

The Reaction of Visnaginone, Khillinone, and *o*-Hydroxyacetophenone with Lawesson's Reagent*

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ABSTRACT

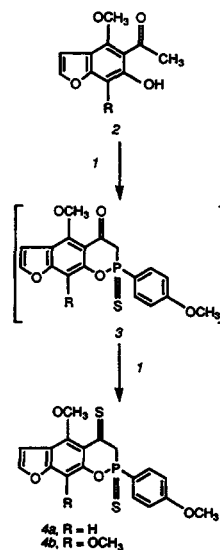
Lawesson's reagent reacts with visnaginone (**2a**), khillinone (**2b**), and *o*-hydroxyacetophenone (**5**) to give the 1,2-oxaphosphinane derivatives **4a**, **4b**, and **6**, respectively.

INTRODUCTION

It is well known that 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide (Lawesson's reagent), (**1**), is the most effective thiation reagent for ketones [1], carboxamides [2–6], esters [7,8], *S*-substituted thioesters [7], enamines [9], lactams [10], and γ - and δ -lactones [11].

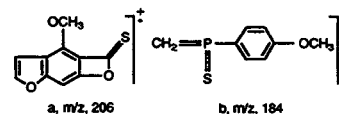
RESULTS AND DISCUSSION

In our attempt to transform visnaginone (**2a**) and khillinone (**2b**) into the corresponding thio-analogues using **1**, the ring systems **4a** and **4b**, respectively, were formed instead (Scheme 1). The structure of **4a**, taken as a representative example, was established by elementary analysis, ^1H and ^{31}P NMR, and Ms and IR spectroscopy. In the ^1H NMR (CDCl_3), **4a** shows signals at $\delta = 3.90$ (3H, s, OCH_3 , para to the phosphorus atom), 4.05 (3H, s, OCH_3 in the visnaginone ring); two double doublets centered at 5.95 and 6.15 for the diastereotopic pro-



SCHEME 1

tons of the CH_2 group with $J_{\text{H}\dots\text{H}} = 3.6$ and $^2J_{\text{P}\dots\text{H}} = 27$ Hz. A multiplet centered at 7 corresponds to 3H (2H, meta to P + 1H of the visnagine part); 7.20 and 7.65 (two doublets for 2H of the furan ring with $J = 2.5$ Hz; 8.05 (2H, dd, ortho protons to P in the aromatic ring with $J_{\text{H}\dots\text{H}} = 9$ Hz and $J_{\text{P}\dots\text{H}} = 15$ Hz). Compound **4a** under electron impact gives the molecular ion peak. The first conspicuous peak, however, corresponds to fragment *a*, formed by ejection of radical cation *b*.

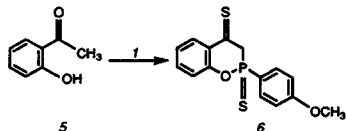


Compound **4a** lacks a band at 1640 cm^{-1} in the IR spectra (CHCl_3) which corresponds to $\text{C}=\text{O}$.

Similarly, the reaction of *o*-hydroxyacetophenone **5** with **1** gave **6**.

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The reaction may start with a nucleophilic attack of the hydroxyl group or of the methylene group of the enol form on the phosphorus [12] with subsequent loss of H_2S to give the intermediate of type **3**. We tried to thiate *o*-hydroxyacetophenone using phosphorus pentasulfide in toluene under reflux for 24 hours, but we only obtained unchanged starting materials.

EXPERIMENTAL

Melting points were determined with the MeI Temp apparatus and are uncorrected as are the boiling points. IR spectra were recorded by using a Unicam SP, 1100, or PU 9712 infrared spectrometer. The ^1H NMR spectra were recorded on a Varian Gemini 200 (200 MHz) or Bruker 250 MHz spectrometer in CDCl_3 . ^1H and ^{31}P chemical shifts are relative to TMS as an internal standard and to external 85% H_3PO_4 . MS data were obtained on a gas chromatography/mass spectrometer (GC/MS) EX 1000, QP Shimadzu–Japan. The reported yields are of pure isolated materials obtained by column chromatography using silica gel 60 (Merck).

