4. A new qualitative test for water in ether has been proposed and is thought to be very satisfactory and quickly made.

MINNEAPOLIS, MINN.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA.]

VERATRINE AND SOME OF ITS DERIVATIVES. II.

BY GEO. B. FRANKFORTER AND W. KRITCHEVSKY.

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The alkaloid known as veratrine, or cevadine, as it has recently been named, has been studied by one of us several years ago.[1] A number of derivatives were studied in order to determine the constitution of the alkaloid.

Among other derivatives, a chloralhydro-veratrine was prepared from chloral and veratrine. As chloral and veratrine are of great importance physiologically, it was thought that a condensation product of the two substances might be interesting pharmacologically. We therefore decided to take up the study of that compound again in order to determine the true nature of the chemical reaction between the two substances. It was obvious that if the reaction is a true condensation reaction, the new compound formed would possess properties entirely different from either of the components. It would therefore quite likely have different physiological properties. If, on the contrary, the substance proved to be an additive product, then its physiological properties would be the result of one or both of the reacting constituents.

Compounds of cevadine and cevine with chloral and bromal were therefore prepared by the following general method:

The alkaloid was dissolved in carbon disulfide and the necessary amount of chloral added. A precipitate formed at once and the reacting mixture became warm. After the reaction had ceased and the solution cooled to room temperature, cold ether was added and the precipitate filtered off. It was washed with ether several times, dried and analyzed. Neither the analysis nor the molecular weight determination proves conclusively that the new compound formed was either a condensation or an additive product. When heated in a drying oven at a temperature of 130–140° for several hours it was found that the compounds lost weight and did not contain either chlorine or bromine. A qualitative study proved that the loss was equal to the percentage of the aldehyde originally present. This shows conclusively that the new compounds are simple additive products. We have not been able to find any definite ratio between the chloral and the alkaloid. We found that by varying the conditions, namely, the quantity of aldehyde, we were able to change the ratio between the reacting components which enter the new molecule.

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[1] *Am. Chem. J.*, **20**, 358.

On the other hand, we found that the halogen aldehydes combine with practically all of the alkaloids soluble in carbon disulfide, forming additive products insoluble in ether. This reaction may be used, therefore, as a class reaction for alkaloids.

Experimental Part.

Cevadine-Chloral, $2C_{32}H_{49}NO_9.CCl_3CHO$.—One part of cevadine was dissolved in ten of carbon disulfide and one part of chloral added. Very little heat was formed. The reaction seemed to be complete in half an hour. Ether was added, when a white, amorphous substance was precipitated. It was washed several times with ether and dried; m. p. 220°.

Calc. for $2C_{32}H_{49}NO_9.CCl_3CHO$: Cl, 7.98; N, 2.11. Found Cl, 8.12; N, 2.32.

The substance was dried at a temperature of 130–140°, until the constant weight was reached. The loss amounts to 10.88% of the original weight of the substance. The percentage of chloral in the substance is 11.06%. The remaining resinous substance shows all the properties of cevadine. A quantitative determination failed to give an appreciable amount of chlorine.

Cevadine-Chloral, $2C_{32}H_{49}NO_9.3CCl_3CHO$.—One part of cevadine was dissolved in five of carbon disulfide and 10 parts of chloral added. A white precipitate was formed at once. It was filtered, washed with ether in order to remove the excess of chloral, and dried; m. p. 209°.

Calc. for $2C_{32}H_{49}NO_9.3CCl_3CHO$: Cl, 19.59; N, 1.73. Found: Cl, 19.50; N, 1.85.
Loss on drying at 130–140°, 26.95; chloral, 27.20.

Cevine-Chloral, $C_{27}H_{43}NO_8.CCl_3CHO$.—One part of cevine was dissolved in five of carbon disulfide and 25 parts of chloral added. The white precipitate formed was filtered, washed with ether to remove the excess of chloral, and dried; m. p. 206–208°. Analyses gave the following:

Calc. for $C_{27}H_{43}NO_8.3CCl_3CHO$: Cl, 33.47; N, 1.47. Found: Cl, 33.68; N, 1.61.
Loss on drying at 130–140°, 46.30; chloral, 46.41.

