

By refluxing 6-ethyl-phenoxarsin with the calculated amount of ethyl iodide for 6 hours, the di-ethyl phenox-arsonium iodide is formed. Pure white translucent needles, not melting below 300°, are obtained by refluxing the reaction mixture with hot water. An aqueous solution of these crystals gives a test for ionic iodine. With silver oxide the arsonium hydroxide apparently results.

Work upon the condensation product of arsenic chloride with mixed and ring substituted amines, diphenyl hydrazine, diphenyl methane, diphenyl sulfide, and similar compounds is being continued.

#### Summary.

1. Diphenyl chloro-arsine and the condensation products of arsenic chloride with diphenyl ether, diphenyl amine and phenyl- $\alpha$ -naphthylamine are briefly contrasted.

2. Derivatives of 6-chloro-phenoxarsin are described and the close resemblance between the chemical properties of this compound and diphenyl chloro-arsine indicated.

3. Properties and directions for preparing the following compounds are submitted: 6-chloro-phenoxarsin, 6-iodo-phenoxarsin, 6-bromo-phenoxarsin, 6-phenoxarsin oxide, 6-phenoxarsin sulfide, 6-thiocyano-phenoxarsin, phenox-cacodyl, phenoxarsinic acid, sodium phenoxarsinate, 6-ethyl-phenoxarsin, and di-ethyl phenoxarsonium iodide and hydroxide.

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## THE PREPARATION OF PARA-DIPHENYL-PROPIOLIC ACID; AND NEW REACTIONS OF DIPHENYL AND ITS DERIVATIVES.<sup>1</sup>

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In connection with a study of some reactions of the propiolic acids, it became desirable to prepare *p*-diphenyl-propionic acid. Before the synthesis of *p*-diphenyl propiolic acid described below was developed, attempts were made to condense both the acid and ester of *p*-diazo-cinnamic and hydrocinnamic with benzene by Molau and Berger's synthesis.<sup>2</sup> It was noted that no condensation took place due to the long side chain or acid radical on the benzene ring carrying the diazo radical. The above mentioned authors state this fact in a later communication.

On attempting to condense *p*-diazo-cinnamic acid and benzene by means of aluminum chloride  $\beta,\beta'$ -diphenyl-propionic acid is formed; m. p. 149°. This compound was first thought to be *p*-diphenyl-acrylic

<sup>1</sup> Summary of a thesis submitted by Chester L. Knowles to the Faculty of Brown University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

<sup>2</sup> Ber., 26, 1198 (1893).

acid, but showed no unsaturation and on oxidation gave benzophenone. It was further identified by preparing its methyl and ethyl esters. Both phenyl groups were found to be attached to the carbon atom *beta* to the carboxyl group. Apparently on condensation the diazo group drops off, the double bond breaks and one hydrogen atom attaches itself to the  $\alpha$ -carbon while the phenyl is joined to the  $\beta$ -carbon. This reaction was but little investigated but seems to be of considerable interest.

The method finally adopted depended on Molau and Berger's condensation of toluene with *p*-diazobenzene chloride to form *p*-methyl-diphenyl, the chlorination and hydrolysis of this, with subsequent formation of the acrylic acid by Perkin's synthesis, followed by bromination and splitting out of hydrobromic acid to form *p*-diphenyl-propionic acid.

The *p*-aldehyde of diphenyl as well as the corresponding acrylic and propionic acids are all compounds not previously described in the literature.

*p*-Diphenyl-aldehyde is a nearly colorless, viscous oil insoluble in cold water, somewhat soluble in hot water, and having a characteristic aldehyde odor. The material boils at 121° and forms a bisulfite addition product very readily. *p*-Diphenyl-acrylic acid is a colorless, crystalline compound, appearing usually in the form of fine needles, slightly soluble in hot water. The material melts at 184° and shows unsaturation. *p*-Diphenyl-propionic acid has physical properties similar to the above, melts at 147° and shows remarkable unsaturation, decolorizing potassium permanganate and absorbing bromine readily. Decomposition takes place at the melting point.

