REACTIVITY OF THE DOUBLE BOND IN COUMARINS AND RELATED $\alpha:\beta$-UNSATURATED CARBONYL COMPOUNDS.

Part V. Action of Mercuric Acetate on Cinnamic Acid and Its Derivatives.

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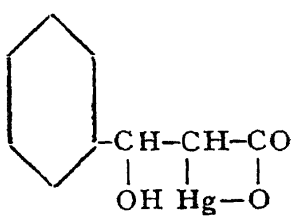
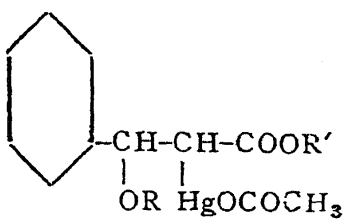
The addition of mercury salts to the double bond present in unsaturated acids was first studied by Biilmann[1] in aqueous solution and he came to the conclusion that high reactivity is associated with the *cis* structure and that *trans*-compounds do not react. He noticed that allocinnamic acid reacted readily with mercuric acetate to form compound (I) whereas ordinary cinnamic acid did not and hence deduced that the latter had the *trans* formula. Schoeller *et al*[2] employed alcoholic solution of esters of cinnamic acid and mercuric acetate and obtained products of the type (II). On saponifying the ester with alkali and subsequently adding acid, they obtained the internal anhydride of α-hydroxy-mercuri-β-alkoxy-β-phenyl-propionic acid (III). Sandborn and Marvel[3] used *l*-methyl cinnamate and were able to prove the formation of diastereoisomers. Wright[4] compared the reactivity of *cis* and *trans* methyl cinnamates and found that the former reacted much more rapidly than the latter and he was also able to collect useful evidence regarding the mechanism of the addition.

Schrauth and Geller[5] and Matejka[6] employed boiling alcoholic solutions of cinnamic acid and mercuric acetate and isolated compound (III). Quite

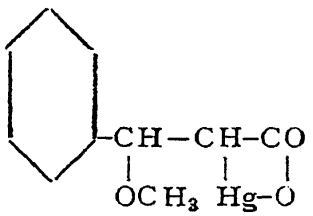


(I)



(II)

where R and R′ represent alkyl groups of the alcohol and ester respy.



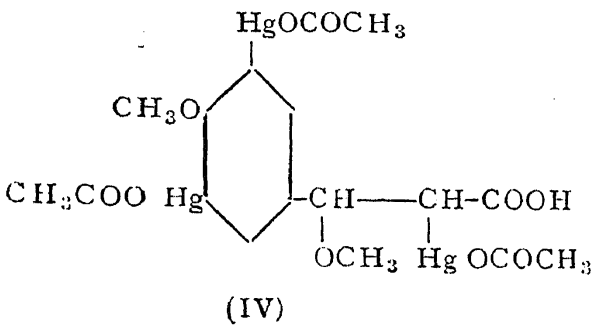
(III)

recently after the work described in the present paper had been completed, Loon and Carter[7] recorded some interesting observations on the effect of impurity in the acid and the time of reaction on the nature of the product.

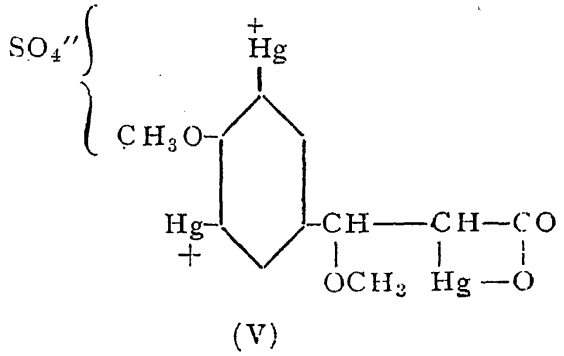
In the previous papers of this series,[8] it was shown that mercuric acetate can, besides adding to the double bond, mercurate the benzene nucleus also. The carboxylic acid form (IV) was frequently met with and the methoxy-dihydro-compounds produced by the action of hydrogen sulphide were found to be rather unstable. With a view to get more information on these aspects, the action of mercuric acetate on cinnamic, *p*-methoxy-cinnamic and *ortho*- and *meta*-nitrocinnamic acids has now been investigated in detail.

On mixing cold methyl alcoholic solutions of cinnamic acid and mercuric acetate, the mercury salt of cinnamic acid immediately separated out as a mass of colourless needles. These slowly dissolved even at the temperature of the room and compound (III) was formed as big rectangular prisms. The change was much quicker at the boiling point. Using very pure cinnamic acid we noticed no change in the chemical composition or properties on allowing the product to stay in the mother liquor for over a week. But even very small quantities of impurities produced definite changes in the solubility of the product though they were not so large as observed by Loon and Carter.

