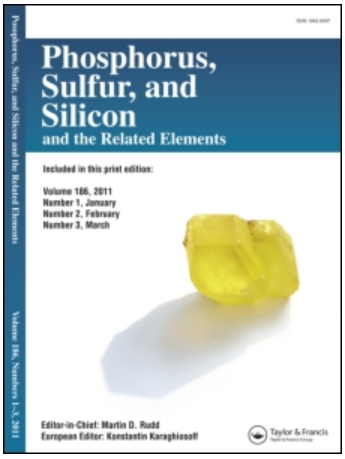

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ORGANOPHOSPHORUS COMPOUNDS XXXI THE REACTION OF TRIALKYL PHOSPHITES WITH THE MONOXIMES OF PHENANTHRENEQUINONE AND ACENAPHTHENEQUINONE

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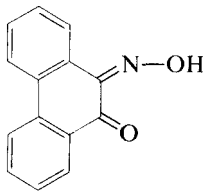
Phenanthrenequinonemonoxime (**1**) reacts with trimethyl-, triethyl-, and triisopropyl phosphites to give the corresponding 1,3,2-oxazaphospholes (**3a–c**). The reaction of acenaphthenequinonemonoxime (**2**) with the same phosphite reagents afforded acenaphthenequinone-ketazine (**5**) in each case. Structural assignments were based upon chemical as well as spectroscopic evidence.

INTRODUCTION

The action of trialkyl phosphites on *o*-quinones, e.g. phenanthrenequinone and acenaphthenequinone, has been extensively studied.[1,2] However, to the best of our knowledge, there appears no information in the literature regarding the behaviour of *o*-quinonemonoximes towards these phosphite esters. It appeared therefore of interest to undertake this study to determine whether phenanthrenequinonemonoxime (**1**) and acenaphthenequinonemonoxime (**2**) would behave in a manner similar to the parent *o*-quinones.



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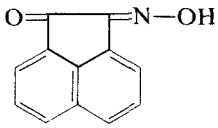

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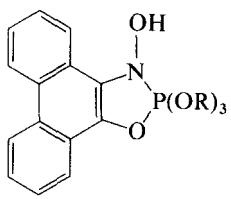
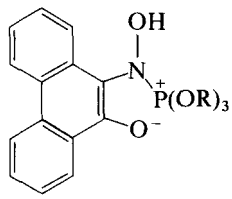
RESULTS AND DISCUSSION

We have found that trialkyl phosphites, namely, trimethyl-, triethyl-, and triisopropyl phosphites, react with phenanthrenequinonemonoxime (**1**), in absence of solvent at room temperature, to give the first reported 2,2,2,3-tetrahydro-3-hydroxy-2,2,2-trialkoxyphenanthro (**9**, **10d**)-1,3,2-oxazaphospholes (**3**). These adducts are colourless crystalline substances with sharp melting points and are stable only for a few days. Correct combustion values are obtained for all new compounds, and the molecular weights correspond to the monomeric formula (*cf.* 3). Compounds (**3a–c**) afford phenanthrenequinone upon oxidation with chromium trioxide in glacial acetic acid or upon hydrolysis with aqueous sodium hydroxide solution. Upon thermolysis, adduct (**3a**) regenerates phenanthrenequinonemonoxime (**1**). The regeneration of the starting *o*-quinonemonoxime **1** upon the pyrolysis of (**3a**) is in agreement with what is known regarding the facile elimination of phosphorus from cyclic compounds.[3]

Supplementary evidence for the assigned structure 3 has been gained from IR and NMR spectroscopic data. The IR spectrum (KBr) of adduct



(**3a**), R=CH_3
(**3b**), R=C_2H_5
(**3c**) R=C_3H_7-*i*

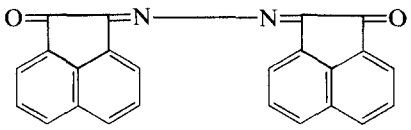


(**4**), R as in 3

(**3b**), taken as example, revealed the absence of absorption in the 1350–1250 cm^{-1} region ($\geqslant P{=}O$) and in the 1585–1570 cm^{-1} region

