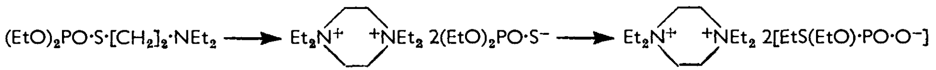
3. *The Reactivity of Organophosphorus Compounds. Part XI.*[1] *High-temperature Decomposition of* S-2-*Diethylaminoethyl Diethyl Phosphorothioate* (" *Amiton* ").

By J. I. G. Cadogan.

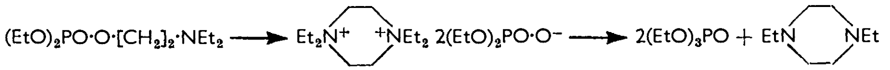
Decomposition of *S*-2-diethylaminoethyl diethyl phosphorothioate (" Amiton ") at 165° gives triethylamine, whereas the product of the low-temperature (60—100°) decomposition, which is a mixture of 1,1,4,4-tetraethylpiperazinium bis-(*OO*-diethyl phosphorothioate) and bis-(*OS*-diethyl phosphorothioate), on decomposition at high temperatures gives triethyl phosphate, triethyl phosphorothiolate, triethyl phosphorothionate, 1,4-diethylpiperazine, diethyl sulphide, and diethyl disulphide. " Amiton " at 150° in the presence of water gives 2-diethylaminoethanol and *NNN'N'*-tetraethylethylenediamine. The modes of formation of these products are discussed.

Decomposition at 60—100° of *S*-2-diethylaminoethyl diethyl phosphorothioate (" Amiton ") (I), an extremely toxic[2] insecticide, has been shown[3] to proceed by way of rearrangement of 1,1,4,4-tetraethylpiperazinium bis-(*OO*-diethyl phosphorothioate) (II) to the isomeric bis-(*OS*-diethyl phosphorothioate) (III).



(I) (II) (III)

The analogous 2-diethylaminoethyl diethyl phosphate (IV) behaves similarly at low temperatures, but at 180° decomposition of the intermediate 1,1,4,4-tetraethylpiperazinium bis-(diethyl phosphate) (V) occurs by way of a reverse Menschutkin reaction to give triethyl phosphate and 1,4-diethylpiperazine.[3]



(i)

(IV) (V)

It was thus of interest to investigate the high-temperature reaction of " Amiton," which in theory would be expected to proceed by way of the bis-(*OO*-diethyl phosphorothioate) (II) and the bis-(*OS*-diethyl phosphorothioate) (III) to give 1,4-diethylpiperazine and triethyl phosphorothiolate. In practice, however, decomposition of " Amiton " above 165° gave a good yield of triethylamine with a small amount of polymer of approximate formula $(\cdot S \cdot CH_2 \cdot CH_2 \cdot)_n$, and a small quantity of an unidentified neutral phosphorus ester. Infrared examination suggested the presence of triethyl phosphate but further

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[1] Part X, Burn, Cadogan, and Moulden, *J.*, 1961, 5542.
[2] Fukoto and Stafford, *J. Amer. Chem. Soc.*, 1957, **79**, 6083.
[3] Cadogan and Thomas, *J.*, 1960, 2248.

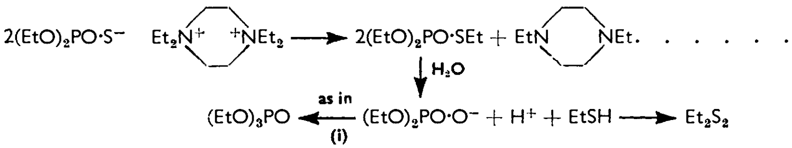
classification of this third product was unsuccessful. Triethylamine is believed to arise from self-alkylation to give an intermediate salt of the type (VI), which undergoes decom-

$$(EtO)_2PO{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}NEt_3^+ \quad Et_2N{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}PO(OEt){\cdot}O^- \quad (VI)$$

position of the reverse Menshutkin type. The other product of this reaction would be a complex product which is assumed to undergo further self-alkylation and subsequent decomposition to give more triethylamine. Similar self-alkylations of diethyl 2-diethylaminoethylphosphonate[4] and of *N*-substituted phosphoramidates[5] have been reported previously.

