The Reaction of Oxymercurials with Active Methylene Compounds and the Demercuration of the Resulting Mercurials with Acid and Base

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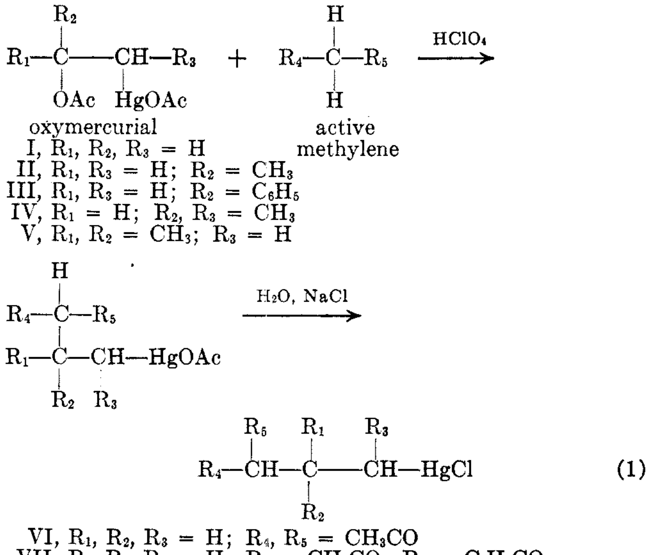
The reaction of oxymercurials with active methylene compounds has been studied in acetic acid, methanol, ethanol, and 2-propanol containing perchloric acid. Active methylene compounds, substituted with alkyls and aralkyls containing mercury, have been obtained in good yields. This reaction proceeds readily in between the oxymercurials from 1-olefins and the active methylene compounds whose keto–enol equilibria are on the side of the enol form. Oxymercurials from inner olefin and substituted olefin failed to react because of side reactions. 3,3-Diacylpropylmercuric chlorides, which were obtained by the reaction of β-diketones, reacted with aqueous potassium hydroxide to give 1,1-diacylcyclopropanes and mercury through an SNi mechanism. In methanol, ethanol, and 2-propanol containing perchloric acid, 3,3-diacetylpropylmercuric acetate gave 1,1-diacetylcyclopropane at lower reaction temperature. At higher temperature, mixtures of the cyclopropane and methyl or ethyl 3,3-diacetylpropyl ether were obtained. The demercuration of the same acetate in acetic acid containing perchloric acid gave pentan-1-ol-4-one acetate and 3-acetyl-2-methyl-4,5-dihydrofuran. For this acid demercuration, a mechanism involving a nonclassical carbonium ion intermediate, which is analogous to phenonium ion, can be described. This was disproved, however, by several experimental results. It is concluded that this reaction proceeds through a classical carbonium ion mechanism.

In a previous paper,[2] it has been shown that an acetoxymercuriethyl group can be introduced into the active methylene by the reaction of β-acetoxyethylmercuric acetate (I) (the oxymercuration product of ethylene with mercuric acetate in acetic acid) with ethyl acetoacetate in acetic acid containing perchloric acid or boron trifluoride. This paper describes the results of experiments to determine the applicability of this reaction to other active methylene compounds and oxymercurials. Some of the resulting mercurials showed interesting behavior toward acid and base. The chemical properties of these new types of mercurials are also reported.

The Reaction of Oxymercurials with Active Methylenes.—According to eq. 1, the reaction proceeds in acetic acid containing perchloric acid (1 *M*) at room temperature. The products have been isolated as chloromercuri derivatives. When reaction did not occur, the olefins were regenerated during the chlorinating procedure.



$$R_1-\underset{OAc}{\overset{R_2}{C}}-\underset{HgOAc}{CH}-R_3 + R_4-\underset{H}{\overset{H}{C}}-R_5 \xrightarrow{HClO_4} \begin{matrix} R_4-\overset{H}{C}-R_5 \\ | \\ R_1-\underset{R_2}{C}-\underset{R_3}{CH}-HgOAc \end{matrix} \xrightarrow{H_2O,\ NaCl} R_4-\overset{R_5}{CH}-\underset{R_2}{\overset{R_1}{C}}-\overset{R_3}{CH}-HgCl \quad (1)$$

I, $R_1, R_2, R_3 = H$
II, $R_1, R_3 = H$; $R_2 = CH_3$
III, $R_1, R_3 = H$; $R_2 = C_6H_5$
IV, $R_1 = H$; $R_2, R_3 = CH_3$
V, $R_1, R_2 = CH_3$; $R_3 = H$

VI, $R_1, R_2, R_3 = H$; $R_4, R_5 = CH_3CO$
VII, $R_1, R_2, R_3 = H$; $R_4 = CH_3CO$; $R_5 = C_6H_5CO$
VIII, $R_1, R_2, R_3 = H$; $R_4, R_5 = C_6H_5CO$
X, $R_1, R_3 = H$; $R_2 = CH_3$; $R_4, R_5 = CH_3CO$
XI, $R_1, R_3 = H$; $R_2 = C_6H_5$; $R_4, R_5 = CH_3CO$
XII, $R_1 = C_6H_5$; $R_2, R_3 = H$; $R_4 = CH_3CO$; $R_5 = C_6H_5CO$
XIII, $R_1 = C_6H_5$; $R_2, R_3 = H$; $R_4 = C_6H_5CO$; $R_5 = EtOCO$

