

diphosgene was heated in a bomb-tube for ten hours at 150–175°. After cooling and opening the tube in the usual manner, the reaction mixture was hydrolyzed with water (over a period of twelve hours at room temperature), and evaporated to dryness on a water-bath. Since phenylmalonic acid is readily decarboxylated, the last traces of water were removed by drying the product over phosphorus pentoxide *in vacuo*. The mixture of phenylacetic acid and phenylmalonic acid thus obtained (3.8 g.) was decarboxylated at 220°. The carbon dioxide evolved was collected quantitatively. From the amount of carbon dioxide formed, it is estimated that the phenylmalonic acid present in the reaction mixture amounted to a 1.4% yield.

Summary

1. It has been demonstrated that the chloroformyl (—COCl) group can be directly introduced (at the α carbon atom) into aliphatic and

aryl-substituted-aliphatic acid chlorides by the use of trichloromethylchloroformate (diphosgene) as the "carboxylating" agent.

2. The experimental conditions requisite for carrying out this type of carboxylation have been determined.

3. The syntheses with good yields of several di-substituted malonyl chlorides have been described.

4. The chloroformyl group (derived from diphosgene) replaces hydrogen atoms attached to the α carbon atoms of acid chlorides most easily when these α carbon atoms are tertiary and least easily when they are primary.

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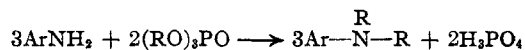
Alkylation of Amines. I¹

BY JOHN H. BULLMAN, A. RADIKE AND B. W. MUNDY

The esters of sulfuric,² sulfurous,³ and *p*-toluenesulfonic acids⁴ have been used frequently for the alkylation of amines. Now that the methyl, ethyl and *n*-butyl esters of orthophosphoric acid have become readily available within recent years,⁵ it was of interest to investigate the possibility of using these esters as alkylating agents for amines since Noller⁶ has shown that they may be used to alkylate phenols.

All of the esters investigated appeared to be non-toxic under normal conditions and were quite stable toward hydrolysis. Three-quarters of an hour was required to saponify triethyl phosphate completely when boiled with the calculated amount of sodium hydroxide.

It was found that all three groups in the ester could be utilized in the alkylation. The reaction may be represented by the equation



Several attempts to alkylate *p*-nitroaniline by this method resulted in failure. The conditions necessary to effect alkylation resulted in decomposition.

(1) Original manuscript received April 13, 1942.

(2) Claesson and Lundwall, *Ber.*, **13**, 1700 (1880); Ullmann and Wenner, **33**, 2476 (1900); Cade, *Chem. Met. Eng.*, **29**, 319 (1923).

(3) Voss and Blanke, *Ann.*, **485**, 258 (1931).

(4) Marvel and Sekera, *This Journal*, **55**, 345 (1933).

(5) Commercial Solvents Corporation, Terre Haute, Indiana.

(6) Noller and Dutton, *This Journal*, **55**, 424 (1933).

When branched chain alkyl orthophosphates such as isopropyl phosphate were used, practically pure isopropylaniline was obtained.

The authors wish to thank the Commercial Solvents Corporation for some of the phosphate esters used in this work.

Experimental

Preparation of Orthophosphate Esters.—The *n*-propyl and the isopropyl esters of orthophosphoric acid were prepared from phosphorus oxychloride and the proper alcohol similar to the method described in "Organic Syntheses."⁷ The yield of *n*-propyl phosphate was 54%, while that of the isopropyl phosphate was 65%.

Procedure for Alkylation of Amines.—A mixture of 0.3 mole of the amine and 0.2 mole of trialkyl phosphate in a 500-cc. flask provided with a condenser and boiling chips was refluxed at a moderate rate for two hours. In most cases, during the early stages of heating, the reaction became vigorous and the temperature rose sharply. As soon as rapid boiling ceased the stream of water in the condenser jacket was replaced by one of air. The mixture was then cooled to 50°, 25 g. of sodium hydroxide in 100 ml. of water added and the whole refluxed one hour, and then poured into a 400-cc. beaker where it was allowed to cool to room temperature. The oily layer of amine, which formed on top, was poured off from the solid sodium phosphate. The latter was extracted with ether and the combined extracts and oil dried over anhydrous sodium sulfate. The ether was then removed, the residue treated with an equal volume of acetic anhydride and allowed to stand overnight.

(7) *Organic Syntheses*, **16**, 10 (1936).

