The mechanism of the reduction of organic halides by means of the alkali metals in liquid ammonia solution is discussed.

WORCESTER, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE ADDITION OF MERCURIC SALTS TO ALPHA-BETA-UNSATURATED KETONES

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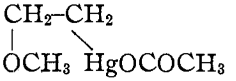
It is well known that mercuric salts react more or less readily with various unsaturated compounds to give products whose compositions are represented by unsaturated compound plus —HgX and —OH, if the reaction is carried out in aqueous solution, or unsaturated compound plus —HgX and —OR if the reaction is carried out in alcohol. There has been some question as to their structure, whether they are saturated compounds formed by addition to the double linkage or complex compounds of the double salt or molecular type.[2] For example, when ethylene is passed into a methyl alcoholic solution of mercuric acetate, it forms a compound whose composition is represented by $C_2H_4.HgOCOCH_3.OCH_3$ and which according to these two views, is either a molecular compound, or the saturated compound,[3]  $\underset{OCH_3}{CH_2}-\underset{HgOCOCH_3}{CH_2}$ The principal reason why substances of this type have been regarded as molecular compounds is the ease with which the unsaturated compounds are regenerated by acids. $C_2H_4.HgX.OCH_3 + HX \longrightarrow C_2H_4 + CH_3OH + HgX_2$. The most recent work of Adams, Roman and Sperry[4] shows conclusively that in some cases these are saturated compounds formed by addition to the double bond. The following investigation of the reaction between mercuric acetate and α,β-unsaturated ketones was undertaken with the purpose of getting further evidence on this point and on the mode of addition. The results show that α,β-unsaturated ketones with one double linkage, such as benzalacetophenone, will react with but one mol. of mercuric acetate while with dibenzalacetone, which has two double linkages, two mols. of mercuric acetate reacted. It appears from this that addition to the double linkages has taken place. Furthermore, all the compounds were white. Cinnamalacetophenone, a ketone which has two double

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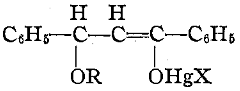
[2] For an account of the arguments in favor of and against 'molecular' structures, see Whitmore, "Organic Compounds of Mercury," The Chemical Catalog Co., 1921, Chap. 5.

[3] Schoeller and Schrauth, *Ber.*, **46**, 2867 (1913). Manchot, *Ber.*, **53**, 986 (1920).

[4] Adams, Roman and Sperry, THIS JOURNAL, **44**, 1781 (1922). Mills and Adams, *ibid.*, **45**, 1842 (1923).

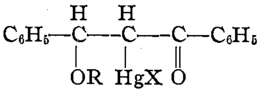
linkages, one of which is γ to the carbonyl, reacted with two molecules of alcoholic mercuric acetate, but the acetate compound has not been obtained in a form suitable for analysis, and when sodium chloride solution was added, insoluble amorphous precipitates of variable composition were obtained.

The simple α,β-unsaturated ketones were found to react readily with mercuric acetate in alcoholic solution. With benzalacetophenone, the products obtained analyzed for the ketone to which the groups —OR and $HgOCOCH_3$ had been added. The addition might have taken place in one of three ways: the groups could add 1, 4 to the conjugated system, like other metallic derivatives, to give a compound of the structure I; or they might possibly add 1, 2, according to either II or III.



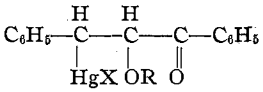
$C_6H_5\text{—}\overset{H}{\underset{OR}{C}}\text{—}\overset{H}{C}\text{=}\underset{OHgX}{C}\text{—}C_6H_5$

I



$C_6H_5\text{—}\overset{H}{\underset{OR}{C}}\text{—}\overset{H}{\underset{HgX}{C}}\text{—}\underset{O}{\underset{\|}{C}}\text{—}C_6H_5$

