

6. The addition product of 2-phenyl-benzothiazole and acetyl chloride loses acetyl chloride readily when heated or on treatment with water.

7. 6-Amino-2-phenyl-benzothiazole was changed into the cyanide, and the latter into the 6-carboxylic acid, which is structurally analogous to Cinchophen (Atophan), and which it is hoped may show useful therapeutic properties.

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ACETYLENE COMPOUNDS WITH SILVER PHOSPHATE AND SILVER ARSENATE

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Unlike the mercury and copper derivatives, silver compounds of acetylene prepared by passing the gas into acid solutions of various silver salts are usually the explosive acetylides or carbides of the metal, but in the case of the phosphate of silver dissolved in phosphoric acid, a compound is formed that is very stable.

This substance prepared by Nieuwland and Maguire¹ is not notably affected by light and is not an aldehyde derivative. The formula $3(C_2Ag_2) \cdot 2H_3PO_4 \cdot Ag_3PO_4 \cdot H_2O$ was applied to the substance, but apparent discrepancies in relationship of analytical results and formula suggested that it might be advisable to go over the matter again with a view of ascertaining whether the original determinations were correct.

Acetylene silver phosphate was prepared according to the method used by Nieuwland and Maguire. Chemically pure silver nitrate which had been recrystallized was treated with chemically pure dibasic sodium phosphate until an excess of the phosphate was present. The yellow silver phosphate was carefully washed by decantation until all traces of disodium phosphate and silver nitrate were removed; it was then filtered by suction and treated with a strong solution of phosphoric acid, and after all had dissolved, saturated with purified acetylene. A cream colored substance was precipitated, which was washed 10 or 12 times by decantation until test showed absence of free phosphoric acid. After being filtered by suction it was dried in an air-bath and desiccator alternately, until repeated weighings showed no more loss.

Four analyses were made. In the first two operations the silver was determined as silver chloride and the filtrates from the silver chloride were used to estimate the amount of phosphate present as magnesium pyrophosphate. In the third and fourth operations the compound was analyzed electrolytically. From the results obtained a formula was cal-

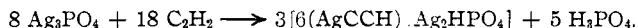
¹ Nieuwland and Maguire, *THIS JOURNAL*, **28**, 1025 (1906).

culated, which answered to the following percentages, agreeing very closely with the values obtained.

Calc.: Ag, 77.95; PO₄, 8.58. Found: Ag, 78.27, 77.72, 77.85, 77.02, Av. 77.92; PO₄, 8.49, 8.26, Av. 8.38.

The average value for silver differs only 0.03% from the theoretical value, while the difference for PO₄ is 0.2%. The formula which was established on the basis of these results is 6(AgCCH).Ag₂HPO₄.

The reaction proceeds probably in the following manner,



This formula is completely at variance with the formula calculated by Nieuwland and Maguire. It seems evident that they had not succeeded in removing all free phosphoric acid, and had not dried the precipitate carefully enough.

Acetylene silver arsenate was prepared by the same method as the compound described above, using the same precautions to free the cream colored substance from every trace of free arsenic acid, and then from water by prolonged drying in a steam-oven and desiccator alternately until successive weighings showed no loss.

The silver was estimated as silver chloride. In the first two operations the substance was dissolved in dil. nitric acid; in the next two operations it was dissolved in aqua regia; in the other cases it was dissolved in conc. nitric acid. In all there were made 7 determinations, taking the precaution to dissolve the precipitated silver chloride in ammonia and reprecipitate it by nitric acid before drying and weighing.

In the estimation of the arsenic content of the compound, the procedure was in general the method worked out by Gooch. Six determinations were made in all. For the first duplicates the filtrates from the silver chloride precipitates were evaporated to dryness, treated with hydrochloric acid and water and then reduced by potassium iodide and sulfuric acid to arsenious acid according to the equation, $\text{H}_3\text{AsO}_4 + 2\text{KI} + \text{H}_2\text{SO}_4 \longrightarrow \text{H}_3\text{AsO}_3 + \text{H}_2\text{O} + \text{K}_2\text{SO}_4$. After the liquid had been diluted to 100 cc. and then boiled down to 40 cc. to drive off most of the free iodine, the remaining free iodine was cautiously bleached by sulfurous acid, the solution at once diluted, nearly neutralized with potassium carbonate, and completely with sodium hydrogen carbonate; it was then titrated against a standardized iodine solution, the starch indicator being added shortly before the end-point was reached to insure a deep blue coloration.

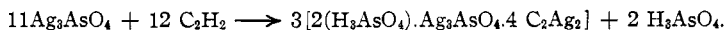
The second duplicate of determinations was made by dissolving the substance in conc. hydrochloric acid to which 1 cc. of conc. nitric acid had been added, filtering from the silver chloride precipitates, and treating again according to Gooch's method. The third duplicate of determinations was made according to the modifications of Gooch's method by

Geo. Ross Robertson² for the estimation of arsenic in arsphenamine and allied products. In this case the silver iodide precipitated by the addition of potassium iodide was not filtered off, but the titration was made after treating the mixture as in the previous determinations.