Ester	Primary amine	Tertiary amine	Yield, %
Methyl phosphate	Aniline	Dimethylaniline	67.9
Methyl phosphate	β -Naphthylamine	Dimethyl- β -naphthylamine	64.4
Ethyl phosphate	Aniline	Diethylaniline	99.0
Ethyl phosphate	α -Naphthylamine	Diethyl- α -naphthylamine	60.0
<i>n</i> -Propyl phosphate	Aniline	Di- <i>n</i> -propylaniline	78.1
Butyl phosphate	Aniline	Di- <i>n</i> -butylaniline	78.5

The mixture was treated with 20 ml. of concd. hydrochloric acid dissolved in 30 ml. of water and shaken until the base dissolved. The solution was extracted with two 30-ml. portions of ether and the water layer treated with a 25% sodium hydroxide solution to free the base. The oil which formed was collected by extracting the mixture with ether. The ether was dried over anhydrous sodium sulfate and distilled to recover the tertiary amine.

The yield of isopropylaniline from isopropyl phosphate and aniline was 80.5%.

The boiling points of the amines and the melting points

of their solid derivatives corresponded to those found in the literature.

Summary

A method has been developed for the preparation of tertiary amines by treating an aromatic amine with alkyl esters of orthophosphoric acid. Six tertiary amines have been prepared in 60 to 99% yield by this procedure.

BLOOMINGTON, INDIANA

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Physical Properties of Terpenes. I. The System α - and β -Pinene^{1a}

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A knowledge of the physical properties of binary mixtures of α - and β -pinene is necessary for some phases of study of American gum turpentine which is composed largely of these two substances.^{1c}

Data in the literature show a wide variation in the values for the physical constants for α - and β -pinene. Since it was desired to make a study of binary mixtures of these compounds, it was necessary first to establish constants for the pure substances.

With efficient fractionating columns it is possible to obtain α - and β -pinenes which, the authors believe, are of a higher degree of purity than has been reported heretofore. In a previous publication² the authors have shown that the spiral screen type of column developed by Lecky and Ewell³ is well suited for the purification of α - and β -pinene.

Preparation of α -Pinene and β -Pinene

α -Pinene was prepared by the careful fractionation of four liters of commercial α -pinene,⁴ from gum turpentine.

(1a) Original manuscript received April 11, 1942.

(1b) Present address, American Cynamid Co., Stamford, Conn.

(1c) Palkin and co-workers, U. S. D. A. Technical Bulletin No. 276, January, 1932.

(2) Stallcup, Fugitt and Hawkins, *Ind. Eng. Chem., Anal. Ed.*, **14**, 503 (1942).

(3) Lecky and Ewell, *ibid.*, **12**, 544 (1940).

(4) Furnished through the courtesy of Southern Pine Chemical Company, Jacksonville, Florida.

through a spiral screen column² at 20-mm. pressure and a reflux ratio of 40 to 1. This column exerted 75 plates upon a mixture of *n*-heptane-methylcyclohexane at total reflux and atmospheric pressure. Fractions were collected at 75-cc. intervals. All fractions with a refractive index in the range 1.4631-1.4633 at 25.0° were combined and refractionated through the same column. Fractions were then collected at 50-cc. intervals and their refractive indices and optical rotations were measured at 25.0°. The fractions which had constant values of refractive index and optical rotation were combined and were considered to be pure α -pinene. In verification, a 100-cc. portion of the latter was fractionated through a column which had 60 plates determined as above. No change in these two physical constants was noted at any point during collection of the distillate.

For comparison, α -pinene from wood turpentine was desired. The preparation of this pure component from wood turpentine involved its separation from a small amount of camphene which boils about 3° higher. The intermediate fractions having constant refractive indices and optical rotations at 25.0° were then combined and refractionated. The material thus obtained had constant physical properties and was of the same purity as the α -pinene from gum turpentine.

The β -pinene used was prepared in an analogous manner from commercial β -pinene⁴ obtained from gum turpentine.

These purified pinenes had the following constants

	B. p., °C. (20.0 mm.)	$n_D^{25.0}$	$d_4^{25.0}$	$[\alpha]_D^{25.0}$
α -(gum)	52.2	1.4631	0.8542	- 3.83
α -(wood)	52.2	1.4631	.8542	+34.07
β -(gum)	59.7	1.4768	.8666	-21.49

These constants are in close agreement with unpublished