### Experimental.

**Condensation of Diazobenzene Chloride with Toluene.**—Seventy g. of solid diazobenzene chloride is slowly added to a suspension of 50 g. of aluminum chloride in 200 cc. of freshly distilled, dry toluene at 75°. The mixture is agitated mechanically in order to keep the aluminum chloride in suspension and to insure good condensation without too great a loss of the diazobenzene chloride through decomposition. The addition requires approximately one hour, after which the mixture is boiled one hour, the flask being fitted with a reflux condenser. The contents of the flask are poured into hydrochloric acid and water to dissolve the inorganic salts, the two layers separated and the toluene and later 35 g. of methyl-diphenyl distilled off; b. p. 258 to 268°; b. p. pure substance, 264°. Yield, 30%. The methyl-diphenyl obtained was a nearly colorless, oily liquid possessing a high index of refraction.

**Chlorination of Methyl-Diphenyl and Hydrolysis.**—Various methods of substituting two atoms of halogen in the side chain were investigated. Bromination in the bright sunlight as well as chlorination in the dark served admirably. The best method was found to be as follows. Dry 5 g. of *p*-methyl-diphenyl over sodium. Heat this material to 210° in an oil-bath in the dark and pass into it sufficient chlorine to replace two hydrogen atoms of the methyl group. Some mono- and tri-chloride are always formed, but without separating these the mixture is sealed in a tube with 10 parts of water after expelling the air with a current of carbon dioxide. The tube is heated for 4 hours at 150°, cooled, opened and sodium carbonate and ether added to extract the aldehyde. Since the next step in the synthesis is the formation of the acrylic acid, acetic anhydride and potassium acetate may be added directly. The aldehyde, how-

ever, can easily be isolated by forming the bisulfite addition compound and decomposing this with alkali or acid. B. p. 121°.

**Formation of Acrylic Acid.**—Four g. of aldehyde, 2.8 g. of potassium acetate and 24 cc. of acetic anhydride are boiled under a reflux condenser for 4 hours, water is added and the mixture evaporated to dryness. The residue is dissolved in sodium carbonate solution, the solution washed with ether and the acid precipitated by the addition of hydrochloric acid. Colorless crystals of *p*-diphenyl-acrylic acid are obtained. After recrystallization from 60% acetic acid, the material melts sharply at 184° and shows unsaturation when added to a potassium permanganate solution. No halogen could be detected. Molecular weight, 222; calc., 224.

**Preparation and Bromination of Ethyl Ester of *p*-Diphenyl-Acrylic Acid.**—1.5 g. acrylic acid is sealed in a tube with the calculated amount of absolute alcohol and sulfuric acid. This mixture is heated for 3 hours on the water-bath and then poured upon sodium carbonate. Yield 1.02 g. of ester. The ester is sealed in a tube with 2 atoms of bromine dissolved in carbon tetrachloride and after heating for 6 hours is entirely decolorized. The tube is opened and the carbon tetrachloride evaporated off. 0.75 g. of potassium hydroxide (10% excess) is added and the mixture heated on a water-bath, whereupon potassium bromide separates. The alcohol is evaporated off, water added, the solution filtered and acidified with dil. hydrochloric acid. The product may be recrystallized from 60% acetic acid. Crystals are obtained which melt between 145–147° with decomposition and evolution of carbon dioxide. The material contains no halogen, and is extremely unsaturated. Molecular weight, 222; calc., 222. The melting point after further recrystallization is 147°.

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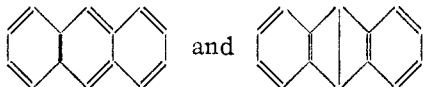

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

## SYNTHESIS OF ANTHRACENE<sup>1</sup> FROM NAPHTHALENE.

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Since the discovery of anthracene in coal tar it has been prepared synthetically a great many times. A synthesis, however, from a derivative of naphthalene in which the naphthalene nucleus has been maintained intact has never been made. Such a synthesis would have considerable interest since it would explain satisfactorily the disposition of the fourth valence of the carbon atoms 9, 10, of anthracene. At the present time the two most common formulas which are given to anthracene are

 and , the latter usually spoken of as the bridge formula. In some cases the experimental evidence seems to indicate that anthracene has the first formula and in others the results are explained just as well by either the first or second formula. Thus the reaction of aluminum chloride with tetrabromoethane in the presence of benzene to give anthracene is in favor of the

<sup>1</sup> An abstract of a thesis submitted by C. W. Colver in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the University of Illinois.