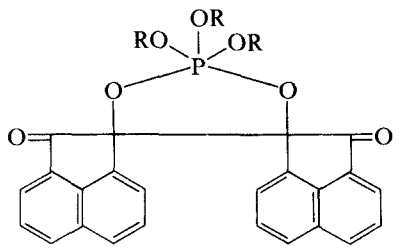
(enolate). Moreover, the strong carbonyl absorption band present in the IR spectrum of phenanthrenequinonemonoxime (**1**) at 1680 cm^{-1}, was absent in the spectrum of (**3b**). However, strong bands at 3200 cm^{-1} (OH), 1625 cm^{-1}, 1610 cm^{-1} (C=C, aromatic) and at 1050 cm^{-1} (P—O—C_2H_5)[4] were present in the spectrum. The ^1H NMR spectrum of (**3b**) (in $CdCl_3$), gave a triplet at $\delta = 1.25$ (9H, for protons of the ethoxy-CH_3 groups), quintet at $\delta = 4.25$ (6H, for protons of the ethoxy-CH_2 groups attached to phosphorus) and a multiplet centered at $\delta = 7.80$ (8H, aromatics). The ^{31}PMR shift (vs. H_3PO_4) recorded for adduct (**3b**) was $\delta = -51.4$ ppm. This latter value which lies in the range of ring-phosphorane shift[5] favours the cyclic structure **3** over the other possible alternative dipolar form (*cf.* 4) for the phenanthrenequinonemonoxime-trialkyl phosphite adducts. There seems to be great tendency for 9:10-derivatives of phenanthrene to form rings.[6,7]

Next, the reaction of acenaphthenequinonemonoxime (**2**) with the aforementioned trialkyl phosphites, was investigated. The reaction proceeded only in the absence of solvent at the boiling point of the phosphite reagent, yielding one and the same product in each case. This latter substance was proved to be acenaphthenequinoneketazine (**5**) (m.p., mixed m.p. and superimposable IR spectra).



5

The formation of a nitrogen-to-nitrogen bond (*cf.* **5**) by the action of trialkyl phosphites on acenaphthenequinonemonoxime (**2**) recalls the production of a carbon-to-carbon linkage in the 2:1 adduct (**6**) formed by the reaction of acenaphthenequinone with the same phosphite esters.[2]



6

EXPERIMENTAL

All melting point are uncorrected. The trialky phosphites were purified by treatment with Na followed by fractional distillation. The IR spectra were recorded in KBr with a Carl Zeiss Spectrophotometer Model "UR 10." The ^1H NMR spectra were run on a Varian A 60 Spectrometer, in $CDCl_3$, using TMS as internal standard.

Reaction of Phenanthrenequinonemoroxime (**1**) with Trialkyl Phosphites. A mixture of compound I[8] (0.001 mol) and trimethyl phosphite[9] (ca. 0.01 mol) was kept at 20° for two hr. After removing the volatile materials, *in a vacuo*, the residual substance was crystallized from benzene-petroleum ether (b.p. 40–60°) to give 2,2,2,3-tetrahydro-3-hydroxy-2,2,2-trimethoxyphenanthro-(**9,10-d**)-1,3,2-oxazaphosphole (**3a**) as colourless crystals, m.p. 85–87° (yield: 0.3 g, 90%). IR: strong absorption bands at 3170 cm^{-1} (OH); 1630 cm^{-1} 1610 cm^{-1} (C=C aromatic) and at 1050 cm^{-1} (P—O—CH_3)[4]. Anal. Calcd for $C_{17}H_{18}NO_5P$: C, 58.80; H, 5.52; N, 4.03; P, 8.90. Found: C, 58.73; H, 5.24; N, 3.97; P, 8.82%.

