(IIc) One gram of condensation product II was dissolved in 5 cc. of 20% sodium hydroxide solution and 2 cc. of dimethyl sulfate added. The mixture was shaken vigorously and allowed to stand for some time. The methylated product was then filtered off, washed with sodium hydroxide solution, and recrystallized from alcohol.

Summary

Crystalline condensation products and their derivatives of resorcinol and saturated aliphatic aldehydes were investigated and subjected to extensive quantitative elementary analysis and molecular weight determinations. The results obtained seem to indicate that resorcinol in these condensations reacted like pyrrole under similar circumstances, giving rise also to crystalline condensation products which seem to possess a similar structural pattern as the "porphyrins" obtainable in pyrrole-carbonyl compounds condensations, but possessing "benzene" instead of "pyrrole" rings.

WASHINGTON SQUARE COLLEGE
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[CONTRIBUTION FROM THE PEARSON MEMORIAL LABORATORY OF TUFTS COLLEGE]

Studies in the Biphenyl Series. IV. Some *o*-Biphenyl Derivatives of Phosphorus, Arsenic and Antimony

BY DAVID E. WORRALL

It has been shown previously[1] that *p*-chlorobiphenyl condenses smoothly with the chlorides of phosphorus, arsenic and antimony in the presence of sodium, that the products exhibit the usual properties of these organo derivatives and that they are unusually tractable. The corresponding reactions in part have been studied with *o*-chlorobiphenyl. While the ortho derivatives react less smoothly and undergo hydrolysis more easily, only minor differences in chemical behavior were discovered.

Tri-*o*-biphenylphosphine (I).—A mixture containing 9 g. of granulated sodium, 25 g. of 2-chlorobiphenyl and 6.1 g. of phosphorus trichloride in 200 cc. of benzene, after adding a crystal of antimony trichloride, was heated to boiling for two hours. It was filtered while still warm, concentrated to a small bulk and mixed with an equal volume of alcohol. An oil separated at first but it became crystalline on standing; yield after washing with alcohol, 8.3 g. After several crystallizations, small colorless plates were obtained, m. p. 151–152°. As with most of the *o*-derivatives, the melting point was not sharp and preliminary softening took place.

Anal. Calcd. for $C_{36}H_{27}P$: P, 6.3. Found: P, 6.3.

Tri-*o*-biphenylphosphine Oxide.—The gummy product obtained by the action of bromine or chlorine on I was heated for a few minutes with alcoholic potassium hydroxide, poured into water and dissolved in a small volume of dilute alcohol. Clumps of tiny needles appeared, m. p. 184–185°.

Anal. Calcd. for $C_{36}H_{27}PO$: P, 6.1. Found: P, 6.1.

Tri-*o*-biphenyl Methylphosphonium Iodide.—On dissolving a portion of I in methyl iodide, bundles of tiny needles almost immediately began to form; yield after several hours, nearly quantitative. It melted indefinitely with decomposition above 250°.

Anal. Calcd. for $C_{37}H_{30}PI$: I, 20.1. Found: I, 20.0.

The odor of biphenyl on heating the phosphonium compound with silver oxide was indicative of the conventional change into dibiphenylmethylphosphine oxide.

Tri-*o*-biphenylarsine (II).—Arsenic chloride, 0.1 g. mole, was heated to boiling for two hours with corresponding quantities of *o*-chlorobiphenyl and sodium in benzene. The filtrate, concentrated to a small volume and mixed with alcohol, yielded 33–34 g. of product. Small glittering plates separated from a benzene–alcohol mixture on recrystallization, m. p. 190°.

Anal. Calcd. for $C_{36}H_{27}As$: As, 14.0. Found: As, 13.9.

Tri-*o*-biphenylarsine Dihydroxide.—Attempts to convert II into the dibromide or dichloride gave gummy products which were heated with alcoholic potassium hydroxide, evaporated to dryness and extracted with water. The residue crystallized in the form of stout needles from alcohol, m. p. 237–238°.

Anal. Calcd. for $C_{36}H_{29}O_2As$: As, 13.2. Found: As, 13.4.

Tri-*o*-biphenylmethylarsonium Iodide.—II dissolved in methyl iodide and heated for a few minutes changed quantitatively into the arsonium iodide. Needle-like crystals separated on crystallization from a small volume of alcohol. It dissociated on heating into methyl iodide and II at approximately 154° when it partially melted and then hardened.

Anal. Calcd. for $C_{36}H_{30}AsI$: I, 18.8. Found: I, 18.5.

Chlorine converted this substance into the corresponding iodochloride, sparkling yellow platelets, m. p. 172–174°, with decompn. A satisfactory analysis for combined halogens was made.