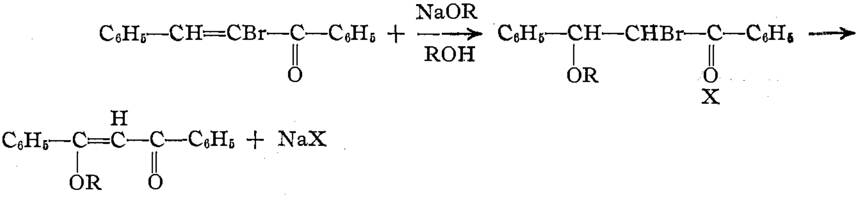
II



$C_6H_5\text{—}\overset{H}{\underset{HgX}{C}}\text{—}\overset{H}{\underset{OR}{C}}\text{—}\underset{O}{\underset{\|}{C}}\text{—}C_6H_5$

III

Structure III may be discarded immediately because the mercury compounds obtained reacted with halogens, the halogen replacing the mercury group and α-halogen-β-alkoxy ketones were obtained. The α-bromo-β-ethoxy and α-bromo-β-methoxy addition products of benzalacetophenone have been isolated recently by Dufraisse and Gerald[5] as intermediate products in the reaction of sodium alcoholate with α-bromobenzalacetophenone. The melting points and other properties given by these workers

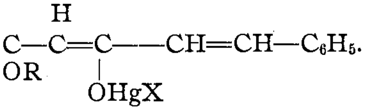


$$C_6H_5\text{—}CH\text{=}CBr\text{—}\underset{O}{\underset{\|}{C}}\text{—}C_6H_5 + \xrightarrow[ROH]{NaOR} C_6H_5\text{—}\underset{OR}{CH}\text{—}CHBr\text{—}\underset{X}{\underset{O}{\underset{\|}{C}}}\text{—}C_6H_5 \longrightarrow$$

$$C_6H_5\text{—}\underset{OR}{C}\text{=}\overset{H}{C}\text{—}\underset{O}{\underset{\|}{C}}\text{—}C_6H_5 + NaX$$

are identical with those of the bromine compounds obtained from the mercury derivatives of benzalacetophenone by replacing the mercury with bromine.

It now remains to distinguish between Structures I and II. In this connection, the reaction of mercuric acetate in alcohol solution with dibenzalacetone was studied. If the groups add 1, 4, we should expect to get only a monomercury compound with dibenzalacetone, $C_6H_5\text{—}$



$\underset{OR}{C}\text{—}\overset{H}{C}\text{=}\underset{OHgX}{C}\text{——}CH\text{=}CH\text{—}C_6H_5$. But the products obtained had two —OR and two $\text{—}HgOCOCH_3$ groups, and a dimercurated product could not have been obtained by 1, 4 addition alone. Furthermore, the com-

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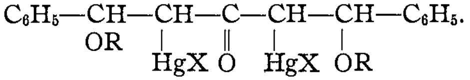
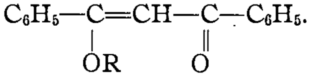
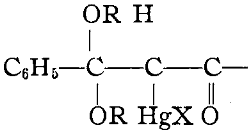
[5] Dufraisse and Gerald, *Compt. rend.*, **174**, 1631 (1922).

pounds did not give mercuric oxide with sodium hydroxide solution as one might expect if they were —OHg— derivatives, so that mercury compounds of benzalacetophenone have Structure II, while the derivatives of dibenzalacetone are  $C_6H_5—\underset{OR}{CH}—\underset{HgX}{CH}—\underset{O}{\overset{\|}{C}}—\underset{HgX}{CH}—\underset{OR}{CH}—C_6H_5$. The mercury derivatives of unsaturated ketones are therefore analogous to the substances derived from the unsaturated esters.[6]

The behavior of these compounds was similar to that of mercury derivatives of other unsaturated compounds. Solutions of the acetates gave precipitates of the bromides or chlorides when treated with sodium bromide or chloride solution and they were decomposed by acids and by sodium iodide in the usual way. Also, they were found to be decomposed by Grignard reagents; ethylmagnesium bromide reacted with the bromomercuri-methoxy derivative of benzalacetophenone giving β-phenylvalerophenone. The last substance is obtained from benzalacetophenone itself and ethylmagnesium bromide.[7]

