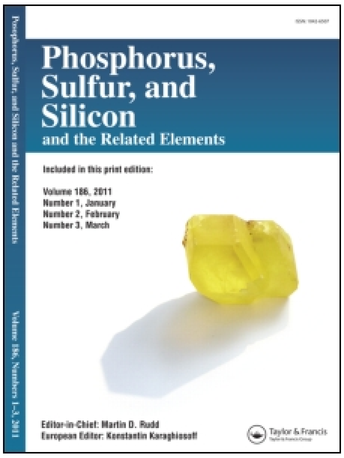

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STUDIES ON ORGANOPHOSPHORUS COMPOUNDS PART IX.[1] THE ACTION OF Di-, TRIALKYL PHOSPHITES AND THIOL ACIDS ON SOME ENAMINOLACTONES

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STUDIES ON ORGANOPHOSPHORUS COMPOUNDS
PART IX.[1] THE ACTION OF Di-, TRIALKYL PHOSPHITES AND THIOL ACIDS ON SOME ENAMINOLACTONES

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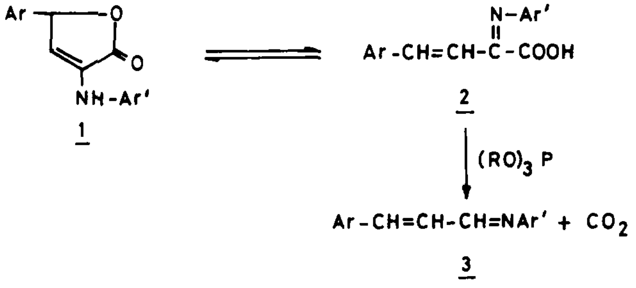
Di-, and trimethylphosphites react with enaminolactone, **4**, only in methanol to give N-benzoyl-3-phenyl-3-phosphonoalanine-trimethylester (**7**) in good yields. Diphenylphosphinodithioic acid also reacts with **4** to give N-benzoyl-3-phenylcysteine-methyl ester-diphenylphosphinodithioate (**9**). A mechanism is proposed to account for the formation of **7**. Compatible analytical and spectroscopic results were obtained for the new compounds.

INTRODUCTION

Although the action of trialkyl phosphites on *β*, and *γ*-lactones is well established,[2] their action on enamino-lactones has hitherto not been well investigated. In a previous paper[3] from this laboratory we have found that 5-aryl-3-arylamino-2-(5H) furanones (1) undergo decarboxylation in the presence of trialkyl phosphite to give the corresponding cinnamylideneanilines, **3**, via the tautomeric open form **2**, while dialkyl phosphites fail to do so. We rationalized that this behaviour is due to the presence of the phosphorus atom in the penta- rather than the trivalent state,[4,5] (Scheme 1).



SCHEME 1

Since 4-benzylidene-2-phenyloxazol-5-one (4)[6] bears formal analogy—a sort of enaminolactone—to 1 and also shows the chemical properties associated with lactones and *α*,*β*-unsaturated ketones, it seems therefore of interest and

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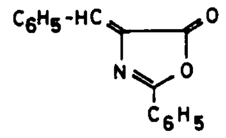
worthwhile to investigate its behaviour towards the action of phosphite esters and thiol acids.



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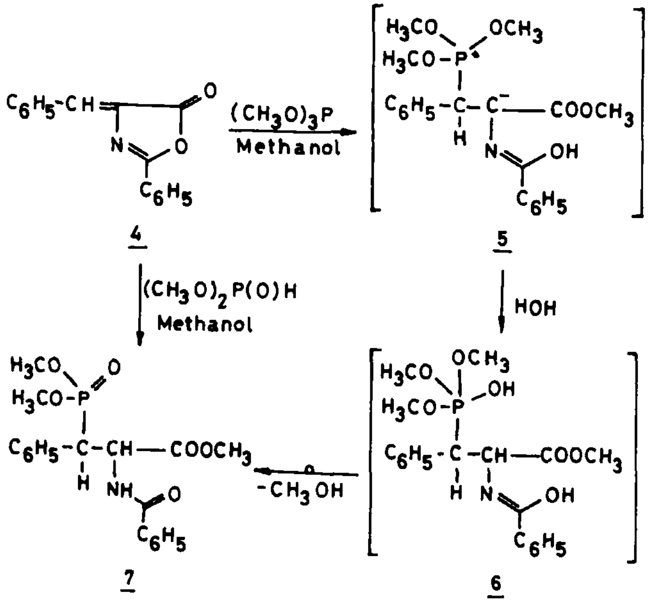
RESULTS AND DISCUSSION

Attempts were made to study the chemical reactivity of compound 4 towards di-, and trialkyl phosphites in different solvents such as benzene, toluene and also without solvent (drastic condition), but in all these conditions the starting 4 was recovered practically unchanged (m.p. and mixed m.p.).