Tri-*o*-biphenylstibine (III).—To a solution of 50 g. of *o*-chloro-biphenyl in 250 cc. of benzene containing 20 g. of

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[1] Worrall, THIS JOURNAL, **52**, 2933 (1930).

antimony chloride was added 20 g. of granulated sodium. The reaction was initiated by heating, after which it became necessary to cool the mixture from time to time. It was filtered while warm, concentrated and mixed with an equal volume of alcohol. The product was dissolved in warm benzene–alcohol mixture. Small glittering plates separated, m. p. 208–209°, yield nearly 33 g.

Anal. Calcd. for $C_{36}H_{27}Sb$: Sb, 21.0. Found: Sb, 20.9.

Tri-*o*-biphenylstibine Dibromide.—Slightly less than the equivalent amount of bromine was mixed with 2 g. of III dissolved in 20 cc. of chloroform. Then petroleum ether was added and the mixture concentrated by distillation until crystallization started. Needle-like clusters appeared, m. p. 152–154°.

Anal. Calcd. for $C_{36}H_{27}SbBr_2 \cdot CHCl_3$: Br, 18.6. Found: Br, 18.8.

The dichloride, prepared in a similar manner, melted at 174–175° but the iodide did not form.

Tri-*o*-biphenylstibine Hydroxide.—Alcoholic ammonia changed the dibromide into a substance separating from alcohol as a powder, m. p. 243–244°.

Anal. Calcd. for $C_{36}H_{29}SbO_2$: Sb, 19.8. Found: Sb, 20.1.

Mono-biphenylstibine Hydroxychloride.[2]—A mixture of 10 g. of tri-biphenylstibine and 8 g. of antimony chloride in 20 cc. of xylene was heated to 220–250° in a sealed tube for one hundred hours. The residue after repeated crystallizations from benzene produced lustrous plates, m. p. 201–202°.

Anal. Calcd. for $C_{12}H_{10}OClSb$: Cl, 10.8; Sb, 37.3. Found: Cl, 10.9; Sb, 37.0.

No traces were found of dibiphenylstibine monochloride.

Mono-biphenylstibine Oxide.—It was obtained in clusters of tiny slender needles by the action of alcoholic ammonia on the hydroxy chloride, m. p. 195–196°.

Anal. Calcd. for $C_{12}H_9OSb$: Sb, 41.9. Found: Sb, 41.5.

Mono-biphenylstibinic Acid.—Chlorination of the basic salt produced a sirupy mixture that was changed into the acid by stirring with water. The resulting white powder was washed thoroughly with cold alcohol, m. p. well above 300°.

Anal. Calcd. for $C_{12}H_{11}SbO_3$: Sb, 37.5. Found: Sb, 37.2.

Summary

Tri-*o*-biphenylphosphine, arsine and stibine have been prepared by the Fittig reaction and their chemical properties investigated.

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[2] Michaelis and Genzken, *Ann.*, **242**, 164 (1887), observed that partial hydrolysis took place in the crystallization of mono-*p*-tolylstibine diiodide from moist chloroform.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BARNARD COLLEGE]

Addition Reactions of Unsaturated *alpha*-Ketonic Acids. VI

BY MARIE REIMER AND ELISE TOBIN

The study of the influence of ring substitution on the reactions of the side-chain of benzalpyruvic acid[1] has been continued with a bromine atom in the *para* position in the benzene ring. As was to have been expected, the influence of the *p*-bromine atom is markedly different from that of the *p*-methoxy[2] and the *p*-methyl[1] groups. Unlike these acids, *p*-bromobenzalpyruvic acid and its esters are sensitive to light, particularly the ethyl ester which polymerizes readily even in the diffused light of the laboratory. In this respect the acid resembles most closely the unsubstituted benzalpyruvic acid. The stability of addition products is greatly increased, the acid forming a stable hydrate so readily that it takes up moisture from the air and a dibromide far less easily decomposed than any other met with in this study of unsaturated α-ketonic acids. There are no brilliant color reactions in sulfuric acid solution as with the methoxy substituted compounds.

The most interesting result of these experiments arises from the unusual stability of the dibromo addition product. The dibromides of the series of six substituted benzalpyruvic acids so far investigated have been unstable, decomposing on standing and losing hydrogen bromide rapidly on contact with moisture. The dibromide here described is not changed after months of exposure to the air and even combines with water to form a hydrate under appropriate conditions. This stability has made it possible to eliminate hydrogen bromide under controlled and reproducible conditions which has led to the preparation of isomeric unsaturated bromo acids. These acids are conspicuously different in properties. The one obtained by heating the dibromide with water has the unusual characteristics of the analogous compounds of the series, prepared in the same way. The compound is pure white in spite of the fact that it has supposedly the same conjugated system as the original bright yellow acid

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[1] Reimer and Chase, THIS JOURNAL, **60**, 2469 (1938).

[2] Reimer, *ibid.*, **48**, 2454 (1926).