

Reaction of Ethyl Orthoformate with Phosphorous Pentasulphide & O,O-Diethyl Dithiophosphoric Acid*

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Ethyl orthoformate reacts with phosphorous pentasulphide to give ethyl formate, ethyl thionoformate and triethyl dithiophosphate. The latter compound has been shown to be O,O-diethyl-S-ethyl dithiophosphate (I) by IR, NMR and mass spectral data. The identity of triethyl dithiophosphate with I has been established by an unambiguous synthesis of I by the alkylation of O,O-diethyl dithiophosphoric acid. The probable mechanism of its formation has been suggested.

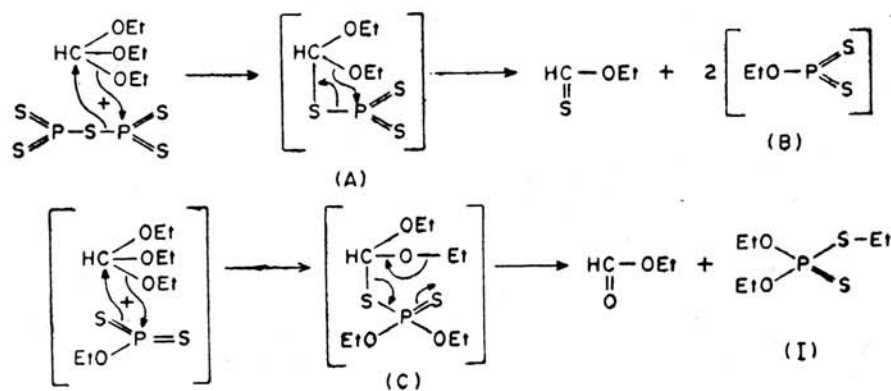
THE reaction of ethyl orthoformate with phosphorous pentasulphide was reported by Brannock¹ to give ethyl formate, ethyl thionoformate and a triethyl dithiophosphate. However, no definite structure was proposed for the latter compound and it was merely stated that it could be either O,O,S-triethyl dithiophosphate or O,S,S-triethyl dithiophosphate.

In the course of our work on the synthesis of heterocyclic compounds using ethyl orthoformate, we decided to reinvestigate the reaction of ethyl orthoformate with phosphorous pentasulphide. The products obtained were found to be identical with those reported by Brannock. The structure of the triethyl dithiophosphate has been elucidated and the possible mechanism of its formation has been suggested.

The NMR spectrum (CDCl₃, τ) of the triethyl dithiophosphate shows a nine-proton triplet centred at 8.85 and a two-proton octet centred at 7.15. The lowest downfield multiplet which also shows eight lines is at 5.9 and accounts for two methylene protons. From this data it is clear that there are three ethyl groups, two of them are identical and one differs in its chemical environment. Further

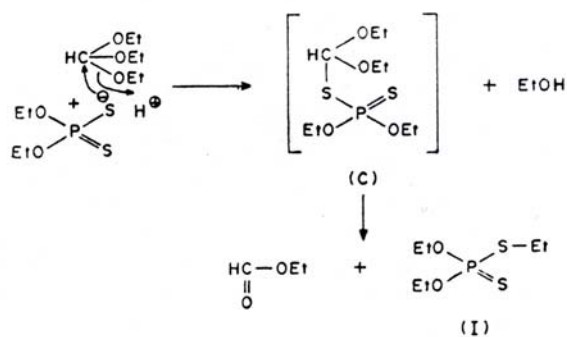
the multiplicities of the methylene groups suggest that they are coupled to phosphorus through either oxygen or sulphur atoms. The multiplet centred at 5.9 and which accords for two methylenes is due to P-(O-CH₂-CH₃)₂ and the upfield methylene at 7.15 can be assigned to P-S-CH₂-CH₃. When the triplet due to methyl groups at 8.85 was irradiated, the two methylene multiplets at 7.15 and 5.9 had collapsed to doublets (*J* = 16 Hz and 10 Hz respectively). The higher coupling constant can be due to *J*_{P-S-CH}, and the smaller one due to *J*_{P-O-CH}, (ref. 2).

Its IR spectrum (liquid film) shows bands at 1165, 1025 and at 660 cm⁻¹. The first two bands are assigned to P-O-alkyl and the last to P=S absorption³. The mass spectrum shows the molecular ion at *m/e* 214 (86.6%) and the base peak at *m/e* 186 due to the loss of an ethyl group. The other significant ions are at *m/e* 121 (90%), 137 (63%), 153 (16%), and at 169 (5%) which can be accounted for (C₂H₅O)₂P⁺, C₂H₅O-P⁺-SC₂H₅, (C₂H₅O)₂P=S and C₂H₅O-P-SC₂H₅, respectively. From these data it is clear that the triethyl dithiophosphate can be represented by structure I.



SCHEME 1

*NCL Communication No. 1870.



SCHEME 2

The mechanism for formation of I can be suggested as shown in Scheme 1. The reaction occurs in two stages. In the first stage, ethyl orthoformate reacts with phosphorous pentasulphide giving rise to one mole of ethyl thionoformate and two moles of (B), through the intermediate (A). In the second stage each mole of (B) reacts with an additional molecule of ethyl orthoformate to give one mole of ethyl formate and one mole of I through the intermediate species (C). Further an intermediate like (C) is really involved in the process is evident from the reaction of O,O-diethyl dithiophosphoric acid with ethyl orthoformate which gives ethyl formate and I as indicated in Scheme 2.

O,O-Diethyl-S-ethyl dithiophosphate (I) has been synthesized unambiguously by reaction of the potassium salt of O,O-diethyl dithiophosphoric acid with ethyl bromide. The product obtained is identical with triethyl dithiophosphate obtained by Brannock¹.

Experimental Procedure

O,O-Diethyl dithiophosphoric acid — Phosphorous pentasulphide (11.1 g, 0.05 mole) was dissolved in absolute ethanol (18 ml, 0.03 mole) with cooling. The clear solution was then refluxed on a steam-bath for 4 hr during which period the evolution of H₂S gas was completely stopped. The excess of ethanol was removed and the viscous liquid was distilled under reduced pressure to give O,O-diethyl dithiophosphoric acid in almost quantitative yield (18 g).

Reaction of ethyl orthoformate with O,O-diethyl dithiophosphoric acid — O,O-Diethyl dithiophosphoric acid (18.6 g, 0.1 mole) and ethyl orthoformate (16.5 ml, 0.1 mole) were refluxed for 2 hr. The mixture was then distilled and the first fraction collected was characterized as ethyl formate and the remaining viscous liquid was distilled under reduced pressure (114°/10 mm) to give O,O-diethyl-S-ethyl dithiophosphate. The IR spectrum of this product was superimposable with the IR spectrum of I obtained by the reaction of ethyl orthoformate with P₂S₅.

O,O-Diethyl-S-ethyl dithiophosphate (I) — O,O-Diethyl dithiophosphoric acid was ethylated with ethyl bromide (excess) in boiling acetone in presence of potassium carbonate. The solvent was removed, water added and the oily liquid was collected and distilled under reduced pressure to yield I.

References

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