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

THE STRUCTURE OF THE COMPOUNDS PRODUCED BY THE ADDITION OF MERCURIC SALTS TO OLEFINS

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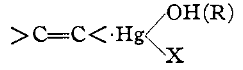
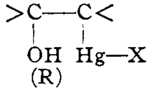
It is a well-known fact that mercuric salts in aqueous or alcoholic solution react more or less readily with compounds containing a carbon-carbon double bond to form addition products. The solvent also enters into the reaction causing hydrolysis or alcoholysis and the final product contains an hydroxyl or alkoxyl group. Considerable work has been done in attempting to establish the structure of these compounds, but as yet no absolute proof of their structure has been published.

Manchot[2] is the most recent advocate of the theory that these products are molecular addition products. He represents their structure by Formula I.



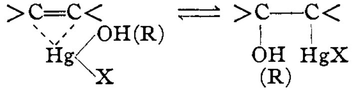
$$>C{=}C{<}\cdot\mathrm{Hg}\begin{matrix}\diagup\mathrm{OH(R)}\\ \diagdown\mathrm{X}\end{matrix}$$

I



$$\begin{matrix}>C & - & C<\\ | & & |\\ \mathrm{OH} & & \mathrm{Hg{-}X}\\ \mathrm{(R)} & & \end{matrix}$$

II



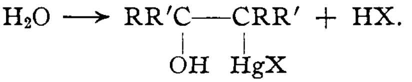
$$\begin{matrix}>C & = & C<\\ & \mathrm{Hg}\begin{matrix}\diagup\mathrm{OH(R)}\\ \diagdown\mathrm{X}\end{matrix} & \end{matrix}\rightleftharpoons\begin{matrix}>C & - & C<\\ | & & |\\ \mathrm{OH} & & \mathrm{HgX}\\ \mathrm{(R)} & & \end{matrix}$$

III

The more common theory concerning the structure of these compounds is that they are true addition products in which the hydroxyl (or alkoxyl) group and the mercury atom are attached in the usual manner to the carbon atoms which were joined by the double union in the original olefin (Formula II). This theory seems to be fairly well established by the work of Adams, Roman and Sperry[3] on the addition of mercuric salts to *o*-allylphenol.

Sand[4] has represented the addition compounds as an equilibrium mixture between some type of molecular addition product and the ordinary type of addition product (Formula III). The merits of these three formulas have been very completely discussed in the paper of Adams, Roman and Sperry[3] and the discussion need not be repeated here.

If the addition products are of the structure represented in Formula II, it should be possible to obtain optically active isomers by the addition of mercuric salts to certain types of olefins. Thus $RR'C{=}CRR' + HgX_2 +$



$$H_2O \longrightarrow \begin{matrix}RR'C & - & CRR'\\ | & & |\\ \mathrm{OH} & & \mathrm{HgX}\end{matrix} + HX.$$

Such isomerism is not possible in compounds of the types represented by

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[1] This communication is an abstract of a thesis submitted by L. T. Sandborn in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] Manchot, *Ber.*, **53**, 984 (1920).

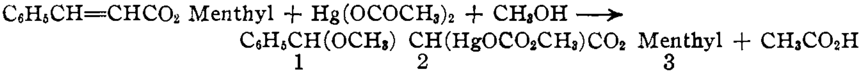
[3] Adams, Roman and Sperry, THIS JOURNAL, **44**, 1781 (1922).

[4] Sand, *Ann.*, **329**, 151 (1903).

Formulas I and III. Hence, if it can be shown that such optically active substances are obtained, the structure of these addition products will be definitely established.

Schrauth, Schoeller and Struensee[5] have shown that mercuric acetate adds easily to methyl cinnamate in methyl alcoholic solution to give a product which is assumed to be methyl β-methoxy-α-acetoxymercuri-hydrocinnamate, $C_6H_5CH(OCH_3)CH(HgOCOCH_3)CO_2CH_3$ (IV). Four optically active, isomeric compounds of this structure are theoretically possible and in the laboratory preparation the two racemic modifications might be expected. Frequently, in similar cases where asymmetric carbon atoms are produced by the addition of other reagents to a carbon-carbon double bond, only one of the possible racemic compounds is produced in large quantities. It is not surprising that Schrauth, Schoeller and Struensee obtained only one product in their work.

