[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

The Reaction of Aniline with Phosphorus Pentoxide: Phosphoric Anilides

BY ALLEN C. BUCK[1] AND HERMAN P. LANKELMA

The reaction of six and four moles of aniline with one mole of phosphorus pentasulfide has been shown to yield thiophosphoric trianilide and dithiophosphoric dianilide, respectively.[1a]

The reaction of six and four moles of aniline with one mole of phosphorus pentoxide under similar conditions gave aniline metaphosphate as the major reaction product along with small amounts of aniline orthophosphate. In addition to aniline metaphosphate, the reaction of four moles of aniline and one mole of phosphorus pentoxide at room temperature in an inert solvent such as toluene gave very low yields of phosphoric dianilide.

The formation of some phosphoric dianilide suggested that the reaction was similar to that with the sulfide, that is, the formation of a dianilide which subsequently reacts with aniline at higher temperatures to form a trianilide. However, the reaction of aniline with phosphorus pentoxide differed in that aniline metaphosphate was formed.

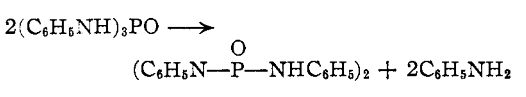
$$2C_6H_5NH_2 + P_2O_5 \longrightarrow (C_6H_5NH)_2POOH + HPO_3 \quad (1)$$

$$C_6H_5NH_2 + HPO_3 \longrightarrow C_6H_5NH_2{\cdot}HPO_3 \quad (2)$$

With phosphorus pentasulfide, however, the formation of dithiophosphoric dianilide was not interfered with by the formation of a salt of aniline.

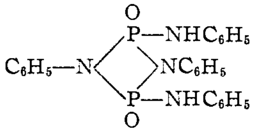
Although phosphoric trianilide was not obtained by the action of aniline on phosphorus pentoxide, it has been prepared by Michaelis and Soden[2] from aniline and phosphorus oxychloride. Phosphoric trianilide, like thiophosphoric trianilide, was stable to prolonged refluxing in water, dilute acids and bases. It was also stable toward glacial acetic acid under conditions which effect a cleavage of thiophosphoric trianilide.[1a]

Michaelis and Silberstein[3,4] observed that phosphoric trianilide was thermally unstable when heated under a vacuum, losing aniline to form dimeric phosphoric anil anilide

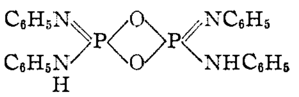


$$2(C_6H_5NH)_3PO \longrightarrow (C_6H_5N{-}\overset{O}{P}{-}NHC_6H_5)_2 + 2C_6H_5NH_2 \quad (3)$$

They recorded a melting point of 357° for this compound and suggested a cyclic amide structure (A), whereas Oddo[5] reported a melting point of 320–325° and suggested a cyclic isoamide structure (B)



(A)



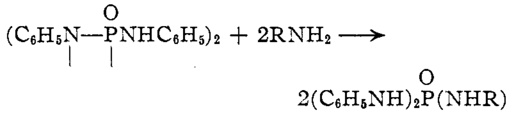
(B)

Dimeric phosphoric anil anilide, prepared in this laboratory by thermal decomposition of phosphoric trianilide, melted at 357–358° as reported by Michaelis and Silberstein. It has been previously shown that thiophosphoric trianilide exhibited similar thermal instability.[1a]

Since dimeric thiophosphoric anil anilide had reacted with aniline to reform thiophosphoric trianilide,[1a] it appeared that phosphoric anil anilide might undergo a similar reaction. When dimeric phosphoric anil anilide was refluxed in excess aniline, it slowly dissolved with the formation of quantitative yields of phosphoric trianilide.

It has previously been shown that the nitrogen–phosphorus bond in thiophosphoric trianilide was ruptured by tributylamine and that aniline could be displaced from it with primary amines.[6] Phosphoric trianilide was not attacked by tributylamine under similar conditions. This suggested that the aniline might not be displaced by primary amines. Accordingly phosphoric trianilide was treated with excess benzylamine under conditions which had displaced aniline from thiophosphoric trianilide to give eighty per cent. yields of tribenzyl thiophosphoric amide.[6] The phosphoric trianilide was recovered unaltered.

