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OXAZAPHOSPHOLES. A NEW CLASS OF COMPOUNDS CONTAINING PHOSPHORUS

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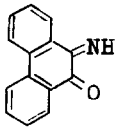
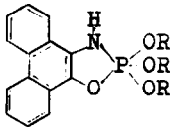
As far as we aware, compounds of the type mentioned in the title have not hitherto been described. Trialkyl phosphites (distilled over Na), namely, trimethyl-, triethyl-, and triisopropyl phosphites react with phenanthrenequinonemonoimine[1](I), in boiling benzene, to give the first reported 2,2,2,3-tetrahydro-2,2,2-trialkoxyphenanthro(9,10-d)-1,3,2-oxazaphospholes (II).



I



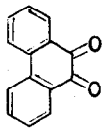
IIa, R=CH_3; b, R=C_2H_5; c, R=C_3H_7-i

The adducts are colourless crystalline substances with sharp m.ps. and are stable[2] only for few days. Correct combustion values are obtained for all the new compounds (IIa-c), and their molecular weights (the ebullioscopic method in benzene) correspond to the monomeric formulae(cf.II).

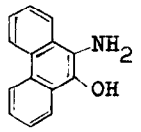
The IR and ^1H n.m.r. spectra[3] of adducts IIa-c are compatible with the oxazaphosphole structure. The IR spectrum of IIa in KBr, for example, shows bands at 3200 cm^{-1} (NH); 1605 cm^{-1} and 1630 cm^{-1}(aromatic bands); 1050 cm^{-1} (P-OCH_3)[4]. No absorption bands are recorded at 1587-1570 cm^{-1} (enolate)[5] or at 1350-1250 cm^{-1} (phosphoryl)[4] and the region near 1680 cm^{-1} characteristic of the C=O vibration of the parent compound I was free of absorption. The ^1H n.m.r. spectrum of IIa ($CDCl_3$, τ) shows the following assignments: multiplet at 2.35 (8 aromatic protons), a doublet at 6.14 (J_{HP} = 11.4 Hz, 9 methoxyl protons).

That the adducts (IIa-c) do not react with diazomethane is also in favour of the cyclic formulae and the regeneration of the starting quinone I upon the pyrolysis of IIa is in agreement with what is known regarding the facile elimination of phosphorus from cyclic compounds[6].

Treatment of adduct IIa with aqueous 10% sodium hydroxide yields phenanthrenequinone (III). It is very probable that this reaction gives first 9-amino-10-phenanthrol (IV), which is further oxidised by the air to phenanthrenequinone[7] (III). Oxidation of IIa with chromium trioxide in glacial acetic acid also results in the formation of III.



III



IV

REFERENCES

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2. All manipulations were carried out under N_2. Moisture and O_2 must be avoided in making and handling the adducts.
3. The IR spectra were recorded with a Carl Zeiss Infracord Spectrophotometer Model "UR 10" and the ^1H n.m.r. spectra were run on Varian A 60 Spectrometer, using TMS as internal standard.
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