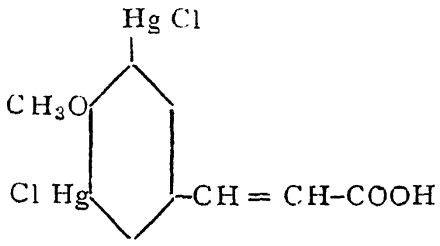
With equimolecular proportions of *p*-methoxycinnamic acid and mercuric acetate the mercury salt was immediately produced but it underwent very rapid conversion into the addition product. Even this could not be obtained pure since at the same time mercuration also took place to some extent. Therefore using excess of mercuric acetate the final product of addition and mercuration (IV), α : 3 : 5-triacetoxy-mercuri-β : 4-dimethoxy-dihydrocinnamic acid was obtained. Analytical results agree with the carboxylic formula. The positions of the acetoxy-mercuri-groups are assumed following the usual orienting influence of the methoxyl group. On adding dilute sulphuric acid to a solution of the substance in sodium hydroxide, sulphatomercuri compound (V) was formed whereas with dilute hydrochloric acid it formed 3 : 5-dichloro-mercuri-4-methoxy-cinnamic acid (VI) in which the addenda had been removed. These derivatives were useful in confirming the constitution of the mercuration product. The use of hydrochloric acid easily enabled a distinction between nuclear mercuration and addition at the double bond to be made since it invariably removed the addenda whereas sulphuric acid had no such influence.



(IV)



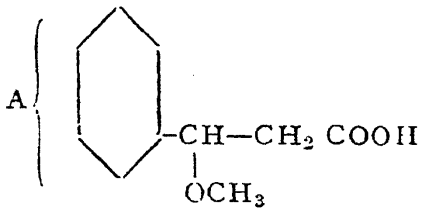
(V)



(VI)

m-Nitrocinnamic acid forms the mercuric salt in the cold immediately. This is quite stable and undergoes no change on long standing, whereas on heating, it slowly dissolves and forms the anhydride corresponding to (III). There is no mercuration. *o*-Nitrocinnamic acid does not react in the cold probably due to its low solubility in alcohol and the consequent high dilution of the solution, and on heating forms a similar addition product. No nuclear substitution could be expected since to the already inactive cinnamic acid the deactivating influence of the nitro group is added.

On treatment with hydrogen sulphide in alkaline solutions the methoxy-mercurials yielded the corresponding β-methoxydihydrocinnamic acids (VII), all the acetoxy-mercuri groups having been replaced by hydrogen atoms. These compounds were stable and were unaffected by prolonged treatment with dilute acid and alkali in the cold.



A—stands for H, OCH_3 or NO_2 group in the benzene nucleus.

(VII)

Experimental.

Para-methoxy- and *ortho*- and *meta*-nitrocinnamic acids were prepared from methoxy- and nitrobenzaldehydes by condensation with malonic acid using pyridine as catalyst.[9]

Action of mercuric acetate.

1. On cinnamic acid. Mercuric cinnamate.—The acid (2 g.) was dissolved in methyl alcohol (20 c.c.) and treated with a solution of mercuric acetate (4 g.) in methyl alcohol (50 c.c.) to which a few drops of acetic acid had been added. A bulky precipitate consisting of colourless fine needles was produced immediately. It was filtered and washed with small quantities of methyl alcohol containing a little acetic acid. It then melted at 194° with sintering at about 160°. (Found: Hg, 41·2; C, 43·1; $C_{18}H_{14}O_4Hg$ required Hg, 40·6; C, 43·7%.) When treated with aqueous sodium hydroxide it underwent decomposition to produce mercuric oxide and on adding dilute sulphuric acid to the alkaline mixture pure cinnamic acid could be isolated.

Anhydride of α-hydroxymercuri-β-methoxydihydrocinnamic acid (III).—When the mercuric salt was not filtered off and was allowed to stay in the mother liquor it underwent very slow conversion at 0° C. but at the temperature of the room (28° C.) it went into the solution again rather rapidly. If the volume of alcohol was sufficient a clear solution was obtained in the course of two hours and subsequently the more sparingly soluble compound (III), was deposited as colourless long rectangular rods. Even though with the volumes of alcohol mentioned in the previous experiment, no clear solution could be produced, the conversion was satisfactory and the anhydride was obtained pure in the course of 24 hours. After filtering and washing with methyl alcohol containing a little acetic acid the product melted at 212° with decomposition. (Found: Hg, 53·0; C, 31·3; $C_{10}H_{10}O_3Hg$ required Hg, 53·0; C, 31·7%.) It was easily soluble in chloroform and could be got into solution in aqueous potassium bromide by repeated treatment. It dissolved in aqueous sodium hydroxide without producing any trace of mercuric oxide and on acidifying the solution with dilute sulphuric acid it was reprecipitated. When aqueous hydrochloric acid was used instead, mercury was eliminated and cinnamic acid was liberated.

