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.

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

The Preparation of Ethers of Triphenylcarbinol from the Triphenylcarbonium Ion

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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

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

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(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 Tochdte, *ibid.*, **56**, 766 (1923).

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

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

may exist in solution, and the effect of increased complexity of the alkyl group may be of such a nature as to shift the equilibrium toward the formation of the carbinol.

The ethers of triphenylcarbinol also form the triphenylcarbonium ion when dissolved in 100% sulfuric acid, and the triphenylcarbinol may be recovered in essentially quantitative yields if such solutions are poured into water.

In attempting to find the most advantageous procedure for the etherification reactions, a study was first made of the esterification of 2,4,6-trimethylbenzoic acid with methanol and ethanol. It was found that Newman's procedure[1] could be greatly simplified. In fact, the study indicated that, under conditions similar to those employed by Newman, both benzoic acid and 2,4,6-trimethylbenzoic acids may be almost completely esterified, but the benzoates are rapidly hydrolyzed. If the reaction mixture is poured into water rather than having water poured into it, good yields of the benzoates may be obtained. Apparently when water is poured into the sulfuric acid solution, local heating causes hydrolysis of the benzoates. A similar but much slower hydrolysis of the esters of the 2,4,6-trimethylbenzoic acid probably causes a slight reduction in the net yield of these esters. Conditions can be established which show that the fundamental differences between benzoic acid and the sterically hindered benzoic acids discussed by Newman do actually exist. This is shown by the fact that the sterically hindered 2,4,6-trimethylbenzoic acid is almost completely esterified in ten minutes, while the unhindered benzoic acid is not. The *i* factor of 4 for the hindered acid in sulfuric acid indicates a carbonium ion reaction while that of 2 for benzoic acid indicates that the ordinary type of acid-catalyzed esterification is involved.

Experimental

The 100% sulfuric acid was prepared by mixing suitable quantities of 96% sulfuric acid and oleum. It froze at 10° and analyzed 100.3% by dilution and titration with standard base.

Preparation of Ethers from Triphenylcarbinol.—For those ethers which were solids, 2 g. of triphenylcarbinol was dissolved in 6 to 12 g. of 100% sulfuric acid. The resulting yellow solution was added dropwise to 30 ml. of cold alcohol held at −10° by means of a salt–ice-bath. As soon as all of the solution was added, the resulting mixture was poured into 100 g. of a mixture of ice and water. The solid which separated was immediately filtered out, washed, and recrystallized from methanol.

For those ethers which were obtained as liquids, the following modifications were introduced. After pouring the sulfuric acid–alcohol solution into water, the organic layer was extracted with ether. The ether solution was treated with sodium carbonate solution, dried, and all readily volatile matter removed. The triphenylcarbinol ether which remained was fractionated in a small Vigreux column.

Hydrolysis of Ethers.—Several of the above ethers were dissolved in 100% sulfuric acid solution, and the resulting yellow solutions poured into ice water. The solid product which separated was filtered from the liquid, and identified as triphenylcarbinol by its melting point and mixed melting point with known triphenylcarbinol.

TABLE I

ETHERS OF TRIPHENYLCARBINOL

Alcohol used	Yield, %	Melting point or boiling point, °C.[b]
Methyl	97	96 -96.5
Ethyl	94	82.5-83
Propyl[a]	88	54.5-55.5
Isopropyl	86	113 -114
n-Butyl	87	208 at 5.5 mm.
Isoamyl	88	217.5 at 5.5 mm.

[a] It was usually necessary to extract this ether because of difficulty in inducing crystallization. [b] See Norris and Young, ref. 5, for melting or boiling points of the compounds.

Attempted Esterification of Triphenylacetic Acid.—Two grams of triphenylacetic acid was dissolved in 25 g. of 100% sulfuric acid. Some frothing was noted, indicating gas evolution. The resulting yellow solution was poured dropwise into 30 cc. of cooled methanol. This mixture was poured into 100 g. of ice and water. The precipitate was filtered and recrystallized from methanol to give 1.77 g. of white crystals, m. p. 96°.[11]

Anal. Calcd. for $C_{20}H_{18}O$: C, 87.6; H, 6.6. Found: C, 87.5, 87.5; H, 6.8, 6.6.

Esterification of Benzoic and 2,4,6-Trimethylbenzoic Acids.—Benzoic and 2,4,6-trimethylbenzoic acids were esterified in the manner described by Newman[1] (Method I) and by a modification of this method (Method II). The main difference between the two was that in the modified method the reaction mixture was poured into ice and water, while Newman added ice water to the reaction mixture. For each esterification, 2-g. samples of benzoic acid and 1-g. samples of 2,4,6-trimethylbenzoic acids were used.

In two parallel experiments using benzoic acid and ethanol, and allowing the mixture of alcohol, sulfuric acid and benzoic acid to stand for twelve hours, the product worked up by Method I showed 62.5% of acid recovered. Using Method II, no acid was obtained. When methanol and benzoic acid were used, and the mixture allowed to stand for only ten minutes, less than 50% of the acid was recovered by Method II. When the mixture was allowed to stand for one hour, only 10% of the acid was recovered.

In experiments with 2,4,6-trimethylbenzoic acid and methanol, using Method II, 6% of the acid was recovered whether the mixture was allowed to stand for ten minutes or for one hour.

It is much easier to estimate the ester yields from the percentage of acid recovered, than from ester yields. However the esters were isolated in a number of cases, and the amounts obtained were in accord with the results indicated on the basis of recovered acid.

Summary

A method for the formation of ethers of triphenylcarbinol from the triphenylcarbonium ion has been described; the method gives good yields of pure ethers. The esterification of benzoic and 2,4,6-trimethylbenzoic acids by Newman's method has been discussed.

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[11] The crystals from some of these preparations first melted at 84°, this being the melting point of a different crystalline form of the methyl ether of triphenylcarbinol. See Hatt, *J. Chem. Soc.*, 483 (1938).