Lawesson's reagent is commercially available and can also be prepared as described earlier [13]. The starting visnaginone (**2a**) and khillinone (**2b**) are prepared from visnagine and khilline, respectively, using a known procedure [14]. *o*-Hydroxyacetophenone (**5**) was commercially available.

4a: 1.03 g (5 mmol) of **2a** and 1.01 g (2.5 mmol) of **1** in 25 mL dry toluene were stirred magnetically at reflux temperature until no more of the starting visnaginone could be detected by TLC (8 hours). The reaction mixture was evaporated on silica gel under reduced pressure and applied to a silica gel column using acetone/petroleum ether mixtures as eluent (starting from 5% up to 25% acetone) to give 1.3 g (70%) of **5a**, mp 132°C . Anal. calcd. for $\text{C}_{18}\text{H}_{15}\text{O}_4\text{PS}_2$ (390.41): C, 55.38; H, 3.87; P, 7.93; S, 16.42%. Found: C, 54.95; H, 3.75; P, 7.79; S, 16.25%. IR (γ , cm^{-1} , group): 642 (P=S); 1595, 1605 (C=C furan and C=C aromatic). MS: m/e (% rel. int.), 390 (M^+ , 2), 206 (fragment *a*, 100), 191 ($\text{C}_{10}\text{H}_7\text{O}_3\text{S}$, 100), 176 ($\text{C}_9\text{H}_6\text{O}_3\text{S}$, 100), 173 (15), 161 (8), 133 (5). ^{31}P NMR $\delta = 91.05$. ^1H NMR was mentioned in the text.

4b: The same method as for **4a** was used to give 1.5 g (72%) of **4b**, mp 140°C . Anal. calcd for $\text{C}_{19}\text{H}_{17}\text{O}_5\text{PS}_2$ (420.43): C, 54.28; H, 4.08; P, 7.37; S, 15.25%. Found: C, 54.11; H, 3.99; P, 7.20; S, 15.07%.

^1H NMR $\delta = 3.8$ (s, 3H, OCH_3 , para to phosphorus), 4.00 (s, 6H, 2 OCH_3 in the khilline ring); two double doublets centered at 6.00 for 2H (p- CH_2); 7.00–7.30 (m, 3H, meta-protons to phosphorus + 1H meta in the furan ring); 7.7–8.00 (m, 3H, ortho-protons to phosphorus and one ortho-proton in furan ring). IR (γ cm^{-1} , group): no OH can be detected at 3150 cm^{-1} , 1570, 1600 (C=C furan and C=C aromatic), 650 (P=S), no C=O in the region 1700. MS: m/e (% rel. int.), 420 (M^+ , 20), 236 (fragment corresponding to *a*, 100), 236 ($\text{C}_{11}\text{H}_8\text{O}_4\text{S}$, 50), 206 ($\text{C}_{10}\text{H}_5\text{O}_4\text{S}$), 191 (24), 175 (23), 147 (12). ^{31}P NMR $\delta = 92.25$.

6: As for **4a** to give 1.6 g (25%) of an oil. Anal. calcd for $\text{C}_{15}\text{H}_{13}\text{O}_2\text{PS}_2$ (320.36): C, 56.24; H, 4.09; P, 9.66; S, 20.02%. Found: C, 55.95; H, 4.00; P, 9.49; S, 20.19%. ^1H NMR $\delta = 3.90$ (s, 3H, OCH_3); two double doublets at 5.70 and 6.20 (CH_2); 7.00 (dd, 2H, m-protons to phosphorus); 7.2–7.5 (m, 4H of the aromatic ring of the acetophenone part); 7.9 (dd, 2H, O-protons to phosphorus). The IR spectra show no bands for C=O in the region of 1700 cm^{-1} . MS: m/e (% rel. int.): 321 ($\text{M}^+ + 1$, 100), 289 ($\text{C}_{15}\text{H}_{13}\text{O}_2\text{PS}$, 25), 206 (fragment *a*, 15); 181 (25), 166 (30); 151 (35); 139 (43); 121 (60); 108 (25); 91 (45); 77 (24); 63 (40).

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