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).

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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 ($n^{25}\text{D}$ 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., $n^{25}\text{D}$ 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.

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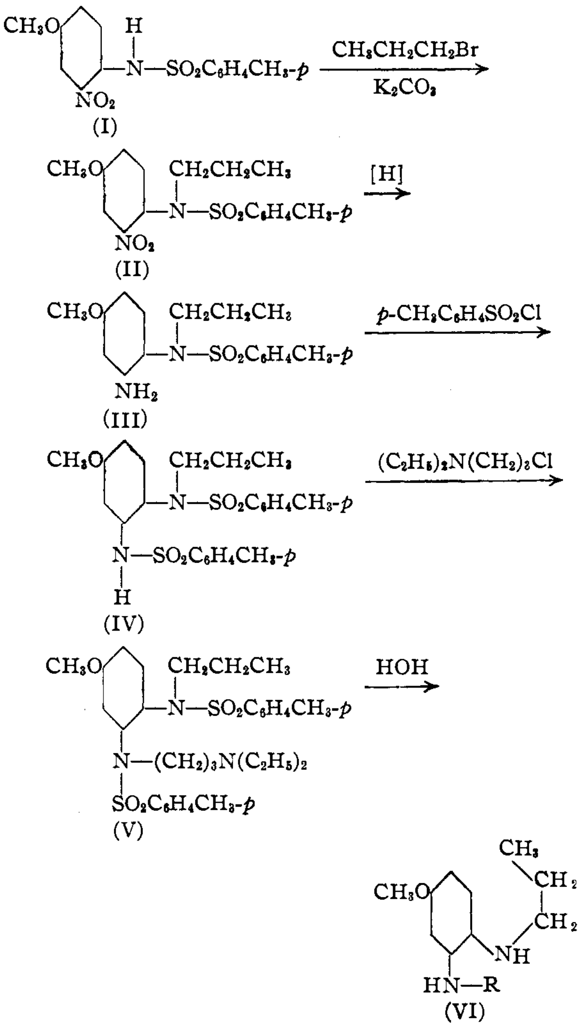
[1] Toy, THIS JOURNAL, **70**, 3882 (1948).

[2] It was necessary to purify trimethyl phosphate by distillation ($n^{25}\text{D}$ 1.3948 to 1.3950). When the regular commercial grade material ($n^{25}\text{D}$ 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.



(VI)

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

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

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

(III) with noval bromide (2-bromo-5-diethylaminopentane) according to the general procedure of Rohrman and Shonle,[3] compound (III) was converted to its *p*-toluenesulfonamido derivative (IV) which was alkylated successfully with 3-diethylaminopropyl chloride. However, hydrolysis of the alkylated product (V) gave material which could not be purified.

Barber and co-workers[2] similarly effected the propylation of compound (I) but the product (II) was then hydrolyzed and reduced. The resulting amine was reacted with 5-diethylamino-2,2-diethoxypentane followed by reduction to form their analog. The product was particularly susceptible to atmospheric oxidation and did not readily yield crystalline salts.[2]

Experimental[4]

3-Nitro-4-(N-*n*-propyl-*p*-toluenesulfonamido)-anisole (II).—A solution of 10 g. (0.032 mole) of 3-nitro-4-(*p*-toluenesulfonamido)-anisole[2] (I) and 4.6 g. (0.037 mole) of *n*-propyl bromide in 35 ml. of commercial absolute ethanol was refluxed with 4.5 g. (0.032 mole) of anhydrous potassium carbonate for seventeen hours.[5] The hot solution was filtered, the alcohol was evaporated and the deep red product was washed with a 10% sodium hydroxide solution and then with water. The yield of compound (II) as a tan-colored powder, melting at 105–106°, was 7.2 g. (64%). Two recrystallizations from ethanol–water gave white crystals melting at 107–108°; reported m. p. 108–109°.

Anal. Calcd. for $C_{17}H_{20}N_2O_5S$: C, 56.08; H, 5.54; N, 7.70; S, 8.81. Found: C, 56.25; H, 5.94; N, 7.85; S, 8.96.

3-Amino-4-(N-*n*-propyl-*p*-toluenesulfonamido)-anisole (III).—To a well stirred refluxing solution of 90 g. (0.247 mole) of 3-nitro-4-(N-*n*-propyl-*p*-toluenesulfonamido)-anisole (II) (m.p. 105–106°) in 1000 ml. of 85% ethanol (in a 2l. three-necked flask fitted with a reflux condenser and a mercury-sealed stirrer) was added 20 g. of ammonium chloride and, in small portions, 130 g. of zinc dust. After the reaction mixture had been stirred and refluxed for five hours, it was filtered and the insoluble material washed several times with small portions of hot 95% ethanol. To the combined ethanol solutions, 250 ml. of water was added and, after chilling, the precipitated white flocculent product was filtered and dried *in vacuo* to give 75 g. (91%) of amine (III) melting at 112°. Two recrystallizations did not raise the melting point.