As Dufraisse and Gerald[5] have shown, the α-bromo-β-alkoxy-β-phenyl propiophenones lose hydrogen bromide with sodium alcoholate giving ketones of the structure,  $C_6H_5—\underset{OR}{C}=CH—\underset{O}{\overset{\|}{C}}—C_6H_5$. These unsaturated ketones reacted with alcoholic mercuric acetate but no "acetal" compound,  $C_6H_5—\underset{OR}{\overset{OR}{C}}—\underset{HgX}{\overset{H}{C}}—\underset{O}{\overset{\|}{C}}—C_6H_5$, was obtained; the analyses indicated that the product was diacetoxymercuri-dibenzoyl methane. The reaction was found to go best in dil. alcohol solution so it probably proceeds first, by the addition of —OH and —$HgOCOCH_3$, second, by the elimination of ROH and third, by the further addition of mercuric acetate.

Substitution in the benzene rings did not affect the reaction of the unsaturated ketones with mercuric acetate. Benzal-*p*-chloro-acetophenone reacted as readily as benzalacetophenone itself. But the reaction failed with benzaldesoxybenzoin. Nor were addition compounds formed with cyclopropane ketones. Dimethyl 2-phenyl-3-benzoyl-cyclopropane-dicarboxylate[8] did not react with mercuric acetate in cold methyl alcohol solution nor did 1,2-dibenzoyl-3-phenyl-cyclopropane.[9] Other cyclopropanes were tried without obtaining addition products.

It is interesting to compare the reactions of unsaturated ketones with

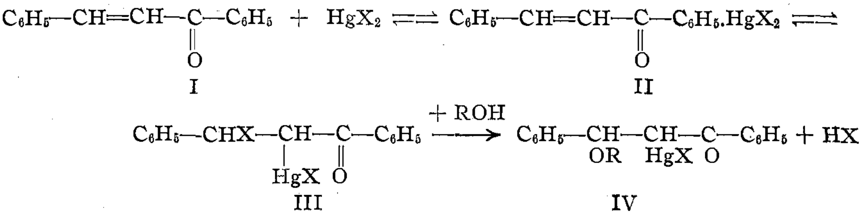
[6] Schoeller, Schrauth and Struensee, *Ber.*, **43**, 695 (1910); **44**, 1048 (1911)

[7] *Am. Chem. J.*, **38**, 548 (1907).

[8] Kohler and Conant, THIS JOURNAL, **39**, 1404 (1917).

[9] Kohler and Jones, *ibid.*, **41**, 1249 (1919).

mercuric acetate and with mercuric halides. Since this work was completed, Vorländer and Eichwald[10] have published an account of more compounds obtained from mercuric chloride and bromide, and unsaturated ketones. The double compounds, composed of one mol. of ketone and one mol. of mercuric halide, were stable towards alcohol, the solvent used; that is, there were no products obtained of the type, unsaturated ketone plus —OR plus —HgX. In hot alcohol they were completely dissociated into their components, mercuric halide and unsaturated ketone. The writer has found by measuring the elevation of the boiling point of acetone, that they are completely dissociated in this solvent, while the compounds described in this paper, while not entirely undecomposed, are not dissociated to this extent. The compounds obtained with mercuric halides are colored and with an unsaturated ketone with two double linkages; dianisalacetone, the product obtained by Vorländer and Eichwald, contained only one mol. of mercuric halide to one of ketone. In view of the facts known, it seems probable that the following equilibrium exists when alcoholic solutions of mercuric salts and of an unsaturated ketone such as benzalacetophenone are brought together.



$$\underset{\text{I}}{C_6H_5{-}CH{=}CH{-}\underset{\underset{O}{\|}}{C}{-}C_6H_5} + HgX_2 \rightleftharpoons \underset{\text{II}}{C_6H_5{-}CH{=}CH{-}\underset{\underset{O}{\|}}{C}{-}C_6H_5.HgX_2} \rightleftharpoons$$

$$\underset{\text{III}}{C_6H_5{-}CHX{-}\underset{\underset{HgX}{|}}{CH}{-}\underset{\underset{O}{\|}}{C}{-}C_6H_5} \xrightarrow{+\,ROH} \underset{\text{IV}}{C_6H_5{-}\underset{OR}{CH}{-}\underset{HgX}{CH}{-}\underset{O}{C}{-}C_6H_5} + HX$$