Since there is no available method for the resolution of a substance of the type represented by Formula IV, it was thought that the addition of mercuric acetate to *l*-menthyl cinnamate in methyl alcoholic solution might lead to more satisfactory results. The reaction would be



$$C_6H_5CH{=}CHCO_2\ \text{Menthyl} + Hg(OCOCH_3)_2 + CH_3OH \longrightarrow C_6H_5\underset{1}{C}H(OCH_3)\ \underset{2}{C}H(HgOCO_2CH_3)CO_2\ \text{Men}\underset{3}{\text{t}}\text{hyl} + CH_3CO_2H$$

V

Four optically active isomers of the *l*-menthyl β-methoxy-α-acetoxy-mercuri-hydrocinnamate would be theoretically possible. Representing them in the usual manner in the order of the numbers in Formula V, these isomers are *ddl, lll, dll, ldl.* Here again in the actual laboratory preparation an asymmetric synthesis may occur which will favor the formation of certain isomers over the others.

When the reaction was carried out the addition product melted over a considerable range even after repeated crystallizations. However, analysis showed that the mercury content agreed with that of the expected product.

The crude *l*-menthyl β-methoxy-α-acetoxymercuri-hydrocinnamate was converted into the chloromercuri compound ($C_6H_5CH(OCH_3)CH(HgCl)$-CO_2 Menthyl) by means of sodium chloride in dil. methyl alcohol and a product of definite melting point and composition was obtained, but only one isomer could be isolated. The corresponding bromomercuri and iodomercuri compounds were obtained by treating the crude acetate, respectively, with solutions of sodium bromide and sodium iodide. Two definite isomers of each of these compounds resulted. One isomer of *l*-menthyl β-methoxy-α-bromomercuri-hydrocinnamate ($C_6H_5CH(OCH_3)$-$CH(HgBr)CO_2$ Menthyl) melted at 145–146° and had a negative rotation $[[\alpha]_D^{25} = -48.6°]$ and the other melted at 134–135° and had a positive

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[5] Schrauth, Schoeller and Struensee, *Ber.*, **43,** 695 (1910); **44,** 1048 (1911).

rotation $[[\alpha]_D^{25} = +61.9°]$. In the case of the iodomercuri compounds one melted at 126–128° and had a rotation of +65.89°, and the other melted at 102–103° and had a rotation of —22.5°. In each case the levorotatory isomer was present in much larger amounts and only a few grams of dextrorotatory compound could be isolated. It seems probable that other isomers were present in the residues but they could not be obtained in crystalline form.

The chloromercuri compound could be converted into the *levo*-bromomercuri compound and this in turn to the *levo*-iodomercuri compound. On account of the small quantities available no attempt was made to convert the *dextro*-bromomercuri compound into the *dextro*-iodomercuri compound.

The existence of these optically active mercury compounds can be explained only by assuming that the mercuric salt has added to the carbon-carbon double bond of *l*-menthyl cinnamate to give a product in which the $—OCH_3$ and the $—HgOCOCH_3$ groups are attached to the carbon atoms by the same type of bond that occurs in the ordinary organic compound.

Experimental Part

***l*-Menthyl Cinnamate.**—*l*-Menthyl cinnamate was prepared by the method of Cohen and Whiteley.[6]

The crude material was distilled under reduced pressure and the pure product collected at 234–237° (28 mm.); yield, 87–91%; $[\alpha]_D^{25} = —59.5°$ for a 7.5% solution in chloroform.

The Addition of Mercuric Acetate to *l*-Menthyl Cinnamate.—A solution of 95 g. of *l*-menthyl cinnamate in about 100 cc. of absolute methyl alcohol was added to a solution of 150 g. of mercuric acetate in 1000 cc. of methyl alcohol. About 3 or 4 cc. of glacial acetic acid was needed to bring the mercuric acetate entirely into solution. After two weeks about 800 cc. of alcohol was distilled and the remaining solution was cooled in an ice-salt bath. The crystals which separated were filtered with suction and then weighed 116 g. The mother liquors were diluted with water and an additional 64 g. of product was obtained. The total yield of crude material weighed 180 g. (94%).

The crude material was recrystallized from petroleum ether (b. p., 50–60°). It then melted at 95–105°; $[\alpha]_D^{21} = —23.1°$ for a 2.5% solution in chloroform.

Anal. Subs., 0.3365: Hg, 0.1167. Calcd. for $C_{22}H_{32}O_5Hg$: **Hg,** 34.78. Found: 34.69.