The stability of phosphoric trianilide to displacement reactions suggested that mixed phosphoric triamides might be prepared by the addition of amines other than aniline to dimeric phosphoric anil anilide



$$(C_6H_5\underset{|}{N}{-}\overset{O}{\underset{|}{P}}NHC_6H_5)_2 + 2RNH_2 \longrightarrow 2(C_6H_5NH)_2\overset{O}{P}(NHR) \quad (4)$$

This reaction was first tried using *n*-propylamine as the amine. The solid product obtained from the reaction was a mixture which exhibited resistance to hot dilute acids and bases, a property of trianilides, from which phosphoric trianilide was isolated after several crystallizations. When this reaction was repeated with secondary amines, di-*n*-propylamine and piperidine, a mixture of products was again obtained and phosphoric trianilide was isolated after two crystallizations.

Theoretically, amines could react with dimeric phosphoric anil anilide in one or both of the following ways depending upon whether nitrogen–

---

[1] Standard Oil Co., Ohio, Fellow in Chemistry 1946–1947; present address, E. I. du Pont de Nemours and Co., Parlin, New Jersey.

[1a] Buck, Bartleson and Lankelma, THIS JOURNAL, **70**, 744 (1948).

[2] Michaelis and Soden, *Ann.*, **229**, 295–340 (1885).

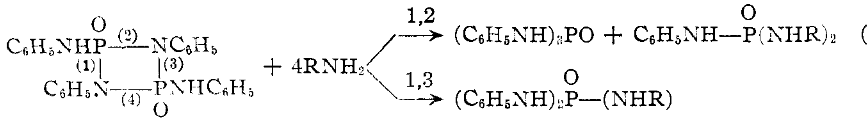
[3] Michaelis, *ibid.*, **407**, 310 (1915).

[4] Michaelis and Silberstein, *Ber.*, **28**, 716–733 (1896).

[5] Oddo, *Gazz. chim. ital.*, **29**, II, 340 (1899).

[6] Buck and Lankelma, THIS JOURNAL, **70**, 2396 (1948).

phosphorus bonds 1,2 or 1,3 of the ring were ruptured



(5)

Each pair of bonds would have an equal chance to be ruptured and a mixture of products would therefore be expected. The presence of phosphoric trianilide as one of the reaction products regardless of the nature of RNH_2 supported the view that the addition of amines to dimeric phosphoric anil anilide did occur by the rupture of bonds 1,2 above.

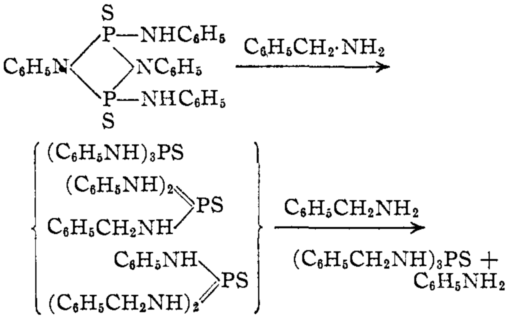
Since mixtures of products were obtained from which phosphoric trianilide was isolated only after repeated crystallization, it appeared quite likely that this mixture contained the two similar mixed phosphoric triamides suggested in equation (5) above. The similar solubilities of these mixed triamides prevented separation into the individual components.

The formation of phosphoric trianilide by the addition of two moles of an amine other than aniline to dimeric phosphoric anil anilide offers proof that the structure proposed by Michaelis[3] for dimeric phosphoric anil anilide is correct. The structure proposed by Oddo would not yield phosphoric trianilide but a mixed triamide.

By analogy with dimeric phosphoric anil anilide, the structure of dimeric thiophosphoric anil anilide previously reported[1a] would contain a four-membered nitrogen–phosphorus ring. This structure was supported by the fact that the addition of aniline gave thiophosphoric trianilide, a reaction comparable to that observed with dimeric phosphoric anil anilide. However, with amines other than aniline there was a difference in the type of triamide obtained. Whereas dimeric phosphoric anil anilide and amines at 180° gave mixtures of phosphoric triamides of which one component was always the trianilide, dimeric thiophosphoric anil anilide and amines such as benzylamine, gave excellent yields of a single triamide, tribenzyl thiophosphoric amide.[6] However, it has been shown previously that the action of excess benzylamine on dimeric thiophosphoric anil anilide at 30 and 60° gave mixtures of thiophosphoric triamides from which no individual triamide could be isolated. Also, displacement of aniline from thiophosphoric trianilide by benzylamine did not occur at 30 and 60° but occurred readily at 180°. It would appear, therefore, that the displacement of aniline in dimeric thiophosphoric anil anilide by benzylamine would not occur at the lower temperatures. The reaction of primary amines, such as benzylamine, with dimeric thiophosphoric anil anilide to form tribenzylthiophosphoric amide would involve severing of the ring to give a mixture of triamides followed by displacement of aniline.