Cevadine-Bromal, $2C_{23}H_{49}NO_9.CBr_3CHO$.—One part of cevadine was dissolved in ten of carbon disulfide and five molecules of bromal added. The precipitate formed in the process was filtered, washed with ether and dried. The precipitate was a bright yellow powder with a m. p. of 162°.

Calc. for $2C_{32}H_{49}NO_9.CBr_3CHO$: Br, 16.30; N, 1.91. Found: Br, 16.50; N, 2.07.
Loss on drying, 19.29; bromal, 19.58.

Cevine-Bromal, $2C_{27}H_{43}NO_8.CBr_3CHO$.—One molecule of cevine was dissolved in ten volumes of carbon disulfide and five molecules of bromal added. The precipitate was filtered, washed and dried. The substance is a bright yellow powder with a m. p. 106°.

Calc. for $C_{27}H_{43}NO_8.CBr_3CHO$: Br, 18.47; N, 2.16. Found: Br, 18.21; N, 2.29.
Loss on drying, 21.45; bromal, 21.63.

The action of chloral on alkaloids in general.—When an alkaloid is dissolved in carbon disulfide and chloral or bromal added to it, a precipitate is formed which is insoluble in ether. This is true of every alkaloid soluble in carbon disulfide which we have studied. The powder formed is an additive compound of the alkaloid and the aldehyde.

The following alkaloids were studied: Cevadine, cevine, nicotine, codeine, brucine, strychnine, cocaine, conine, chinchonine and papaverine. In every case the precipitate formed was insoluble in ether.

MINNEAPOLIS, MINN.

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

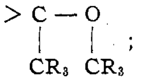
TRIPHENYLMETHYL. XXIV. THE ADDITIVE COMPOUNDS OF TRIPHENYLMETHYL AND SOME SATURATED HYDROCARBONS.

BY M. GOMBERG AND C. S. SCHOEPFLE.

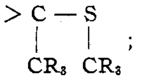
Received August 26, 1915.

The unsaturated character of triphenylmethyl is strikingly illustrated by its tendency to unite spontaneously with compounds of various types. In fact, it is rather difficult to find solvents from which triphenylmethyl crystallizes without taking up solvent of crystallization. Triphenylmethyl has been found to unite in this manner with ethers, esters, ketones, aldehydes, and nitriles; with olefines and with aromatic hydrocarbons; with carbon disulfide, with chloroform, etc.[1]

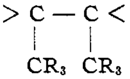
The trivalency of carbon in triphenylmethyl is sufficient in itself to account for the additive tendencies of the free radical. On the other hand, it seems rather difficult to find a plausible explanation in terms of graphic formulas for the additive compounds thus produced. In the esters, ketones, and aldehydes, we have the double linking C = O; in carbon disulfide, the corresponding C = S; while in the aromatic hydrocarbons and in the olefines, we have the grouping C = C. But it seems hardly probable that in all these instances triphenylmethyl adds itself in virtue of the double bond in the various compounds. If this were the case, we should expect the addition to result in fairly stable substances, as for example, in the addition of the Grignard reagent to aldehydes, ketones, esters, etc.



$$>\underset{\displaystyle CR_3}{\underset{|}{C}}-\underset{\displaystyle CR_3}{\underset{|}{O}};$$



$$>\underset{\displaystyle CR_3}{\underset{|}{C}}-\underset{\displaystyle CR_3}{\underset{|}{S}};$$



$$>\underset{\displaystyle CR_3}{\underset{|}{C}}-\underset{\displaystyle CR_3}{\underset{|}{C}}<$$

But as a matter of fact, the addition compounds in the triphenylmethyl series are extremely unstable, dissociating readily at temperatures of 50–100°, into the original components. Indeed, the stability of these additive compounds is apparently no greater than that of the additive com-

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[1] THIS JOURNAL, 36, 1147 (1914).