Compound (III) could be obtained more readily by heating the solutions as follows: cinnamic acid (4 g.) was dissolved in hot methyl alcohol (16 c.c.) and mixed with a similar solution of mercuric acetate (8 g.) in methyl alcohol (50 c.c.). A bulky precipitate of mercuric cinnamate was formed immediately. It however went into solution in the course of 10 minutes when the mixture was heated under reflux on a water-bath and the anhydride began to separate pure after another 10 minutes. The heating was stopped after half an hour, the mixture allowed to stand overnight and the product filtered and washed with methyl alcohol. The yield was about 9 g. and the

substance was identical in all respects with the sample obtained in the cold.

In one experiment the mixture was allowed to stand for a week and the solid product was isolated. It had undergone no change in its composition or properties. When a sample of cinnamic acid which was slightly coloured was employed and the mixture allowed to stand for seven days the composition was practically the same (Found : Hg, 52·9%) and its solubility in potassium bromide was also practically unchanged, but it did not dissolve completely in chloroform and it left behind a small insoluble residue.

With a view to examine the possibility of mercuration, cinnamic acid was boiled in methyl alcoholic solution with 4 molecular proportions of mercuric acetate for 40 hours. However the same anhydride (III) was obtained and there was no mercuration of the benzene nucleus.

β-Methoxydihydrocinnamic acid.—The mercury compound (2 g.) was dissolved in normal sodium hydroxide solution (20 c.c.) and hydrogen sulphide passed into it till all the mercury was precipitated as the sulphide ($\frac{1}{2}$ hour). After allowing the mixture to stand overnight the sulphide was filtered off and the clear filtrate acidified with dilute sulphuric acid. The solid that separated out in a crystalline form was recrystallised from hot water. It was obtained as colourless prisms melting at 97–8°. (Found : C, 66·3 ; H, 6·5 ; $C_{10}H_{12}O_3$ required C, 66·7 ; H, 6·7%.) The methoxy acid was readily soluble in all solvents and was unaffected in the presence of dilute acids and alkalies for several days.

2. *On para-methoxy-cinnamic acid.*—When equi-molecular proportions of the methoxycinnamic acid and mercuric acetate were mixed together in methyl-alcoholic solution in the cold the mercuric salt was immediately formed. But it underwent change so rapidly into the addition product that it could not be obtained pure. It decomposed at 161° and reacted with aqueous sodium hydroxide to produce mercuric oxide, but on further adding sulphuric acid the methoxycinnamic acid that was recovered was contaminated with a little combined mercury. In the course of 15 minutes the mercuric salt underwent complete transformation into a new product which decomposed at 204°. When filtered and washed with alcohol it dissolved in aqueous alkali to give a clear solution and most of the mercury was removed by adding hydrochloric acid. The methoxy acid that was obtained contained some mercury due to nuclear mercuration. The solid product was therefore mostly the addition compound with a portion that had further undergone mercuration in the benzene nucleus.

α : 3 : 5-*Triacetoxymercuri-β* : 4-*dimethoxy-dihydrocinnamic acid* (*IV*).—This was obtained by heating the acid with 4 molecular proportions of mercuric acetate as follows : the methoxy acid (5 g.) was dissolved in methyl alcohol (50 c.c.) and mixed with a solution of mercuric acetate (30 g.) in methyl alcohol (150 c.c.). No solid separated out in the cold as before. The mixture was heated under reflux for about 20 hours. Even then no solid was formed. It was only on adding more methyl alcohol to the solution after cooling that a crystalline looking solid was obtained. After the addition of sufficient amount of alcohol the product was filtered and washed with alcohol. It was then found to be very sparingly soluble in all organic solvents and to decompose at 181° (Found : Hg, 61·6 ; C, 20·7 ; $C_{17}H_{20}O_{10}Hg_3$ required Hg, 61·1 ; C, 20·7%.) It readily dissolved in aqueous sodium hydroxide to form a clear solution which deposited a colourless solid on adding dilute sulphuric acid. After filtering and washing repeatedly with water it was found to decompose at 223° and to correspond to formula (V). (Found : Hg, 66·2 ; $C_{11}H_{10}O_8Hg_3S$ required Hg, 66·6%.) If, on the other hand, the alkaline solution was acidified with dilute hydrochloric acid a different compound was obtained decomposing at 204°. This corresponded with 3 : 5-dichloro-mercuri-4-methoxy-cinnamic acid, the addenda having been removed by the acid. (Found : Hg, 62·4 ; $C_{10}H_8O_3Hg_2Cl_2$ required Hg, 61·9%.)

