** and fluorenone **4** (Scheme 1).



Scheme 1

## Results and Discussion

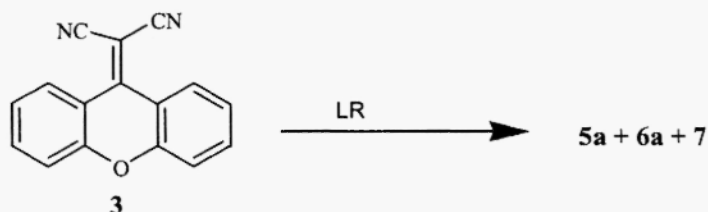
We have found that, when one mole of xanthen-9-ylidenemalononitrile **3** was allowed to react with half an equivalent of **1** in refluxing toluene for 10 hr, products **5a**, **6a**, **7** and the starting ylidenemalononitrile **3** were isolated. Carrying out the reaction using one mole of Lawesson's reagent instead of half a mole, led to the formation of **5a**, **6a** and **7** in good yields (Scheme 2).



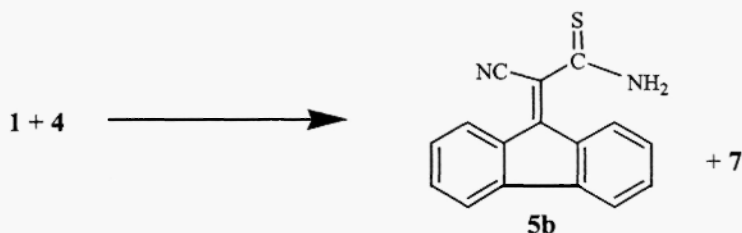
(Scheme 2)

Compounds **5a**, **6a** and **7** are chromatographically pure and possess sharp melting points. Compound **5a** (yield 30%) was formulated as 3-amino-2-xanthen-9-ylidene-3-thioxopropanenitrile based upon analytical and spectroscopic arguments (cf. Experimental). The second product **6a**, (yield 35%) was formulated as the cyclic 3-amino-2-[(4-methoxyphenyl)-methylthiothioxophosphino]-3-thioxo-2-xanthen-9-ylpropanenitrile for the following reasons: Elemental and mass spectral analyses for compound **6a** corresponded to an empirical formula of C<sub>23</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub>PS<sub>3</sub>. The structure assigned for compound **6a** was based on the <sup>31</sup>P NMR shifts (+92.78 ppm, 85% H<sub>3</sub>PO<sub>4</sub>), which corresponds to a cyclic structure incorporating a 1,2-thiaphosphate-2-sulfide moiety (3,4). The IR spectrum of **6a** (KBr, cm<sup>-1</sup>) showed two bands at 3410 cm<sup>-1</sup> and 3425 cm<sup>-1</sup> due to the stretching vibration of the NH<sub>2</sub> group, signals at 1250 cm<sup>-1</sup> (C=S), 2220 cm<sup>-1</sup> (C=N) and at 1580 cm<sup>-1</sup> (C=C, aromatic). The <sup>1</sup>H NMR spectrum of **6a** (in CDCl<sub>3</sub>, δ ppm) revealed the presence of signals at 8.45 ppm (2H, NH<sub>2</sub>, bs exchangeable with D<sub>2</sub>O), at 6.75-7.95 ppm (m, 11H) corresponding to the aromatic protons and at 3.85 ppm (s, 3H, OCH<sub>3</sub>). Moreover, the <sup>1</sup>H NMR of **6a** showed the presence of signals at 6.35 ppm (d, 1H, <sup>3</sup>J<sub>HP</sub> = 11.5 Hz). The mass spectrum of **6a** contains a prominent peak for M<sup>+</sup> at m/z 480 (85%) which supports the cyclic structure **6a**.

Moreover, compound **7** was isolated from the reaction mixture as colorless crystalline phosphorus-containing product and proved to be trimer by comparing its melting point as well as IR and <sup>1</sup>H NMR spectra with those of an authentic specimen (5-7). Formation of compound **7** is frequently observed during the thiation processes initiated by Lawesson's reagent **1**.