In the case of dimeric phosphoric anil anilide the triamides resulting from the first reaction are stable.

Phosphoric dianilide, $(C_6H_5NH)_2POOH$, obtained in very low yields from aniline and phosphorus pentoxide has previously been prepared by Michaelis and Soden[2] from aniline and phosphorus oxychloride. Phosphoric dianilide was observed by Michaelis to be readily hydrolyzed by hot water and hot dilute acids to give aniline and phosphoric acid. It has previously been shown that thiophosphoric dianilide underwent a similar decomposition with these reagents.[1a]



(6)

Experimental

Reactions of Aniline with Phosphorus Pentoxide.—37.2 g. (0.4 mole) of aniline and 14.2 g. (0.1 mole) of phosphorus pentoxide in 100 ml. of toluene were heated at 50° for three hours with stirring. The principal product was aniline phosphate from which the aniline was liberated by treatment with cold 5% sodium hydroxide solution. The aniline was identified as benzene sulfonanilide, the phosphate ion as ammonium phosphomolybdate. In addition 3 g., a 6% yield, of phosphoric dianilide, m. p. 199–200°, was obtained. It was identified by a mixed melting point with a sample of the dianilide prepared by the method of Michaelis and Soden.[2] Using a 6:1 molar ratio of aniline and phosphorus pentoxide and heating at 200° for three hours only aniline phosphate was obtained.

Attempts to Hydrolyze Phosphoric Trianilide.—One gram samples of phosphoric trianilide were refluxed in water, 5% sodium hydroxide, 5% hydrochloric acid and glacial acetic acid for twenty hours without change.

Preparation of Dimeric Phosphoric Anil Anilide and its Reaction with Primary and Secondary Amines.—Nine grams of phosphoric trianilide was heated for thirty minutes at 225° under a vacuum of 30 mm. of mercury; 2.5 g. of aniline distilled over. The residual solid was washed with alcohol and filtered. Six grams of phosphoric anil anilide, m. p. 357–359°, was obtained. This is a yield of 94%.

Three grams of phosphoric anil anilide was heated with 15 g. of aniline at the boiling point for five hours. The excess aniline was removed by steam distillation and the residual solid recrystallized from alcohol and gave 3.9 g. (a 93% yield) of phosphoric trianilide, m. p. 213–215°.

Two grams of phosphoric anil anilide and 15 g. of *n*-propylamine heated at 180–190° in a sealed tube for five hours gave 1.0 g. of product melting at 70–205°. Recrystallizations from alcohol gave 0.2 g. of phosphoric trianilide. No other product could be separated.

Two grams of phosphoric anil anilide with 15 g. of di-*n*-propylamine gave 0.8 g. of phosphoric trianilide, and 7 g. of phosphoric anil anilide with 30 g. of piperidine gave 2 g. of phosphoric trianilide.

Stability of Phosphoric Acid Trianilide to Amines.—Phosphoric trianilide was heated with excess tributylamine for twenty hours at 130° and also with excess benzylamine for four hours at 170°. Unchanged trianilide was recovered in high yield and no reaction products were detected.

Summary

The reaction of aniline with phosphorus pentoxide gave aniline metaphosphate as the principal product.

A comparison of the properties of phosphoric and thiophosphoric anilides has been made.

Proof of structure of the dimeric phosphoric and thiophosphoric anil anilides has been given.