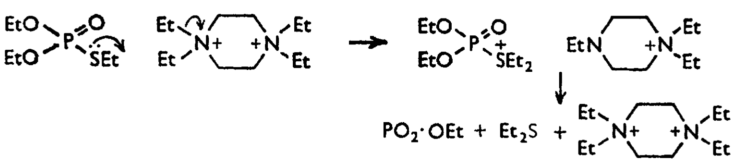
The decompositions at high temperature of the piperazinium bis-(*OO*-diethyl phosphorothioate) (II) and bis-(*OS*-diethyl phosphorothioate) (III) have also been studied. The former, on dry distillation, gave a product (30%) which contained triethyl phosphate (40%), triethyl phosphorothiolate (38%), triethyl phosphorothionate (2%), 1,4-diethylpiperazine (5%), diethyl sulphide (5%), and diethyl disulphide (10%), and the odour of ethanethiol was noticed during the reaction.

The presence of triethyl phosphoro-thiolate and -thionate and of 1,4-diethylpiperazine is explicable in terms of reaction as in (ii), where the very small amount of thionate formed reflects the smaller nucleophilicity towards carbon of the $>PS{\cdot}O^-$ ion than of the $>PO{\cdot}S^-$ anion. The formation of triethyl phosphate, diethyl disulphide, and diethyl sulphide is, however, less easily rationalised. The first two products are assumed to arise from the ease with which water is absorbed by the parent piperazinium bis-(*OO*-diethyl phosphorothioate) (II) to give the crystalline dihydrate. The first step in the decomposition of the salt is the formation of triethyl phosphorothiolate and 1,4-diethylpiperazine [reaction (ii)]; hydrolysis of the former would give ethanethiol, and hence the disulphide, and the diethyl phosphate anion, which in turn can dealkylate unreacted 1,1,4,4-tetraethylpiperazinium cation [as in reaction (i)] or the newly formed 1,4-diethylpiperazinium cation



. . . . . . (ii)

to give triethyl phosphate. Diethyl sulphide is unlikely to have been formed under the conditions of this reaction by dealkylation by thioethoxide ion. It is more likely to have arisen by *S*-alkylation of triethyl phosphorothiolate by the 1,1,4,4-tetraethylpiperazinium cation, thus resembling the recently reported alkylation of phosphorothiolates by alkyl iodides.[1]



In support of the above interpretation is the observation that significantly more triethyl phosphorothiolate, at the expense of triethyl phosphate and diethyl disulphide, is formed in a reaction under anhydrous conditions. On the other hand, decomposition of the dihydrate gave a higher yield of triethyl phosphate. Dry distillation of the isomeric 1,1,4,4-tetraethylpiperazinium bis-(*OS*-diethyl phosphorothiolate) (III), which is not so readily hydrated, gave triethyl phosphorothiolate (9 parts) and triethyl phosphate (1 part).

In accord with these observations the product of the low-temperature isomerisation

[4] Cadogan, *J.*, 1957, 4154.
[5] Cadogan, *J.*, 1957, 1079.

of " Amiton," which has been shown to be a mixture of the piperazinium phosphorothioates (II) and (III),[3] gave on dry distillation the expected mixture of triethyl phosphate, phosphorothiolate, and phosphorothionate and diethyl sulphide and disulphide.

Decomposition of the piperazinium salts in each case led to the formation of an involatile salt-like residue which could not be resolved. It is possible that the low accountance of piperazine derivatives is related to the appearance of these residues.