Similarly, 2,2,2,3-tetrahydro-3-hydroxy-2,2,2-triethoxyphenanthro(**9,10-d**)-1,3,2-oxazaphosphole (**3b**) and 2,2,2,3-tetrahydro-3-hydroxy-2,2,2-triisopropyloxyphenanthro(**9,10-d**)-1,3,2-oxazaphosphole (**3c**) were obtained by the action of triethyl phosphite[10] and triisopropyl phosphite,[10] respectively on phenanthrenequinonemonoxime (**1**).

Adduct 3b was recrystallized from benzene-petroleum ether (b.p. 40–60°) to give colourless crystals, m.p. 116–118°, (yield: 0.34 g, 90%). Anal. Calcd for $C_{20}H_{24}NO_5P$: C, 61.70; H, 6.20; N, 3.59; P, 7.94. Found: C, 61.55; H, 6.18; N, 3.65; P, 7.87%.

The colourless crystals of adduct **3c** were obtained from benzene-petroleum ether (b.p. 40–60°), m.p. 135–137°; (yield: 0.40 g, 90%). IR: strong bands at 3150 cm^{-1} (OH), 1625 cm^{-1}, 1610 cm^{-1} (C=C, aromatic) and at 1040 cm^{-1} (P—O – C_3H_7-i).[4] Anal. Calcd for $C_{23}H_{30}NO_5P$: C, 64.04; H, 7.00; N, 3.24; P, 7.16%. Found: C, 64.12; H, 7.05; N, 3.19; P, 7.22%.

Action of Chromium trioxide on adducts **3a-c**

Adduct **3a**, taken as example, (0.4 g) in glacial acetic acid (30 ml) was treated with a solution of chromium trioxide (0.4 g) in 20 ml of hot glacial acetic acid and the mixture was heated for 10 minutes on the steam bath then cooled. After extraction with hot concentrated solium bisulphite solution, dilute sulphuric acid solution (10%) was added to the extracts. The orange substance that separated was collected (0.2 g, 90%), recrystallized from acetic acid and proved to be phenanthrenequinone (m.p. and mixed m.p. 205°).[11]

Alkali hydrolysis of adducts **3a-c**

The adduct (0.4 g) was treated with aqueous sodium hydroxide solution (10 ml, 10%) at room temperature. The colourless crystals of the adduct decomposed within 15 minutes to yellowish-green crystals. These were filtered off, washed with water, recrystallized from acetic acid and proved to be 9,10-phenanthrenequinone (m.p. and mixed m.p. 205°).[11]

Thermal decomposition of Compounds **3a-c**

Adduct **3a**, taken as example, (0.2 g) was heated in a cold-finger sublimator at 120° (bath temperature) under reduced pressure (1mm/Hg) for about 15 minutes. After cooling, the residual substance was recrystallized from glacial acetic acid to give golden-yellow neeldes proved to be phenanthrenequinonemonoxime (1) (m.p. and mixed m.p. 150°)[8]; (yield: 1.4 g 95%).

The action of Trialky Phosphites on Acenaphthenequinonemonoxime (**2**)

A mixture of acenaphthenequinonemonoxime (**2**) (1.9 g, 0.001 mol) and trimethyl phosphite (2.7 g, 0.003 mol) was boiled under reflux for 24 hr. After evaporation of the volatile material, *in a vacuo*, the residual substance was treated with petroleum ether (b.p. 60–80°) then left to cool in the refrigerator. The pale pink crystals that separated (1.7 g, 95%) were recrystallized from benzene and proved to be acenaphthenequinone-ketazine (**5**) (m.p. and mixed m.p. 295°)[12].

Similarly, ketazine 5 was obtained and identified (m.p. and mixed m.p.) in ca. 95% yield, upon reacting triethyl phosphite and/or triisopropyl phosphite with acenaphthenequinonemonoxime (**2**).

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