the yellow of a stable chelate. The addition of acid to the solution of the chelate regenerates the ferricinium ion at the same optical density as that previous to chelate formation. In a similar medium the addition of 1:2-diaminocyclohexanetetra-acetic acid, citric acid, oxalic acid and tartaric acid gives rise to yellow chelates in solution.

The ferricinium ion in this medium gives rise to a polarographic wave at +0·16 V(1) whilst on addition of EDTA and adjustment of pH to 3·5 a wave is obtained at −0·14 V with a similar diffusion current to that of the ferricinium ion. The addition of 1:2 diaminocyclohexanetetra-acetic acid at pH 3·5 leads to a wave at −0·13 V. No well-defined waves were obtained with the other reagents at various pH's, although there was a considerable modification of the ferricinium response at +0·16 V.

A Job plot for each reagent showed that a 1:1 chelate was formed in each case, and a spectrophotometric study of ferricinium ion—EDTA solutions at pH 1·90 indicated partial dissociation of the chelate. By the technique described previously,(2) and from measurements of the extinction coefficients of the chelate and of free ferricinium ion log K_s for the ferricinium chelate of EDTA was found to be 17·4. The values of the acid dissociation constants of EDTA used in this determination were those obtained by SCHWARZENBACH(3). Similar quantitative measurements of optical densities with the other reagents indicated that the strength of chelation is in the decreasing order 1:2 diaminocyclohexanetetra-acetic acid > EDTA > citric acid > oxalic acid > tartaric acid.

In each case, upon increasing the pH the yellow colour of the solution remained substantially the same until pH 7·5, when the solutions assumed a brown coloration which was complete at pH 8·5. Addition of acid to these solutions indicated that the ferricinium ion could be regenerated. On standing, a brown precipitate was formed which consisted substantially of ferric hydroxide.

Experimental

Stock solutions of ferricinium perchlorate in 95% ethanol were obtained by oxidation of ferrocene in 95% ethanol containing perchloric acid at a platinum anode.(1) Reagents were of A.R. grade where possible. The amino carboxylic acids were purified as described previously.(2) Spectrophotometric and polarographic data were obtained as previously indicated, the strength of the solutions being adjusted to 0·1 M by addition of ammonium chloride.

T. D. SMITH

Chemistry Department
The Royal College of Science and Technology
Glasgow

(1) J. A. PAGE and G. WILKINSON, *J. Amer. Chem. Soc.* **74**, 6149 (1952).
(2) J. K. FOREMAN and T. D. SMITH, *J. Chem. Soc.* 1758 (1957).
(3) G. SCHWARZENBACH, R. GUT and G. ANDEREGG, *Helv. Chim. Acta* **37**, 937 (1954).

A new synthesis of tetramethylethylenediphosphine

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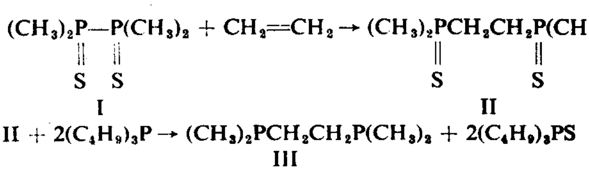
P,P,P′,P′-Tetraalkylethylenediphosphines, a group of powerful chelating agents,(1) have been prepared by stepwise alkylation of phosphine and by addition of tetraalkylbiphosphines to ethylene.(2) A more convenient synthesis has now been found and involves addition of tetramethylbiphosphine disulphide(I), obtainable in 85 per cent yield from methylmagnesium bromide and thiophosphoryl chloride,(3) to ethylene to give P,P,P′,P′-tetramethylethylenediphosphine disulphide(II).



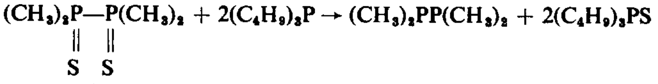
$$\underset{\text{I}}{(CH_3)_2\underset{\underset{S}{\|}}{P}-\underset{\underset{S}{\|}}{P}(CH_3)_2} + CH_2{=}CH_2 \rightarrow \underset{\text{II}}{(CH_3)_2\underset{\underset{S}{\|}}{P}CH_2CH_2\underset{\underset{S}{\|}}{P}(CH_3)_2}$$

$$\text{II} + 2(C_4H_9)_3P \rightarrow \underset{\text{III}}{(CH_3)_2PCH_2CH_2P(CH_3)_2} + 2(C_4H_9)_3PS$$

(1) C. E. WYMORE, Ph.D. Thesis, University of Illinois (1957).
(2) A. B. BURG, Wright Air Force Development Center Conference on High Temperature Polymers and Fluid Research, May, 1959.
(3) H. REINHARDT, D. BIANCHI and D. MÖLLE, *Ber.* **90**, 1657 (1957).