When a mercuric salt such as the acetate, which is alcoholized to a relatively large extent, is used, the reaction finally goes to IV. But when HgX_2 is one of the mercuric halides, the compounds first formed are not affected by the alcohol and the equilibrium represented by Steps I, II and III may be present. In solution such an equilibrium may exist, but the compounds which finally precipitate when mercuric acetate is used are the result of the addition of —OR and $HgOCOCH_3$ to the double linkage.

Experimental Part

α-Acetoxymercuri-β-methoxy-β-phenylpropiophenone.—A solution of 25 g. of benzalacetophenone and 38 g. of mercuric acetate in 250 cc. of absolute methyl alcohol was allowed to stand until a sample no longer gave a precipitate of mercuric oxide with sodium hydroxide solution. The solution was concentrated by evaporation and the mercury compound crystallized; weight, 53 g. After recrystallization from methyl alcohol it melted at 115°.

Analyses. Calc. for $C_{18}H_{18}O_4Hg$: C, 43.31; H, 3.63; Hg, 40.2. Found: C, 43.13; H, 3.54; Hg, 40.2, 40.0.

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[10] Vorländer and Eichwald, *Ber.*, **56B**, 1153 (1923).

α-Acetoxymercuri-β-ethoxy-β-phenylpropiophenone.—In a similar manner, benzalacetophenone reacted with mercuric acetate in absolute ethyl alcohol; 25 g. of ketone gave 54 g. of mercury compound. Recrystallized from ethyl alcohol, it melted at 134°.

Analyses. Calc. for $C_{19}H_{20}O_4Hg$: Hg, 39.1. Found: 39.3, 39.1.

α-Bromomercuri-β-methoxy-β-phenylpropiophenone.—To 25 g. of the acetate dissolved in alcohol was added drop by drop while the mixture was stirred exactly one molecular equivalent of potassium bromide dissolved in a little water. The bromide was precipitated as an oily product but solidified on standing. It was recrystallized from methyl alcohol; yield, 20 g.; m. p., 141°.

Analyses. Calc. for $C_{16}H_{15}O_2BrHg$: C, 36.94; Hg, 38.6. Found: C, 36.91, Hg, 39.3.

α-Bromomercuri-β-ethoxy-β-phenylpropiophenone.—In a similar manner, the bromomercuri-ethoxy derivative was prepared by treating the acetate with one molecular equivalent of potassium bromide. The product, recrystallized from ethyl alcohol, melted at 138°.

Analysis. Calc. for $C_{17}H_{17}O_2BrHg$: Hg, 37.6. Found: 37.7.

α-Bromo-β-methoxy-β-phenylpropiophenone.—To 50 g. of the acetoxymercuric methoxy derivative of benzalacetophenone dissolved in methyl alcohol one molecular equivalent of bromine was added slowly while the mixture was stirred, and the flask containing the mercury compound was cooled with ice water. After a half hour most of the alcohol was removed by distillation and the residue dissolved in ether. The ethereal solution was washed several times with strong aqueous potassium bromide to remove mercuric bromide, and then with water. After evaporation of the ether an oil remained, most of which solidified on standing. Recrystallized from methyl alcohol, it melted at 76°.

Analysis. Calc. for $C_{16}H_{15}O_2Br$: Br, 25.0. Found: 24.4.

α-Bromo-β-ethoxy-β-phenylpropiophenone.—The ethoxy compound was prepared in a similar manner by bromination of the ethoxy-mercury compound in alcohol or ether. Recrystallized from ethyl alcohol, it melted at 60–61°; 55 g. of mercury compound gave 18 g. of product.

Analyses. Calc. for $C_{17}H_{17}O_2Br$: C, 61.26; H, 5.10. Found: C, 61.49, 61.36; H, 5.18, 5.14.