The product was again crystallized from petroleum ether and separated into four fractions in an attempt to obtain pure products. However, each fraction melted over a range and the rotations were nearly identical.

***l*-Menthyl β-Methoxy-α-bromomercuri-hydrocinnamate.**—To a solution of 50 g. of *l*-menthyl β-methoxy-α-acetoxymercuri-hydrocinnamate (m. p., 100–105°) in 250 cc. of methyl alcohol was added a solution of 15 g. of sodium bromide in 100 cc. of methyl alcohol. White needle-shaped crystals separated at once. These crystals were filtered off and dried; yield, 27 g.; m. p., 145–146°. The melting point was not changed by

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[6] Cohen and Whiteley, *J. Chem. Soc.*, **79**, 1308 (1901). Hilditch, *ibid.*, **93**, 1 (1908).

further crystallization. A 0.3272g. sample dissolved in 15 cc. of chloroform gave a rotation of —1.06° in a 1dcm. tube; $[\alpha]_D^{25} = -48.6°$.

Anal. Subs., 0.2249: HgS, 0.0880. Subs., 0.1918: AgBr, 0.0603. Calcd. for $C_{20}H_{29}O_3BrHg$: Hg, 33.50; Br, 13.39. Found: Hg, 33.72; Br, 13.42.

The mother liquors from the first crop of crystals were evaporated and a gummy residue was obtained. After several crystallizations from petroleum ether 5 g. of a pure product, m. p. 134–135°, was obtained. About 20 g. of material could not be obtained in a crystalline condition. A 0.3658g. sample of the second crop of crystals in 15 cc. of chloroform gave a rotation of +1.51°; $[\alpha]_D^{25} = +61.9°$.

Anal. Subs., 0.2216: HgS, 0.0863. Subs., 0.2024: AgBr, 0.0641. Calcd. for $C_{20}H_{29}O_3BrHg$: Hg, 33.50; Br, 13.39. Found: Hg, 33.57; Br, 13.51.

The gummy residue was analyzed for mercury and was found to contain about 5% less mercury than should be present in the expected product.

***l*-Menthyl β-Methoxy-α-chloromercuri-hydrocinnamate.**—A solution of 28.6 g. of *l*-menthyl cinnamate in 50 cc. of methyl alcohol was treated with a solution of 32 g. of mercuric acetate in 300 cc. of methyl alcohol. After twenty-four hours a slight precipitate was apparent, but this dissolved when the solution was warmed. A solution of 11.6 g. of sodium chloride in 200 cc. of 50% methyl alcohol was added, and a white, gummy precipitate separated at once. This was filtered and recrystallized from methyl alcohol. Small needle-shaped crystals melting at 150–152° were thus obtained; yield, 28 g., or 51%. Further crystallization did not change the melting point. A 0.2g. sample in 10 cc. of chloroform gave a rotation of —2.6° (Ventzke scale) in a 1dcm. tube; $[\alpha]_D^{25} = -45.08°$.

Anal. Subs., 0.2027: HgS, 0.0850. Subs., 0.2081: AgCl, 0.0542. Calcd. for $C_{20}H_{29}O_3ClHg$: Hg, 36.26; Cl, 6.41. Found: Hg, 36.16; Cl, 6.44.

No other isomers could be isolated from the mother liquors. This chloromercuri compound was converted into the corresponding bromomercuri compound by treating a solution of 5 g. of the product in 50 cc. of acetone with a solution of 2 g. of sodium bromide in 75 cc. of acetone. Sodium chloride separated and was removed by filtration. The acetone was evaporated and the residue washed with water and crystallized from methyl alcohol. In this way 4 g. of bromomercuri compound melting at 144–145° was obtained. This product was identical with the levorotatory bromomercuri isomer described before.

In a similar manner 3 g. of the chloromercuri compound in 50 cc. of acetone was treated with a solution of 1 g. of sodium iodide in 25 cc. of acetone. The product (iodomercuri compound) was isolated as before and crystallized from petroleum ether (b. p., 50–60°); yield, 1.5 g.; m. p., 101–102°. A mixed-melting-point determination and the optical rotation showed that this product was identical with the levorotatory iodomercuri compound obtained directly from the acetoxymercuri compound and the bromomercuri compound.