Desulphurization of II with tributylphosphine gave P,P,P′,P′-tetramethylethylenediphosphine(III) in 78 per cent yield. Although the overall yield is similar to that reported by BURG,(2) this reaction sequence is more suitable for large-scale preparations because it involves no spontaneously flammable materials.

It was also found that tetramethylbiphosphine disulphide(I) itself can be desulphurized with tributylphosphine to give tetramethylbiphosphine(IV) in 69 per cent yield. Triethyl phosphite also serves as a desulphurizing agent in this reaction but gives a lower yield of IV.



$$\underset{\underset{S}{\|}}{(CH_3)_2P}—\underset{\underset{S}{\|}}{P}(CH_3)_2 + 2(C_4H_9)_3P \rightarrow (CH_3)_2PP(CH_3)_2 + 2(C_4H_9)_3PS$$

I IV

Experimental

P,P,P′,P′-*Tetramethylethylenediphosphine disulphide*. Each of four 165 ml Carius tubes was charged with 11·2 g of tetramethylbiphosphine disulphide, 0·3 g of iodide and 2·0 g of ethylene. The tubes were heated at 275° for 48 hr. The light yellow, crystalline product was recrystallized from ethanol to give fine, off-white needles, m.p. 257–263°; yield, 30·5 g (60%). Two more recrystallizations gave pure white P,P,P′,P′-tetramethylethylenediphosphine disulphide, m.p. 260–263°. (Found: C, 33·53; H, 7·55; P, 29·07; S, 30·30. Calc. for $C_6H_{16}P_2S_2$: C, 33·63; H, 7·53; P, 28·92; S, 29·93.)

P,P,P′,P′-Tetramethylethylenediphosphine. A mixture of 19 g of P,P,P′,P′-tetramethylethylenediphosphine disulphide and 40 g of tri-n-butylphosphine(4) was heated to 245° in a nitrogen atmosphere in a 100 ml flask fitted to a 12 in. spinning-band column. The mixture soon became homogeneous and 20 ml of a clear, colourless liquid distilled at 160–190° over a period of 1 hr. Redistillation gave 10·4 g (78%) of P,P,P′,P′-tetramethylethylenediphosphine, b.p. 104°/60 mm; n_D^{25} 1·4887, m.p. −5 to −1° (Lit. values:(2) b.p. 188°, m.p. 0°). The proton magnetic resonance spectrum was identical to that of an authentic sample prepared by addition of tetramethylbiphosphine to ethylene.(2)

A 1·0 g sample of the diphosphine was dissolved in 50 ml of ether and stirred in a nitrogen atmosphere while methyl bromide was bubbled through the solution for 30 min. A white precipitate formed and was collected by filtration. Recrystallization from ethanol gave colourless crystals of P,P,P,P′,P′,P′-hexamethylethylenediphosphonium bromide, m.p. 355–365° with decomposition (Found: C, 28·48; H, 6·58; Br, 47·13. Calc. for $C_8H_{22}Br_2P_2$: C, 28·25; H, 6·52; Br, 47·00.)

Tetramethylbiphosphine. A mixture of 37 g of tetramethylbiphosphine disulphide and 120 ml of tributylphosphine(4) was heated in a nitrogen atmosphere in a flask attached to a 24 in. spinning-band column. When the pot temperature reached 130°, the solid dissolved. A vigorous reaction occurred and 26 ml of cloudy liquid distilled over a period of 15 min. Redistillation gave 16·8 g (69%) of clear, colourless tetramethylbiphosphine, b.p. 139–141°, m.p. −5 to −1° (Lit. vlaues:(5) b.p. 140°, m.p. −2·1°). The proton magnetic resonance spectrum contained a 1–2–1 triplet like that reported by BURG *et al.*(6) The infra-red spectrum contained strong bands assignable to methyl CH and CP bonds and was identical with that of an authentic sample of tetramethylbiphosphine.(7)

When tetramethylbiphosphine disulphide was heated with triethyl phosphite, crude tetramethylbiphosphine, b.p. 139–143°, distilled in 45 per cent yield. However, the infra-red spectrum indicated that the product was contaminated with triethyl phosphite (b.p. 155°).

G. W. PARSHALL

Contribution No. 607 from the
Central Research Department
Experimental Station
E. I. du Pont de Nemours and Co.
Wilmington, Delaware

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(4) The tributylphosphine used in these experiments was supplied by Metal and Thermit Corporation.

(5) A. B. BURG, *J. Inorg. Nucl. Chem.* 11, 258 (1959).

(6) A. B. BURG, P. J. SLOTA and W. MAHLER, Abstracts of Papers presented at the 134th Meeting of the American Chemical Society, September, 1958, p. 78P.

(7) The author is indebted to Dr. WALTER MAHLER for this comparison of the infra-red spectra.