merely decreases gradually to a very low value approaching that of water.

The photochemical process giving rise to the continuum has been discussed by Urey, Dawsey and Rice[7] and again recently by Holt, McLane and Oldenberg.[8]

[8] R. B. Holt, C. K. McLane and O. Oldenberg, *J. Chem. Phys.*, **16**, 225 (1948).

METCALF RESEARCH LABORATORY
BROWN UNIVERSITY
PROVIDENCE, R. I.

RECEIVED MARCH 23, 1949

Preparation of Tetramethyl Pyrophosphate

BY A. D. F. TOY

Previous investigations[1] have shown that the tetra-alkyl esters of pyrophosphoric acid, with the exception of the methyl ester, may be readily prepared in good yields by the controlled hydrolysis of the dialkyl chlorophosphates in the presence of pyridine. It has now been found that tetramethyl pyrophosphate may be prepared in the pure state and in good yield by the action of dimethyl chlorophosphate on trimethyl phosphate with the evolution of methyl chloride.

Procedure.—A mixture of 72.3 g. (0.5 mole) of dimethyl chlorophosphate, 350 g. (2.5 mole or 400% excess) of redistilled[2] trimethyl phosphate (n^{25}D 1.3948), containing a porous porcelain boiling chip was heated with occasional stirring, in a 500-cc. 3-necked flask equipped with a thermometer, a stirrer and a condenser fitted with a calcium chloride tube. Gaseous evolution began slowly at 105° and became steady at 113°. The temperature was maintained at 113° for two and one-half hours. When the rate of gas evolution slowed down the temperature was raised to 122°. After thirty minutes at 122° gas evolution had practically ceased. A portion of the mixture gave only a faint test for chloride indicating that the reaction had gone essentially to completion. The loss of methyl chloride amounted to 24.3 g. compared with a theoretical loss of 25.3 g. The product was fractionally distilled under reduced pressure and after the removal of the excess trimethyl phosphate (279 g., n^{25}D 1.3950), the fraction boiling at 106-108° and 0.3 mm., weighed 99.6 g. (85%). The residue weighed 9.5 g. Analysis and toxicity data showed the product to be identical with the tetramethyl pyrophosphate described previously.[1]

When only an equivalent quantity (0.5 mole) of trimethyl phosphate was used a somewhat lower yield of 86 g. (73.5%) of tetramethyl pyrophosphate was obtained. When the higher temperature of 130° was used with the 400% excess of trimethyl phosphate the gaseous evolution was much more rapid and the reaction was complete after one hour and ten minutes, the same high yield (84.3%) being obtained in the shorter time.

It has been previously pointed out,[1] that the analogous reaction between diethyl chlorophosphate and triethyl phosphate does not produce tetraethyl pyrophosphate in satisfactory yield.

RESEARCH LABORATORY
VICTOR CHEMICAL WORKS
CHICAGO HEIGHTS, ILL.

RECEIVED JANUARY 29, 1949

---

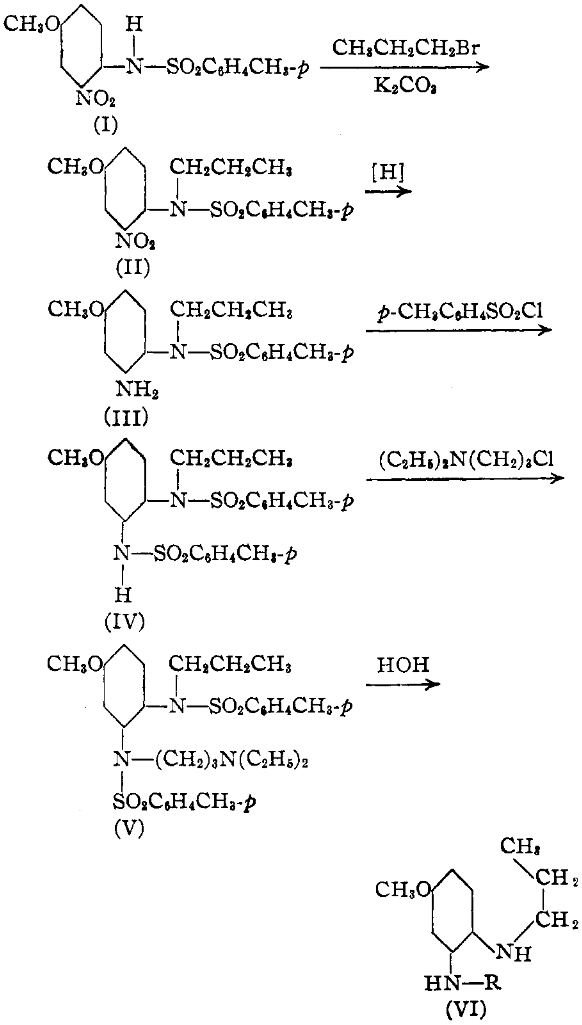
[1] Toy, THIS JOURNAL, **70**, 3882 (1948).

[2] It was necessary to purify trimethyl phosphate by distillation (n^{25}D 1.3948 to 1.3950). When the regular commercial grade material (n^{25}D 1.3928), was used without previous purification the gaseous bubbling began at a much lower temperature and only very low yields of tetramethyl pyrophosphate were obtained.

Attempted Synthesis of an Aliphatic Analog of Plasmochin[1]

BY MARTIN J. WEISS AND CHARLES R. HAUSER

Barber, Major and Wragg[2] have recently reported the synthesis of an aliphatic analog (VI, R = $-CH(CH_3)(CH_2)_3N(C_2H_5)_2$) of plasmochin. Before the appearance of this paper we had attempted the synthesis of a similar analog (VI, R = $-(CH_2)_3N(C_2H_5)_2$). Although this analog was not isolated in the pure condition, the reactions employed are of some interest.



Each of these steps, except the last, was effected in good yield. An attempt to propylate 2-nitro-4-methoxyaniline was unsuccessful but the *p*-toluenesulfonamido derivative (I) was readily alkylated. The nitro group of compound (II) was reduced in ethanol with zinc and ammonium chloride. After an unsuccessful attempt had been made to alkylate the amino group of compound

---

[1] This work was supported by a grant from the Duke University Research Council.

[2] Barber, Major and Wragg, *J. Chem. Soc.*, 613 (1946).