Anal. Calcd. for $C_{17}H_{22}N_2O_3S$: C, 61.05; H, 6.63; N, 8.38; S, 9.59. Found: C, 61.08; H, 6.76; N, 8.41; S, 9.53.

3-(*p*-Toluenesulfonamido)-4-(N-*n*-propyl-*p*-toluenesulfonamido)-anisole (IV).—A solution of 60 g. (0.18 mole) of 3-amino-4-(N-*n*-propyl-*p*-toluenesulfonamido)-anisole (III) and 33.6 g. (0.18 mole) of *p*-toluenesulfonyl chloride in 120 ml. of pyridine was refluxed seven and one-half hours and allowed to stand overnight at room temperature. The addition of 120 ml. of 95% ethanol followed by the slow addition of 500 ml. of ice–water gave a heavy precipitate, which, after filtering, was washed with several portions of a 6 *N* hydrochloric acid until a sample of the washings, when made basic, was only slightly cloudy. After washing several times with water and drying in the oven at 70°, 78.5 g. (90%) of compound (IV) (m. p. 162–164°) was obtained. Several recrystallizations from ethanol–water gave white crystals melting at 167° cor.

Anal. Calcd. for $C_{24}H_{28}N_2O_5S_2$: C, 58.99; H, 5.78; N, 5.74; S, 13.12. Found: C, 59.21; H 6.01; N, 5.81; S, 13.05.

3-(N-γ-Diethylaminopropyl-*p*-toluenesulfonamido)-4-(N-*n*-propyl-*p*-toluenesulfonamido)-anisole (V).—A solution containing 78.5 g. (0.16 mole) of 3-(*p*-toluenesulfonamido)-4-(N-*n*-propyl-*p*-toluenesulfonamido)-anisole (IV) and 27.2 g. (0.184 mole) of 3-diethylaminopropyl chloride[6] in 215 ml. of dioxane was refluxed with 22.4 g. (0.16 mole) of anhydrous potassium carbonate for seventeen hours.[5] After the reaction mixture had been allowed to cool to room temperature, it was slowly poured with stirring into 600 ml. of ice–water. The resulting oil soon solidified. The solid was filtered, washed with water and dried in the oven at 80° to give 92.1 g. (96%) of product (V) melting at 152–154°. Rather surprisingly, several recrystallizations from dioxane–water gave white crystals melting at 130–133° which, however, analyzed for compound (V).

Anal. Calcd. for $C_{31}H_{43}N_3O_5S_2$: C, 61.87; H, 7.01; N, 6.98; S, 10.65. Found: C, 61.40; H, 7.28; N, 7.12; S, 10.88.

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[3] Rohrman and Shonle, THIS JOURNAL, **66**, 1640 (1944).

[4] Microanalyses by Oakwold Laboratories, Alexandria, Virginia. Melting points are uncorrected.

[5] See Izmail'skii and Simonov, *J. Gen. Chem.* (*U.S.S.R.*), **10**, 1580 (1940); *C. A.*, **35**, 2870 (1941).

[6] Breslow, Walker, Yost and Hauser, THIS JOURNAL, **67**, 1472 (1945).

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The Catalytic Oxidation of Piperonyloin to Piperil

BY MARVIN WEISS AND MILDRED APPEL

In a previous article,[1] a statement was made that piperonyloin could not be oxidized to piperil by cupric acetate and ammonium nitrate in acetic acid, due to the formation of tars. This was similar to the observation of Perkin,[2] that when dilute nitric acid reacted with piperonyloin a large amount of oxalic acid was formed.

A study of the effects of increasing amounts of catalyst showed that a point could be reached where the reaction rate of cupric ion with a benzoin (reaction A) exceeded the reaction rate of ammonium nitrate with cuprous ion (reaction B). This manifested itself by the formation of a reddish-brown precipitate of copper oxide, which did not redissolve unless more ammonium nitrate was added.

$$\text{(A)}\quad \mathrm{RCH(OH)COR + 2Cu(OAc)_2 \longrightarrow RCOCOR + 2CuOAc + 2AcOH}$$

$$\text{(B)}\quad \mathrm{2CuOAc + NH_4NO_3 + 2AcOH \longrightarrow 2Cu(OAc)_2 + NH_4NO_2 + H_2O}$$

$$\text{(C)}\quad \mathrm{CH_2O_2C_6H_3CH(OH)COC_6H_3O_2CH_2 + NH_4NO_3 \longrightarrow (COOH)_2} + \text{decomposition}$$

This reversal of reaction rates led to the interesting speculation that, in the event the oxidation of piperonyloin was carried out under conditions just short of copper oxide formation, that is, where the reaction rate of A equalled B, one might expect that reaction C, being slower than a combination of A plus B, would be suppressed. That reaction C might be slower is suggested by the re-

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[1] Weiss and Appel, THIS JOURNAL, **70**, 3666 (1948).

[2] Perkin, *J. Chem. Soc.*, **59**, 164 (1891).