However, it has been found that when compound **4** was allowed to react with trimethyl phosphite in absolute methanol as a solvent a colourless crystalline product was produced in 70% yield which was proved to be N-benzoyl-3-phenyl-3-phosphonoalanine, trimethyl ester (7). The structure of compound **7** was established by microanalysis, Ms, IR, ^{1}H and ^{31}P NMR. In the mass spectra compound 7 showed a peak at 391 which corresponds to M^+ and also shows the following fragments: M/e (%) 391(M^+, 20); 360 ($C_{18}H_{19}O_5NP$, 4); 332($C_{17}H_{19}O_4NP$, 66); 200($C_9H_{13}O_3P$, 100); 105(C_7H_5O, 100); 77(C_6H_5, 40) which fits well the above structure. The IR spectrum in $CHCl_3$ shows absorption bands at 3320 (S, NH), 3 bands at 3080, 3020, and 2860 cm^{-1} (sat. CH); 1740 and 1670 cm^{-1} for both $>C{=}O$ ester and amide respectively, 1605 cm^{-1} for $C{=}C$ aromatic, 1250 cm^{-1} ($P{=}O$ free) and 1055 cm^{-1} for $(POCH_3)^7$. In the ^{1}H NMR

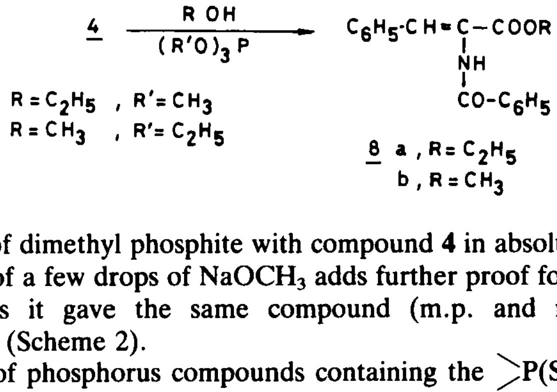


SCHEME 2.

($CDCl_3$), compound 7 shows aromatic protons in the region of 7.20–7.80 ppm, a doublet at 7 ppm for —CH— attached to the ester group with $J = 5$ Hz., and a complex pattern at 4.66 ppm which is assigned to the H—C—P proton. The protons of the two methoxy groups attached to phosphorus appear in the spectrum as a pair of doublets with $J = 11$ Hz centered at 3.70–3.90 ppm, and the methoxy group of the ester is seen at 3.85 as a singlet. In the ^{31}P NMR compound 7 absorbs at +23.7 which corresponds to the phosphonate structure.[8]

A mechanism for the formation of compound **7** from **4** is presented in Scheme 2. This involves an initial attack at the terminal carbon atom of the conjugated system (α,β- unsaturated) by trimethyl phosphite to form the dipolar structure **5**. The unstable ylide **5** in presence of unavoidable moisture can add elements of water to furnish the transient intermediate **6** which collapses and rearranges to give **7**.[9] It should be noted here that the opening of the lactone ring in **4** takes place in methanol enhanced by the presence of trimethyl phosphite, as compound **4** was separated practically unchanged when boiled in methanol alone for 24 hrs.

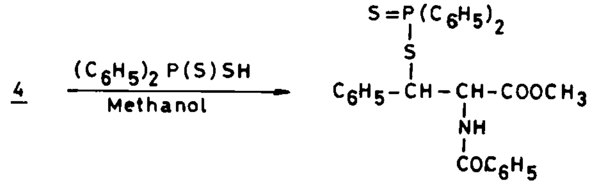
It is necessary to mention that the addition product **7** can be formed only when using trimethyl phosphite and methanol as a solvent. This was confirmed by performing the reaction of trimethyl-, and triethyl phosphites in ethanol and methanol respectively where the products were opening of the ring and formation of ethyl- or methyl α-benzamidocinnamate (8). The role of trialkyl phosphite is just a base for the formation of the ester



8 a, $R = C_2H_5$
b, $R = CH_3$

The reaction of dimethyl phosphite with compound **4** in absolute methanol and in the presence of a few drops of $NaOCH_3$ adds further proof for the structure of compound **7**, as it gave the same compound (m.p. and mixed m.p. and comparative IR) (Scheme 2).

The addition of phosphorus compounds containing the $\rangle$P(S)SH grouping to carbon–carbon multiple linkages has been used to prepare a variety of sulphides[10] a number of which are important oil additives[11] and potential insecticides.[12] Diphenylphosphinodithioic acid is now found to add to the exocyclic conjugated double bond in **4**, using methanol as a solvent to give a colourless 1:1 adduct formulated as **9**.