Apparently, formation of compounds **5a** and **6a** can be interpreted in terms of partial hydrolysis of **3** to yield the respective  $\alpha$ -cyano- $\beta$ -xanthen-2-acetamide which undergo ketone to thioketone conversion under the thiation effect of LR to give **5a** which reacts with another molecule of LR forming product **6a** possibly via 1,3-H-shift (8). On the other hand, when one mole of fluoren-9-ylidenemalononitrile **4** was allowed to react with half an equivalent of Lawesson's reagent, in refluxing toluene for 12 hr, products **5b**, **7** and the starting nitrile **4** were isolated. Carrying out the reaction using one and a half mole of Lawesson's reagent instead of half a mole, led to the formation of product **5b** in 80% yield together with trimer **7** in 12% yield. Compound **5b** was formulated as 3-amino-2-fluoren-9-ylidene-3-thioxopropanenitrile.



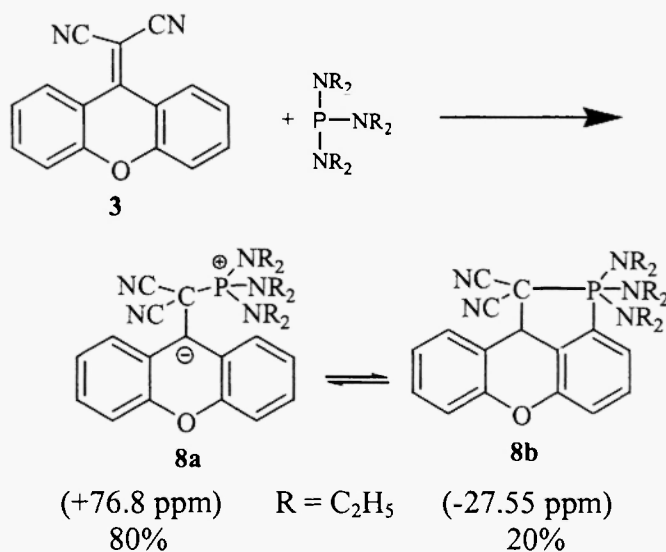
Compound **5b** is a chromatographically pure yellow crystalline compound and possesses a sharp melting point. Compatible analytical and spectral data (IR,  $^1\text{H}$ NMR and MS) were obtained for the new compound **5b** (cf. Experimental).

Previously, we reported (2) the action of Wittig and Wittig-Honer reagents on dicyanomethylene of xanthen-9-ylidenemalononitrile **3** and fluoren-9-ylidenemalononitrile **4**. Therefore, it was of interest to investigate the behaviour of these nitriles towards trivalent phosphorus reagents namely, trisdialkylaminophosphines **2a** and **2b**, respectively (Scheme 1).

We have found that xanthen-9-ylidenemalononitrile **3** reacts with excess trisdiethylamino phosphine **2a** without solvent at  $105^\circ\text{C}$  to give adduct **8** in 87% yield (Scheme 3). Structure elucidation of adduct **8** is based on the following evidences: Elemental analyses and molecular weight determination (MS) for compound **8** support the molecular formula  $\text{C}_{28}\text{H}_{38}\text{N}_5\text{OP}$ . The IR spectrum of **8**, in KBr, exhibits strong absorption bands at  $1312, 854\text{cm}^{-1}$   $\text{P}[\text{N}(\text{Et})_2]_3$  and at  $2195\text{cm}^{-1}$  (CN). Moreover, its IR spectrum revealed the absence of the  $(\text{P}=\text{O})$  absorption bands at  $1240\text{ cm}^{-1}$ . The  $^1\text{H}$ NMR spectrum of **8** shows signals at 1.07, 1.65 ppm (2t, 18H),  $\text{P}[\text{N}(\text{Et})_2]_3$ , 3.02, 4.04 ppm (m, 12H,  $\text{P}[\text{N}(\text{Et})_2]_3$ ), corresponding to the hydrogens of the three magnetically unequivalent diethylamino groups attached to the phosphorus atom of the  $\text{N}[(\text{CH}_2\text{CH}_3)_3]$  moiety (9). The  $^{31}\text{P}$ NMR spectrum of **8** exhibits two signals at +76.8 ppm (80%) and at -27.55 ppm (20%). These observations strongly suggest an equilibrium between the open dipolar structure with quadruply connected

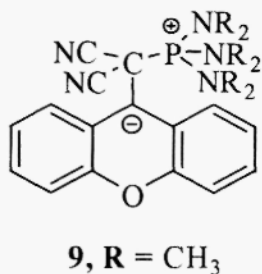
phosphorus **8a** (4) (+76.8ppm) and the cyclic structure having quintuply connected phosphorus **8b** (-27.55ppm).