CLEVELAND, OHIO RECEIVED SEPTEMBER 10, 1947

[CONTRIBUTION NO. 53 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

The Preparation of Ethers of Triphenylcarbinol from the Triphenylcarbonium Ion

BY HILTON A. SMITH AND ROBERT J. SMITH

Several years ago Newman[1] reported a new method for the esterification of certain sterically hindered acids. The acids were dissolved in 100% sulfuric acid where they formed carbonium ions. The resulting solutions were poured into alcohols and the esters formed were subsequently recovered. Triphenylacetic acid is a sterically hindered acid which cannot be esterified by heating with an alcohol in the presence of an acid catalyst.[2] When an attempt was made to esterify this acid with methanol by Newman's method, the product was identified as the methyl ether of triphenylcarbinol. This is, perhaps, not surprising since it has already been shown[3] that triphenylacetic acid loses carbon monoxide quantitatively when treated with concentrated sulfuric acid. The mechanism for the formation of the ether is presumably

$$(C_6H_5)_3CCOOH + 2H_2SO_4 \longrightarrow (C_6H_5)_3CCO^+ + H_3O^+ + 2HSO_4^- \quad (1)$$

$$(C_6H_5)_3CCO^+ \longrightarrow (C_6H_5)_3C^+ + CO \quad (2)$$

$$(C_6H_5)_3C^+ + CH_3OH \longrightarrow (C_6H_5)_3COCH_3 + H^+ \quad (3)$$

While this method is a failure as far as the production of esters of triphenylacetic acid is concerned, it does indicate a quick and useful method for the preparation of ethers of triphenylcarbinol. The carbinol is dissolved in 100% sulfuric acid, where it forms the triphenylcarbonium ion according to the equation

$$(C_6H_5)_3COH + 2H_2SO_4 \longrightarrow (C_6H_5)_3C^+ + H_3O^+ + 2HSO_4^- \quad (4)$$ [4,5]

The carbonium ion may then be made to react with various alcohols in the manner indicated by equation (3). The yield of ether is essentially quantitative, and the product may be obtained in very pure form.

A search of the literature indicated that other methods which have been used to prepare ethers of triphenylcarbinol are usually quite long, and give smaller yields of impure products. Such methods include the reaction of triphenylmethyl chloride with an alcohol,[6,7,8] and the reaction of the chloride with sodium alcoholates. This latter method was employed by Norris and Young,[9] who prepared eleven different ethers of triphenylcarbinol in yields ranging from 10 to 60%. In the present research, six such ethers were prepared, the yields of purified products ranging from 86 to 97%. The same method could presumably be used for the formation of ethers of other carbinols which form similar carbonium ions in sulfuric acid (*i. e.*, have *i* factors of 4).

The preparation of pure ethers of triphenylcarbinol is, unfortunately, complicated by their decomposition into triphenylmethane and an aldehyde, as indicated for the ethyl ether by the equation

$$(C_6H_5)_3COC_2H_5 \longrightarrow (C_6H_5)_3CH + CH_3CHO \quad (5)$$

This reaction was extensively studied by Norris and Young[9] who found that the ease of decomposition increased with increasing complexity of the ether. In addition, the reaction is catalyzed by several ions, the most efficient of those studied being the bisulfate ion. The preparation of ethers of triphenylcarbinol from carbonium ions formed in sulfuric acid gives the product in the presence of bisulfate ions, and decomposition will occur for the higher members of the series unless the product is quickly removed.

Conditions were not found which would give the *s*-butyl, *t*-butyl and benzyl ethers. It might also be noted that Newman[1] was unable to prepare the *t*-butyl ester of trimethylbenzoic acid by an analogous method. The failure of such alcohols to give esters or ethers by reaction with the carbonium ions may be due to one of two reasons:

1. The effect of these branched-chain alcohols may be such as to materially decrease the rate of reaction (3).[10]
2. An equilibrium of the type

$$(C_6H_5)_3COR + H_2O \rightleftharpoons (C_6H_5)_3COH + ROH$$

---

[1] Newman, THIS JOURNAL, **63**, 2431 (1941).

[2] Smith and Burn, *ibid.*, **66**, 1494 (1944).

[3] Bistrzycki and Reintki, *Ber.*, **38**, 839 (1905); Bistrzycki and Mouron, *ibid.*, **43**, 2883 (1910); Dittmar, *J. Phys. Chem.*, **33**, 533 (1929); Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p. 283.

[4] Hantzsch, *Z. physik. Chem.*, **61**, 257 (1908).

[5] Hammett and Deyrup, THIS JOURNAL, **55**, 1900 (1933).

[6] Friedel and Crafts, *Ann. chim. phys.*, [6] **1**, 502 (1884).

[7] Hemilian, *Ber.*, **7**, 1208 (1874).

[8] Helferich, Speidel and Toehdte, *ibid.*, **56**, 766 (1923).

[9] Norris and Young, THIS JOURNAL, **52**, 753 (1930).

[10] Smith, *ibid.*, **62**, 1136 (1940).