The combustion of this compound was troublesome. When burned carefully in an ordinary combustion tube, a certain portion of material always came through undecomposed. It was necessary to use the cerium oxide-asbestos catalyst described by Reimer.[11]

The compound melting at 60–61° (small needles) was always obtained except in the last run made when flat crystals melting at 74° resulted. This was evidently the other racemate possible.

Analyses (compound melting at 74°). Calc. for $C_{17}H_{17}O_2Br$: Br, 24.0. Found: 23.9, 24.2.

α-Iodo-β-methoxy-β-phenylpropiophenone and the Ethoxy Compound.—Treatment of the mercury compounds with iodine instead of bromine gave the iodo-alkoxy addition products of benzalacetophenone.

The ethoxy compound melted at 75–76°.

Analysis. Calc. for $C_{17}H_{17}O_2I$: I, 33.4. Found: 33.4.

The methoxy compound melted at 96°.

Analysis. Calc. for $C_{16}H_{15}O_2I$: I, 34.7. Found: 34.6.

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[11] Reimer, THIS JOURNAL, **37**, 1636 (1915).

Action of Alkali on α-Bromo-β-methoxy-β-phenylpropiophenone and Addition of Mercuric Acetate to the Product.—A solution of 13.8 g. of the bromine compound in methyl alcohol was treated with one molecular equivalent of sodium methylate. The solution was heated until it became neutral. It was then poured into water and extracted with ether. The oil obtained from the ether layer was distilled at 6 mm. The fraction boiling at 200–205° was collected; yield, 8 g. The ethoxy compound was prepared in the same way, by the action of sodium ethylate on the α-bromo-β-ethoxy ketone.

The methoxy compound was dissolved in 90% methyl alcohol and treated with two molecular equivalents of mercuric acetate. As the solution stood, a white crystalline substance was gradually deposited. After 24 hours 80% of the calculated amount had crystallized. It was only very slightly soluble in alcohol; m. p., 237°. The analysis indicated that the product was the diacetoxymercuri derivative of dibenzoyl methane.

Analyses. Calc. for $C_{19}H_{16}O_6Hg_2$: C, 30.75; H, 2.14; Hg, 54.1. Found: C, 30.20; H, 2.21; Hg, 54.5, 54.6.

The ethoxy compound reacted with mercuric acetate in ethyl alcohol to give the same mercury compound, shown by analysis and by a mixed-melting-point determination.

A suspension of 10 g. of the compound melting at 237° in an excess of dil. hydrochloric acid was warmed until it had completely decomposed. The oil which remained was separated and crystallized from alcohol; yield, 90%. It melted at 80°, gave a red color with ferric chloride, and a copper derivative. A mixed-melting-point determination showed it to be dibenzoyl-methane.

Reaction of Ethylmagnesium Bromide with α-Bromomercuri-β-methoxy-β-phenylpropiophenone.—The mercury compound was only very slightly soluble in ether; 5 g. was ground to a fine powder and added slowly to three molecular equivalents of ethylmagnesium bromide. A vigorous reaction took place. When all of the solid had been added, the clear solution was poured into ice water. The ether solution contained an oil which later solidified. It was recrystallized several times from alcohol to free it from mercury diethyl; m. p., 63°. The substance proved to be β-phenyl-valerophenone.[7]

Analyses. Calc. for $C_{17}H_{18}O$: C, 85.7; H, 7.61. Found: C, 85.7; H, 7.54.

Reaction of α-Acetoxymercuri-β-alkoxy-β-phenylpropiophenone with Acids and with Potassium Iodide.—The mercury compounds were slowly decomposed by cold hydrochloric acid and rapidly by hot acid. The products were mercuric chloride and benzalacetophenone. When the mercury compounds were dissolved in alcohol and hydrogen sulfide was passed through the solution, there was an immediate precipitate of mercuric sulfide. The filtrate from the sulfide on concentration yielded benzalacetophenone. When boiled with an excess of aqueous potassium iodide, the mercury compounds were decomposed, the solution became alkaline and on cooling benzalacetophenone was recovered from the solution by extraction with ether.