The  $^{31}\text{P}$ NMR signals suggest that the dipolar form **8a** (80%) greatly predominates over the cyclic structure {1-[1-phospha-1,1,1-tris (diethyl-amino)ethyl]xanthen 9-yl} methane-1,1-dicarbonitrile **8b** (20%). A similar finding has been reported for the coexistence in solutions of a similar structure containing quadruply-connected phosphorus and the corresponding valence tautomer containing quintuply-connected phosphorus (10).



Scheme 3

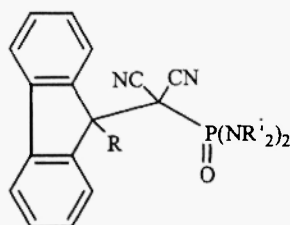
The mass spectrum of **8** yields a prominent ion peak for  $\text{M}^+$  at  $m/z = 491$  (95%). Similarly trisdimethylaminophosphine **2b** reacts with **3** without solvent at  $105^\circ\text{C}$  to give the open dipolar structure **9**. The structure of **9** is deduced from its analysis, IR,  $^1\text{H}$ ,  $^{31}\text{P}$ NMR and mass spectral data (cf. Experimental).



Also, this study has been extended to include the reaction of fluoren-9-ylidenemalononitrile **4** with the same phosphorus reagents **2a** and **2b** to establish whether it would behave in a similar manner.

We have found that the reaction of trisdimethylaminophosphine **2a** with fluoren-9-ylidenemalononitrile **4** proceeds in boiling toluene to give chromatographically pure adduct

assigned the dialkylphosphanate structure [bis(dimethylamino)carbonyl]fluoren-9-ylmethane-1,1-dicarbo-nitrile **10a**. Elemental analyses and molecular weight determination (MS) for compound **10a** support the molecular formula  $C_{20}H_{21}N_4OP$ . The IR spectrum of **10a**, in KBr, exhibits strong absorption bands at  $2200\text{ cm}^{-1}$  (C N),  $1312$ ,  $865\text{ cm}^{-1}$   $P[N(CH_3)_2]_2$  and at  $1240\text{ cm}^{-1}$  (P=O). Moreover, the IR spectrum of **10a** lacks the strong ethylenic ( $-C=C-$ ) band at  $1600\text{ cm}^{-1}$  in the IR spectrum of **4**.



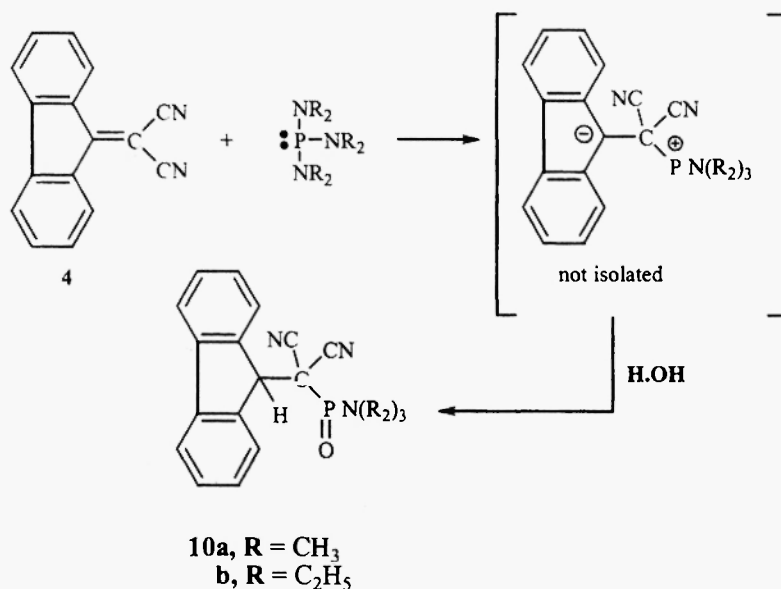
**10a**,  $R' = CH_3$ ,  $R = H$   
**b**,  $R' = C_2H_5$ ,  $R = H$

The  $^1H$ NMR spectrum of **10a** reveals signals at  $\delta = 2.70$  ppm (d, 12H)  $^3J_{HP} = 10.5$  Hz, P  $[N(CH_3)_2]_2$  corresponding to the two magnetically equivalent dimethylamino groups attached to the phosphorus atom. Also, the  $^1H$ NMR spectrum of **10a** shows signals at 4.75 ppm (d, 1H,  $^3J_{HP} = 11.5$  Hz, CH), and at 7.38-7.85 ppm (m, 8H, Ar). The  $^{31}P$ NMR spectrum of **10a** exhibits signal at  $\delta = +23.73$  ppm, a value that falls in the range frequently recorded for the dialkylphosphanate adduct. The mass spectrum of **10a** yields a prominent ion peak at  $m/z$  364 ( $M^+$ , 90).