Calculation of the molecular formula according to the results obtained for silver and arsenic presented great difficulties. It had been assumed that a molecule of silver arsenate might combine with 1, 2 or 3 molecules of acetylene. The percentage of silver found was, however, in each instance too high, while that of arsenic seemed to be too low. Comparison with the acetylene silver phosphate compound described above, as well as the fact that the acetylene silver arsenate puffed up on being heated, pointed to the possibility of the compound being a mixture, and a calculation made on this assumption gave the following result, with which those of the various analyses agreed very closely.

Calc.: Ag, 69.57; As, 13.08. Found: Ag, 69.46, 69.39, 69.06, 69.19, 69.83, 69.28, 69.47, Av. 69.38; As, 12.58, 12.63, 12.47, 12.57, 12.72, 12.61, Av. 12.66.

The average result for silver is within 0.19% of the calculated value; that of arsenic within 0.48%. The formula may therefore be written, $2(\text{H}_3\text{AsO}_4) \cdot \text{Ag}_3\text{AsO}_4 \cdot 4\text{C}_2\text{Ag}_2$. The equation for this particular reaction may be written, $2 \text{Ag}_3\text{AsO}_4 + 3(\text{C}_2\text{H}_2) \longrightarrow 3 \text{C}_2\text{Ag}_2 + 2 \text{H}_3\text{AsO}_4$; and for the entire reaction thus,



The properties of acetylene silver arsenate are analogous to those of acetylene silver phosphate described by Nieuwland and Maguire. When the arsenate was exposed to direct sunlight, it changed from a cream color to a purplish-violet in a short time. In diffused daylight it took several days for a change in color to become noticeable; it did not give up aldehyde as in the case of the acetylene compound of mercuric chromate prepared by the authors mentioned above, nor did it respond to the iodoform reaction, but an iodine derivation of acetylene was formed, which could be recognized by its characteristic odor. The compound is insoluble in ammonia, alcohol and ether, but very soluble in potassium cyanide with decomposition, acetylene being evolved. When heated to about 400°, it deflagrated quietly, and in this regard it differs, like acetylene silver phosphate, from other silver acetylene compounds.

Summary

1. The correctness of the formula of acetylene silver phosphate prepared and described by J. A. Nieuwland and J. A. Maguire was tested, and it was found that their formula was defective owing to the presence of free phosphoric acid and water which had not been removed. Analytical results assign the following formula to the compound: $6(\text{AgCCH}) \cdot \text{Ag}_2\text{HPO}_4$.

² Robertson, *THIS JOURNAL*, **43**, 182 (1921).

2. Acetylene silver arsenate was prepared according to the method used for acetylene silver phosphate. The analysis of the compound points to the following formula: $2(\text{H}_3\text{AsO}_4) \cdot \text{Ag}_3\text{AsO}_4 \cdot 4\text{C}_2\text{Ag}_2$.

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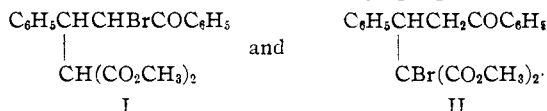
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY]

THE ACTION OF BROMINE ON CERTAIN DELTA KETONIC ESTERS

BY E. P. KOHLER

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When bromine acts on δ -ketonic esters of the type obtained by adding malonic esters to α, β unsaturated ketones it replaces one hydrogen atom with the greatest ease.¹ In the cold the bromination stops sharply at this point. If the reaction is carried out in chloroform or carbon tetrachloride it invariably gives a mixture of 2 isomeric monobromo compounds in nearly equal amounts. As both of these readily lose hydrogen bromide and form a cyclopropane derivative² the bromine in each must be either in the α - or the γ -position. Thus the only possible formulas for the products obtained from dimethyl-benzoyl-phenyl-propylmalonate are,



Since the γ -bromo compound has 2 dissimilar asymmetric carbon atoms, the 2 bromo compounds may be stereo-isomeric forms represented by Formula I, or one may be a γ derivative and the other the α derivative represented by Formula II. When these substances were first encountered it was assumed that they were stereo-isomers because, on treatment with reagents that do not cause isomeric change, both gave the same unsaturated compound.³ Later investigations⁴ showed that this unsaturated compound in reality is a cyclopropane derivative which in nearly all respects behaves like an ethylenic compound. Although the cyclopropane derivative might be formed from an α - as well as from a γ -bromo compound, it nevertheless seemed most probable that the two substances were stereo-isomers. As the substances are formed in nearly equal amounts structural isomerism implied that the α - and γ -hydrogen atoms were replaceable with equal ease and if this were the case there seemed to be no adequate reason why the reaction should stop so sharply with the replacement of one hydrogen atom.

¹ *Am. Chem. J.*, **46**, 482 (1911).

² *THIS JOURNAL*, **39**, 1410 (1917).

³ Ref. 1, p. 483.

⁴ Ref. 2, p. 1404.