When " Amiton " was decomposed in the presence of water at 150° the products included 2-diethylaminoethanol, 1,1,2,2-tetraethylethylenediamine, and a gas. In this case dimerisation to 1,1,4,4-tetraethylpiperazinium bis-(*OO*-diethyl phosphorothioate) (II) is invoked, followed by base-catalysed degradation of the cation. Alkaline decompositions of tetra-alkylpiperazinium salts to give these products and acetylene have been previously reported.[3,6]

EXPERIMENTAL

" Amiton " (*S*-2-diethylaminoethyl diethyl phosphorothioate) being very toxic, precautions against personal contamination are needed.

Infrared spectra in the region of 2—15 μ were obtained by using a Perkin–Elmer model 21 double-beam spectrophotometer, with a rock salt prism. Those in the region 15—25 μ were recorded on a Hilger H 800 double-beam spectrophotometer with potassium bromide prisms. Liquids were examined as capillary films between potassium bromide plates, and solids as Nujol mulls or in potassium chloride or bromide discs. Mr. L. C. Thomas is thanked for the provision of these facilities and his help in interpretation of the spectra is gratefully acknowledged.

Gas–liquid chromatography was carried out on a Perkin–Elmer " Fraktometer " model 116, with a sensitive dual thermal conductivity detector, the response of which was tested by the use of mixtures of known composition.

Preparations.—" Amiton " [7] had b. p. 88°/0·04 mm., n_D^{25} 1·4666 (purity 99% by titration). Triethyl phosphorothiolate [8] had b. p. 100°/12 mm., n_D^{25} 1·4555. Triethyl phosphorothionate [8] had b. p. 98—100°/13 mm., n_D^{25} 1·4460. 1,4-Diethylpiperazine, b. p. 68°/10 mm., n_D^{25} 1·4520, was prepared as described by Cadogan.[9] 1,1,4,4-Tetraethylpiperazinium bis-(*OS*-diethyl phosphorothioate), m. p. 203°, 1,1,4,4-tetraethylpiperazinium bis-(*OO*-diethyl phosphorothioate), m. p. 148°, and the corresponding dihydrate, m. p. 90—116°, were prepared as described by Cadogan and Thomas.[3]

Decomposition of " Amiton " at 150° *in the Presence of Water.*—" Amiton " (10 g.) with water (1 g.) was kept at 150—160° for 16 hr. A gas was evolved which satisfied qualitative tests for acetylene which were, however, inconclusive owing to the small quantity. A small amount (0·2 g.) of a white sublimate was formed. The residual yellow liquid was distilled to give a range of fractions of b. p. 70—120°/10 mm. (4 ml.). These were combined and boiled with methyl iodide in methanol. Most of the solvent was removed and the crystals which separated were recrystallised to constant m. p. 263—264° from methanol–acetone. The m. p. was undepressed on admixture with 2-diethylaminoethanol methiodide, m. p. 263—264°. The mother liquors yielded 1,1,2,2-tetraethylethylenediamine dimethiodide, m. p. and mixed m. p. 203—204° (Found: C, 31·7; H, 6·4. Calc. for $C_{12}H_{30}I_2N_2$: C, 31·6; H, 6·6%). The sublimate had m. p. 183° and was polymeric [Found: C, 39·6; H, 6·8. Calc. for $(C_2H_4S)_n$: C, 40·0; H, 6·7%].

Decomposition of " Amiton " at 165°.—" Amiton " (10 ml.) under nitrogen was kept at 165°. After 1 hr. a white sublimate (0·1 g.), m. p. 184°, was formed, which was identical with that formed in the experiment involving " Amiton " and water at 150°. No more polymer was formed after further heating (15 hr.). The residue, on distillation, gave triethylamine (1·5 g.; methiodide, m. p. and mixed m. p. 295°). A higher-boiling fraction, b. p. 100—180°/760 mm., was dissolved in ether and extracted with acid to remove bases. The basic fraction contained triethylamine and unchanged " Amiton." The neutral fraction, which was a phosphorus compound or mixture of compounds, was not identified.

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[6] Knorr, *Ber.*, 1905, **38**, 3135; 1906, **39**, 1420; Harley-Mason, *J.*, 1947, 321.
[7] Calderbank and Ghosh, *J.*, 1960, 637.
[8] Stirling, *J.*, 1957, 3597.
[9] Cadogan, *J.*, 1955, 2971.