***l*-Menthyl β-Methoxy-α-iodomercuri-hydrocinnamate.**—To a solution of 9 g. of *l*-menthyl cinnamate in 25 cc. of methyl alcohol was added a solution of 15 g. of mercuric acetate in 150 cc. of methyl alcohol. After 48 hours a solution of 15 g. of potassium iodide in methyl alcohol was added. On cooling the solution in an ice-salt bath, a precipitate separated. This was filtered off and recrystallized from ethyl alcohol. In this way there was obtained 1 g. of product; m. p., 126–128°. A 0.2g. sample in 10 cc. of chloroform gave a rotation of +3.8° (Ventzke scale) in a 1dcm. tube; $[\alpha]_D^{25} = +65.89°$.

Anal. Subs., 0.1900: HgS, 0.0690. Subs., 0.2017, 0.0643: AgI, 0.0727, 0.0231. Calcd. for $C_{20}H_{29}O_3HgI$: Hg, 31.11; I, 19.68. Found: Hg, 31.31; I, 19.49, 19.53.

The methyl alcoholic mother liquors were poured into cold water and the precipitate thus obtained was filtered off and crystallized from petroleum ether (b. p., 50–60°). About 0.5 g. of product melting at 96–99° was obtained. A 0.2g. sample in 10 cc. of chloroform gave a rotation of —1.4° (Ventzke scale) in a 1dcm. tube; $[\alpha]_{\mathrm{D}}^{25} = -24.27°$. This material was not purified further, but its physical constants were very close to those of the levorotatory iodomercuri compound obtained from the corresponding bromomercuri derivative.

A solution of 5 g. of *l*-menthyl β-methoxy-α-bromomercuri-hydrocinnamate (m. p., 144–145°) was dissolved in 150 cc. of methyl alcohol and added to a solution of 2.5 g. of sodium iodide in 50 cc. of methyl alcohol. The precipitate of sodium bromide was filtered off, and the methyl alcoholic solution was diluted with water. The precipitated mercury compound was filtered off and recrystallized from petroleum ether (b. p., 50–60°); m. p., 102–103°. When mixed with a sample of the levorotatory iodomercuri isomer obtained from the acetoxymercuri compound the melting point was not depressed. A 0.2g. sample in 10 cc. of chloroform gave an observed rotation of —1.3° (Ventzke scale) in a 1dcm. tube; $[\alpha]_{\mathrm{D}}^{25} = -22.5°$.

Anal. Subs., 0.2017: HgS, 0.0731. Subs., 0.2048: AgI, 0.0743. Calcd. for $C_{20}H_{29}O_3HgI$: Hg, 31.11; I, 19.68. Found: Hg, 31.25; I, 19.60.

Summary

The addition of mercuric salts to olefins of the type RR′C=CRR′ leads to the production of optically active isomers which can be explained only by the assumption that these addition products are true organic mercury compounds and not molecular addition products.

URBANA, ILLINOIS

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

A STUDY OF THE METHYLATION OF XYLENE. THE PREPARATION OF DURENE, PENTAMETHYLBENZENE AND HEXAMETHYLBENZENE

BY LEE IRVIN SMITH AND F. J. DOBROVOLNY[1]

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The method of Friedel and Crafts has been used many times for the methylation of benzene and its homologs, and the reaction has been investigated in some detail by a number of workers.[2]

The quantities methylated were usually small, however, and the object was not primarily to obtain efficient methylation for the production of

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[1] Abstracted from a thesis by F. J. Dobrovolny, presented to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the degree of Master of Science.

[2] Friedel and Crafts, *Ann. chim. phys.*, **1**, 449 (1884). Jannasch and Fittig, *Z. Chem.*, **6**, 161 (1870). Jannasch, *Ber.*, **7**, 692 (1874); *Ann.*, **161**, 79 (1872); *Ber.*, **8**, 355 (1875); **10**, 1355 (1877); **11**, 30 (1878). Ador and Rilliet, *Ber.*, **11**, 1627 (1878); **12**, 329 (1879). Jacobsen, *Ber.*, **9**, 256 (1876); **10**, 1009 (1877); **14**, 2624 (1881); **18**, 338 (1885). Anschütz, *Ann.*, **235**, 177 (1886). Claus, *Ber.*, **20**, 3097 (1887). Beaurepaire, *Bull. Soc. Chim.*, **50**, 677 (1888). See also Jacobsen, *Ber.*, **21**, 2824 (1888), and Beilstein, *Ann.*, **137**, 326 (1866).