β : 4-*dimethoxydihydrocinnamic acid.*—By passing hydrogen sulphide into an alkaline solution of the above triacetoxy-mercuri-compound all the mercury was precipitated as the sulphide and filtered. On adding dilute hydrochloric acid, the dimethoxy-dihydrocinnamic acid was obtained as a crystalline solid which on recrystallisation from hot water appeared as colourless elongated needles melting at 144–45°. (Found : C, 62·6 ; H, 6·4 ; $C_{11}H_{14}O_4$ required C, 62·9 ; H, 6·7%.) The compound was quite stable in the presence of aqueous alkali and dilute hydrochloric acid.

3. On meta-nitrocinnamic acid. The mercuric salt.—On mixing methyl alcoholic solutions of the acid and mercuric acetate in the cold a bulky white precipitate was formed immediately. It was very sparingly soluble in the solvent and did not undergo any change over long periods. A sample of the salt collected after allowing the mixture to stand for 4 hours decomposed at 189°. It readily gave mercuric oxide on treatment with aqueous sodium hydroxide and the pure cinnamic acid was recovered on further addition of dilute sulphuric acid. (Found : Hg, 34·7 ; $C_{18}H_{12}O_8HgN_2$ required Hg, 34·3%.)

Anhydride of α-hydroxymercuri-β-methoxy-3-nitrodihydrocinnamic acid (corresponding to III).—If the alcoholic solutions of the acid and mercuric acetate were heated under reflux after mixing, the precipitated mercury salt redissolved and in the course of half an hour a fresh compound began to separate. The product was collected after heating for 10 hours and washed with methyl alcohol. It was found advisable to discard the first precipitate formed during the first half an hour as it was rather impure. The pure compound decomposed at 214°. (Found : Hg, 47·8; $C_{10}H_9O_5HgN$ required Hg, 47·4%.) It dissolved in alkali to form a clear solution and was reprecipitated on adding dilute sulphuric acid. With dilute hydrochloric acid the addenda were removed and *meta*-nitro cinnamic acid was obtained.

The same addition product was obtained on boiling the nitrocinnamic acid with a large excess of mercuric acetate for over 40 hours. No mercuration of the benzene ring could be noticed.

β-Methoxy-3-nitrodihydrocinnamic acid was obtained in the usual way from the above mercury compound by the action of hydrogen sulphide. When recrystallised from hot water it appeared as pale yellow needles melting at 117–18°. (Found : C, 53·2; H, 4·8; $C_{10}H_{11}O_5N$ required C, 53·3; H, 4·9%.) The compound was easily soluble in all the common organic solvents and was quite stable in the presence of dilute mineral acid and alkali solutions over long periods.

4. On orthonitrocinnamic acid. Anhydride of α-hydroxymercuri-β-methoxy-2-nitrocinnamic acid.—*Ortho*-nitrocinnamic acid is rather sparingly soluble in cold methyl alcohol and consequently there was no reaction with mercuric acetate in the cold probably due to the low concentrations of the reactants. However on boiling the nitrocinnamic acid with excess of mercuric acetate in methyl alcoholic solution for about 30 hours, a good yield of the addition product (anhydride) was obtained. In this case also the first precipitate was filtered off and discarded. The substance decomposed at 215°. (Found : Hg, 47·5; N, 3·5; $C_{10}H_9O_5HgN$ required Hg, 47·4; N, 3·3%.) It behaved quite similar to the *meta*-nitro-compound.

β-Methoxy-2-nitrodihydrocinnamic acid obtained from the above compound crystallised from hot water as yellow rectangular plates melting at 151–52° and was very similar to the 3-nitrocompound in behaviour. (Found : C, 53·6; H, 5·0; $C_{10}H_{11}O_5N$ required C, 53·3; H, 4·9%.)

Summary.

The action of mercuric acetate on cinnamic acid, *p*-methoxy and *o*- and *m*-nitrocinnamic acids in methyl alcoholic solutions has been examined.

In general they form at first the mercuric salts which subsequently undergo further change. With cinnamic acid there is no mercuration of the benzene ring; only addition at the double bond takes place and the product has the anhydride form. In the cold *p*-methoxycinnamic acid undergoes mainly addition whereas on heating with excess of the reagent two acetoxy-mercuri groups further enter the nucleus. The compound has a free carboxyl group. The nitrocinnamic acids do not undergo mercuration; they form addition compounds only on heating and these have the anhydride structure. All the methoxymercurials yield β-methoxydihydrocinnamic acids on treatment with hydrogen sulphide and they are found to be stable in the presence of cold acids and alkalis.

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