The experiment was repeated on a 50 g. scale. After 6½ hr. at 160—170°, the sublimate (0·5 g.) was removed and triethylamine (7 g.) was isolated. The residue was heated at 190° for a further 5 hr., more triethylamine (3 g.) being obtained together with a liquid, b. p. 98°/20 mm. (4 g.). The residue could not be resolved. The second fraction, dissolved in ether, was washed free from base and redistilled; it had b. p. 90°/20 mm., n_D^{25} 1·4770 (0·5 g.) (Found: C, 43·7; H, 8·5%). Repeated distillation of this neutral phosphorus compound did not alter these figures. Infrared examination indicated the presence of the $(EtO)_2P$ group.

Distillation of 1,1,4,4-*Tetraethylpiperazinium Bis-*(OO-*Diethyl Phosphorothioate*).—The anhydrous salt (3·56 g.) was distilled from an oil bath. Vigorous decomposition began at 210° and a brown liquid, b. p. 140—195° (1·61 g.), was collected in an ice-cold receiver. The gummy residue proved to be intractable. Gas–liquid chromatography of the distillate, through a 2-m. column packed with Silicone oil on Celite at 190°, showed the presence of the following components (relative retention times and yields are given): diethyl sulphide (1·0; *ca.* 5%), diethyl disulphide (1·9; 10%), 1,4-diethylpiperazine (2·6; *ca.* 5%), triethyl phosphate (3·1; 30%), triethyl phosphorothionate (3·9; *ca.* 1%), unknown component (4·3), triethyl phosphorothiolate (5·6; 38%). The qualitative composition of the mixture was confirmed by carrying out gas–liquid chromatography under different conditions, *e.g.*, by using a 1-m. Apiezon grease–Celite column at 170° and a 2-m. Apiezon grease–Celite column at 168°. The mixture in ether was extracted with dilute hydrochloric acid, dried ($MgSO_4$), and distilled. The phosphate ester fraction was found by gas–liquid chromatography to contain triethyl phosphate (41·2%), triethyl phosphorothionate (*ca.* 1%), and triethyl phosphorothiolate (47·7%); this was confirmed by infrared spectroscopy.

Related experiments were carried out under different conditions. In each case the neutral phosphorus ester fraction was isolated and analysed as described above. The results of typical experiments are summarised below.

(*a*) The dihydrate (6·38 g.) gave a distillate (2·22 g.) which gave an ester fraction of the following composition (%): triethyl phosphate (51·4), phosphorothionate (3·0), and phosphorothiolate (40·6).

(*b*) The anhydrous salt was dried (P_2O_5) in the distillation apparatus at 70°/0·1 mm. for 2 hr. before distillation. The ester fraction had the following composition (%): triethyl phosphate (28·0), phosphorothionate (3·0), phosphorothiolate (63·0). This was confirmed by infrared spectroscopy. The experiment was repeated after drying for 36 hr. to give the following results: phosphate (15·0), phosphorothionate (5·0), and phosphorothiolate (77·0%). The absence of dry-box facilities for weighing and transference of samples precluded the complete exclusion of moisture from the experiments, so that it was not practicable to obtain conditions under which phosphate was not formed.

(*c*) Decomposition of 1,1,4,4-tetraethylpiperazinium bis-(*OS*-diethyl phosphorothioate) (0·6 g.) gave a product, b. p. 150—195° (0·3 g.), the neutral portion of which had an infrared spectrum identical with that of triethyl phosphorothiolate (9 parts) and triethylphosphate (1 part).

(*d*) The product of isomerisation of " Amiton " at 60°, prepared as described by Cadogan and Thomas,[3] gave a product the neutral portion of which contained triethyl phosphate (25·0), triethyl phosphorothionate (*ca.* 1·0), triethyl phosphorothiolate (60·0), diethyl disulphide (5·0) and diethyl sulphide (5·0%).

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