Similarly, the reaction of **4** with trisdiethylaminophosphine **2b** proceeds in dry toluene to give chromatographically pure adduct formulated as the dialkylaminophosphanate [bis(diethylamino)carbonyl] fluoren-9-ylmethane-1,1-dicarbonitrile **10b**. Structure elucidation for compound **10b** was attested by analytical and spectral data (IR,  $^1H$ ,  $^{31}P$ NMR and MS) (cf. Experimental). A possible explanation of the course of the reaction of trisdialkylaminophosphine **2a,b** with nitrile **4** is shown in Scheme 4.

## Conclusion

The results of the present investigation are of particular significance since they report on a novel route for the production of the cyclic 3-amino-2-[(4-methoxyphenyl)methylthiothioxphosphino]-3-thioxo-2-xanthen-9-ylpropanenitrile **6a** by the utilization of lawesson's reagent.



Scheme 4

### Experimental

All melting points are uncorrected. Lawesson's reagent **1**, dicyano-methylene derivatives of xanthone **3** and fluorenone **4** were prepared according to established procedures. The dialkylaminophosphines **2a,b** were commercially available. The IR spectra were obtained with a Perkin-Elmer Infracord spectrometer Model 157 (Grating) in KBr discs. The <sup>1</sup>H-NMR spectra were recorded in CDCl<sub>3</sub> as solvent on a Joel-270 MHz spectrometer and the chemical shifts were recorded in δ ppm relative to TMS. The <sup>31</sup>P-NMR spectra were taken with a Varian CFT-20 (vs. external 85% H<sub>3</sub>PO<sub>4</sub> standard). The mass spectra were performed at 70 ev on a shimadzu GCS-OP 1000 Ex spectrometer provided with data system.

### Reaction of Lawesson's reagent **1** with xanthen-9-ylidene-malononitrile **3**.

A mixture of **3** (0.24g, 0.001 mol) and LR **1** (0.4g, 0.001 mol) in dry toluene (25 ml) was refluxed for 10 hr. The reaction mixture was evaporated on a silica gel under reduced pressure and applied to a silica gel column using acetone/petroleum ether (40:60, v:v) as eluent to give products **5a**, **6a** and the trimer **7**, respectively.

3-amino-2-xanthen-9-ylidene-3-thioxopropanitrile **5a**, was obtained as dark yellow crystals, yield (30%), m.p. 211-212°C. Calcd. For C<sub>16</sub>H<sub>10</sub>N<sub>2</sub>OS (278.27): C 69.06, H 3.59, N 10.06, S 11.52. Found: C 69.09, H 3.56, N 10.08, S 11.56. MS: m/z = 278 (100%). IR: 2200 (CN), 1620 (C=C), 1256cm<sup>-1</sup> (C=S). <sup>1</sup>H-NMR: δ 10.3, 10.6 (2H, NH<sub>2</sub>, two broad singlets). 7.5-8.2 (8H, Ar, m) ppm.

3-amino-2-[(4-methoxyphenyl)methylthiothioxophosphino]-3-thioxo-2-xanthen-9-ylpropanenitrile **6a**, was obtained as orange crystals, yield (35%), mp. 204-205°C. Calcd. For C<sub>23</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub>PS<sub>3</sub> (480.57) C 57.48, H 3.35, N 5.82, P 6.44, S 20.01. Found: C 57.46, H 3.32, N 5.79, P 6.42, S 20.04. MS: m/z = 480 (85%).

The trimer **7**, was isolated as colorless crystals and identified (mixed mp. and comparative IR spectra).

#### Reaction of LR **1** with fluoren-9-ylidene-malononitrile **4**.

A mixture of **4** (0.22 g, 0.001 mol) and LR **1** (0.6 g, 0.0015 mol) was performed in boiling toluene (25 ml) for 12 hr. The reaction mixture was evaporated under reduced pressure and the residue was applied to a silica gel column chromatography, using acetone/petroleum ether as eluent (40:60, v:v) to give compound **5b** and the trimer **7**.