9

The structure of **9** has been established by microanalyses, IR, Ms and ^1H NMR. In the IR spectra compound **9** showed bands at 3300 cm^{-1} (NH), 1740 cm^{-1} (CO amide) and 1640 cm^{-1} (CO ester), it gave also a molecular peak at M/e = 531 (base peak). In the ^1H NMR it showed a singlet at 3.6 ppm for $\underline{CH_3}$ (ester group), a complex pattern in the region 4.9–5.4 ppm for two ^1H protons (—CH—CH—), and the aromatic protons in the area 6.8–8.0 ppm with integral of 21 protons (aromatic + NH proton).

The result of this investigation allows certain conclusions to be drawn. The reaction product depends not only on the solvent but also on the phosphite used. Thus whereas the reaction of trimethyl phosphite and dimethyl phosphite with 4-benzylidene-2-phenyloxazol-5-one in methanol gave the trimethyl ester of N-benzoyl-3-phenyl-3-phosphonoalanine, the reaction of trimethyl and triethyl phosphite in ethanol and methanol respectively gave ethyl or methyl α-benzamidocinnamate. Also, diphenylphosphinodithioic acid reacts with **4** to give N-benzoyl-3-phenylcysteine, methyl ester, diphenylphosphinodithioate.

EXPERIMENTAL

Melting points are uncorrected. The trialkyl phosphites were purified by prolonged treatment with sodium ribbon, followed by fractional distillation and the dimethyl phosphite was freshly prepared. The starting compound **4** was prepared by a known procedure.[6] ^1H NMR spectra were recorded at 60 MHz on a Varian A-60 Spectrometer. $CDCl_3$ was used as internal standard, chemical shifts are in ppm—values. Mass spectra were recorded on a Micromass 7070f Spectrometer operating at 70 eV using direct inlet. The ^{31}P chemical shift is reported positive when found downfield relative to the external H_3PO_4. The light petroleum used boiled at 40–60° and benzene (thiophene-free) was dried over metallic sodium.

1. *Reaction of Trimethyl Phosphite with 4-Benzylidene-2-phenyloxazol-5-one* (**4**)). *Preparation of N-Benzoyl-3-phenyl-3-phosphonoalanine—trimethyl ester* (**7**). A mixture of the title compound **4** (0.01 mole) and trimethyl phosphite[13] (0.012 mole) in absolute methanol (25 ml) was refluxed for six hrs on a water-bath. After removal of the solvent under reduced pressure, the residue thus obtained, was treated with pet. ether and the precipitated material was collected, dried and crystallized from benzene–lightpetroleum to give the title compound **7**, m.p. 80° (70% yield). Calcd. for $C_{19}H_{22}NO_6P$: C, 58.31; H, 5.63; N, 3.58; P, 7.93. Found: C, 57.98; H, 5.70, N, 3.48; P, 8.05.

2. *Action of Heat on* **4**. Compound **4** (0.2 g) was heated in methanol at reflux temperature for 24 hrs. After evaporation of the solvent the residue was crystallized from benzene to give the starting compound **4** (m.p. and mixed m.p.)

3. *Reaction of Trimethyl Phosphite with* **4** *using Ethyl Alcohol as a Solvent.* This experiment was performed using the same procedure as in reaction (**1**) but using ethyl alcohol as solvent to give ethyl α-benzamido-cinnamate, m.p. 110° [14] (m.p. and mixed m.p.).

4. *Reaction of Triethyl Phosphite with* **4** *Using methyl Alcohol as a Solvent.* Using the same molar ratio as above and methyl alcohol as solvent gave methyl α-benzamido-cinnamate m.p. 138° [14] (m.p. and mixed m.p. and comparative IR).

5. *Reaction of Dimethyl Phosphite with* **4**. A mixture of 4 (0.01 mole), dimethyl phosphite[15] (0.012 mole) and two drops of saturated solution of $NaOCH_3$ methanol was heated for 3 hrs. After removal of the solvent, the residue was crystallized from benzene to give 7 in 75% yield (identified by m.p. and mixed m.p. with compound **7** prepared from experiment 1).

6. *Reaction of diphenylphosphinodithioic Acid with* **4**. To a cold solution of 4 (0.01 mole) in methanol (25 ml) was added diphenylphosphinodithioic acid[16] (0.012 mole) in 5 ml methanol and a few drops of a saturated solution of $NaOCH_3$ in methanol. The mixture was refluxed under N_2 for 6 hrs. After removal of the volatile materials under reduced pressure, the residue was crystallized from benzene-light petroleum to give compound **9** as colourless crystals, m.p. 100°, (80% yield). Calcd. for

$C_{29}H_{26}NO_3PS_2$ C, 65.54; H, 4.90; N, 2.63, P, 5.84, S, 12.05. Found: C, 65.25 H, 4.85; N, 2.70, P, 5.89, S, 12.15.

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