Reaction of Dibenzalacetone with Mercuric Acetate.—To 5 g. of dibenzalacetone was added 13.6 g. of mercuric acetate in 100 cc. of absolute methyl alcohol. After 48 hours 15 g. of product had precipitated. Recrystallized from methyl alcohol, in which it is somewhat soluble, the compound melted at 183°. Analyses showed it to be the dimercurated compound, two methoxyl and two mercury groups having been added.

Analyses. Calc. for $C_{23}H_{26}O_7Hg_2$: C, 33.85; H, 3.21; Hg, 49.2. Found: C, 33.74; H, 3.10; Hg, 49.0, 49.2.

The acetoxymercuri-ethoxy derivative of dibenzalacetone was prepared by carrying out the reaction in ethyl instead of methyl alcohol. The acetate melted at 188–190°.

Analysis. Calc. for $C_{25}H_{30}O_7Hg_2$: Hg, 47.6. Found: 47.7.

α-Acetoxymercuri-β-methoxy-β-phenyl-*p*-chloropropiophenone.—A solution of 10 g. of benzal-*p*-chloro-acetophenone and 13 g. of mercuric acetate in 300 cc. of absolute methyl alcohol, prepared by heating the mixture for a short time on the steam-bath, was allowed to stand several days, concentrated to 50 cc. and again allowed to stand, when about 50% of the mercury compound was slowly precipitated. Recrystallized from methyl alcohol. it melted at 124°.

Analysis. Calc. for $C_{18}H_{17}O_4ClHg$: Hg, 37.6. Found: 37.6.

Sodium chloride solution was added to the filtrate from the acetate and the chloride precipitated. Recrystallized from methyl alcohol, it melted at 160°.

Analysis. Calc. for $C_{16}H_{14}O_2Cl_2Hg$: Hg, 39.3. Found: 39.0.

Summary

1. The reaction of several α,β-unsaturated ketones with alcoholic mercuric acetate has been studied. The products obtained were saturated ketones formed by the addition of the groups —HgX and —OR to the double linkage.

2. The reaction of unsaturated ketones with mercuric acetate has been compared with that of mercuric halides.

3. Reactions and derivatives of the mercury compounds have been described.

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NOTES

Absorption of Halogens by Mercurous Salts: Preliminary Note.—The present work grew out of an attempt to make a more effective mercurial preparation for external application by treating calomel with iodine. In spite of the large amount of work which has been done on various complex mercuric compounds,[1] the mixed mercuric salts, X—Hg—Y, have not been prepared by the action of halogens on mercurous compounds. During the present study, mercurous chloride, sulfate, and nitrate have been treated with alcoholic solutions of iodine and bromine in excess. Mercurous chloride yields mercuric iodochloride, HgICl, and mercuric bromochloride, HgBrCl. The sulfate yields di-iodomercuric sulfate, $(IHg)_2SO_4$, and a perbromide, $(BrHg)_2SO_4.Br_2$. The latter compound reacts with dry chlorine to give dichloromercuric sulfate, $(ClHg)_2SO_4$. The nitrate gives a per-iodide, $(IHgNO_3)_2.I_2$, and a perbromide, $(BrHgNO_3)_2.Br_2$. The former compound, when treated with chlorine, differs from the corresponding sulfate by giving a perchloride, $(ClHgNO_3)_2.Cl_2$.

It is too early to discuss definitely the constitution of this series of compounds of mercury. They exhibit a number of interesting peculiarities

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[1] Ditte, *Compt. rend.*, **87**, 794 (1879); **92**, 353 (1881). Varet, *ibid.*, **123**, 497 (1896). Harth, *Z. anorg. Chem.*, **14**, 323 (1897). Dobrosserdoff, *J. Russ. Phys. Chem. Soc.*, **33**, 303, 387 (1901). Sherrill, *Z. physik. Chem.*, **43**, 705 (1903). Borelli, *Gazz. chim. ital.*, **38**, I, 361 (1908); **38**, II, 421 (1908).