3-amino-2-fluoren-9-ylidene-3-thioxopropanenitrile **5b**, was obtained as yellow crystals yield (80%), mp. 240-241°C. Calcd for  $C_{16}H_{10}N_2S$  (262.26): C 73.27, H 3.81, N 10.68, S 12.22%. Found: C 73.25, H 3.78, N 10.65, S 12.18%. MS:  $m/z = 262$  (65%). IR: 2220 (CN), 1620 (C=C), 1255  $cm^{-1}$  (C=S).  $^1H$ NMR:  $\delta$  10.55, 10.85 (2H,  $NH_2$ , two broad singlets), 7.45-8.35 ppm (8H, Ar, m). **7** was isolated and identified.

#### Reaction of trisdiethylaminophosphine **2b** with xanthen-9-ylidene-malononitrile **3**.

A mixture of **3** (0.24 gm, 0.001 mol) and excess of the reagent **2b** (2 ml) using as solvent was heated at 105°C for 3hr. The reaction mixture was evaporated under reduced pressure and the residue was subjected to a silica gel column chromatography using ethylacetate/petroleum ether (80:20, v:v) as eluent to give adduct **8** as colorless crystals, yield (87%), mp. 235-236°C. Calcd. For  $C_{28}H_{38}N_5OP$  (491.62): C 68.4, H 7.79, N 14.24, P 6.3. Found: C 68.42, H 7.81, N 14.25, P 6.35.

MS:  $m/z = 491$  (95%).

Similarly, trisdimethylaminophosphine **2a** reacts with **3** to give adduct **9** as colorless crystals, yield (75%), mp 221-222°C. Calcd. For  $C_{22}H_{26}N_5OP$  (407.45): C 64.85, H 6.43, N 17.18, P 7.6. Found: C 64.83, H 6.41, N 17.2, P 7.64. MS:  $m/z = 407$  (85%). IR: 2198 (CN), 1310, 863  $cm^{-1}$  ( $P[N(CH_3)_2]_3$ ).  $^1H$ NMR:  $\delta$  2.75, 3.15 (18H,  $J_{HP} = 11.21$  Hz,  $P[N(CH_3)_2]_3$ , 2d) 7.25-7.55 ppm (8H, Ar, m).  $^{31}P$ NMR:  $\delta + 65.3$  ppm.

#### Reaction of trisdimethylaminophosphine **2a** with fluoren-9-ylidene-malononitrile **4**.

A mixture of **4** (0.22 g, 0.001 mol) and the reagent **2a** (0.16g, 0.001mol) in dry toluene (30ml) was refluxed for 25hr. The volatile materials were evaporated under reduced pressure and the residual substance was chromatographed on a silica gel column using acetone/petroleum ether (40:60, v:v) as eluent to give adduct [bis(dimethylamino)carbonyl]fluoren-9-ylmethane-1,1-dicarbonitrile **10a** as colorless crystals, yield (67%), m.p. 227-228°C. Calcd. For  $C_{20}H_{21}N_4OP$  (364.38): C 65.92, H 5.8, N 15.37, P 8.5. Found: C 65.94, H 5.82, N 15.32, P 8.54. MS:  $m/z = 364$  (90%).

Similarly, trisdiethylaminophosphine **2b** reacts with **4** in refluxing toluene for 25 hr to give [bis(diethylamino)carbonyl]fluoren-9-ylmethane-1,1-dicarbonitrile **10b** as colorless crystals, yield (60%), mp. 295-296°C. Calcd. For  $C_{24}H_{29}N_4OP$  (420.49): C 68.55, H 6.95, N 13.32, P 7.36. Found: C 68.53, H 6.97, N 13.28, P 7.32. MS:  $m/z = 420$  (95%). IR: 2200 (CN), 1245 (P=O), 1250, 940  $cm^{-1}$  ( $P[N(C_2H_5)_2]_2$ ).  $^1H$ NMR:  $\delta$  1.05 (12H, =  $P[N(C_2H_5)_2]_2$ , t), 3.01

(8H, = P[N(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, m), 4.85 ppm (1H, J<sub>HP</sub> = 11.5 Hz, CH, d), 7.39-7.87 ppm (8H, Ar, m). <sup>31</sup>P-NMR: δ + 22.98.

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**Received on June 8, 2003.**