The structures of the oxymercurials I–V, which are prepared from ethylene, propylene, styrene, 2-butene, and isobutylene, are well known and represented as shown.[3]

To determine the limitation on active methylene, the oxymercurial of ethylene (I) was used as the standard reactant, because this is the most stable to acid among the oxymercurials and reaction 1 proceeded without side reactions. The active methylene compounds, the enol forms of which are preferred to the keto forms, such as acetylacetone and benzoylacetone, gave the expected products, 3,3-diacetylpropylmercuric chloride (VI) and 3-acetyl-3-benzoylpropylmercuric chloride in 87 and 95% yields, respectively. Dibenzoylmethane gave a mixture of two kinds of mercurials which could be separated by the difference in solubilities in boiling ethanol. The soluble mercurial is estimated to be 3,3-dibenzoylpropylmercuric chloride from the results of mercury analysis, and the yield was 19%. The insoluble one (11% yield) could be recrystallized from benzene and was tentatively assigned to be the enol acetate of VIII (VIII′) on the basis of analytical data. However, further experiments are required to establish the structure. The yields mentioned above are those of the purified products after recrystallization. In the case of ethyl benzoylacetate, several attempts to obtain the crystalline product, 3-benzoyl-3-ethoxycarbonylpropylmercuric chloride, were unsuccessful. The oily product (before treating with sodium chloride), therefore, was decarboxylated by dissolving into 5% aqueous sodium hydroxide and subsequent acidification with hydrochloric acid. The crystalline product, thus obtained in 63% yield, was found to be 3-benzoylpropylmercuric chloride (IX).

With acetone and cyclohexanone, reaction 1 appears to proceed slowly, because the concentration of I decreased slowly and could not be detected after 2 weeks. The expected products, however, could not be obtained because of the subsequent side reactions

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[1] To whom inquiries and reprint requests should be sent.

[2] K. Ichikawa, H. Ouchi, and S. Fukushima, *J. Org. Chem.*, **24**, 1129 (1959).

[3] J. Chatt, *Chem. Rev.*, **48**, 7 (1951); G. F. Wright, *Ann. N. Y. Acad. Sci.*, **65**, 436 (1957); K. Ichikawa, *Kogyo Kagaku Zasshi*, **66**, 1037 (1963).

to form resinous products. These results show that reaction 1 proceeds only slowly with ketones whose keto–enol equilibria are on the side of the keto form.

Diethyl malonate, diethyl acetylmalonate, nitromethane, 2-nitropropane, dimethyl sulfoxide, and picoline have so-called active methylene groups, but, since they do not form enols in a sense of the first group of active methylene mentioned above, they did not react with I. Even after 1 month, the starting active methylenes were recovered and ethylene was regenerated upon adding sodium chloride.

The limitation on the structure of oxymercurials has been studied by using acetylacetone as the standard substrate, because the best results have been obtained with this active methylene. The result with the oxymercurial from ethylene (I) has been mentioned already. 2-Acetoxypropylmercuric acetate (II) from the next 1-olefin, *i.e.*, propylene, reacted to give 3,3-diacetyl-2-methylpropylmercuric chloride (X) in 75% yield. The oxymercurial of styrene, β-acetoxy-β-phenylethylmercuric acetate (III), gave 3,3-diacetyl-2-phenylpropylmercuric chloride (XI) in 75% yield. Further examples were obtained by the reaction of III with benzoylacetone and ethyl benzoylacetate. The products were 3-acetyl-3-benzoyl-2-phenylpropylmercuric chloride (XII) (98% yield) and 3-benzoyl-3-ethoxycarbonyl-2-phenylpropylmercuric chloride (XIII) (48% yield), respectively. Although experiments were not extended to other 1-olefins because of the lack of materials, it can be concluded that the oxymercurials of 1-olefins react with active methylenes generally as shown by eq. 1.

The mercury atom of the oxymercurial prepared from inner olefin is attached to a secondary carbon. In this case, the decomposition of the oxymercurial with acid to form mercurous salt and glycol is much faster than those of 1-olefin derivatives.[4] Thus, 2-acetoxybutylmercuric acetate (IV) and 2-acetoxycyclohexylmercuric acetate, which were prepared from 2-butene and cyclohexene, respectively, decomposed before reacting with acetylacetone. The expected product could not be obtained.

In the case of substituted olefin, *i.e.*, isobutylene, the oxymercuration accompanied the formation of a yellow precipitate. This is a kind of Dénige reaction that is a familiar qualitative test for substituted olefin. Under proper conditions, however, this side reaction can be suppressed to a minimum, and the preparation of the acetic acid solution of 2-acetoxy-2-methylpropylmercuric acetate (V) from isobutylene is not so difficult.[5] Addition of perchloric acid, which is the catalyst in this reaction, however, resulted in an instantaneous formation of the yellow precipitate. Thus, it is impossible to expect reaction 1 with the oxymercurials from substituted olefins.

From the results mentioned above, it is concluded that reaction 1 proceeds only between the oxymercurials of terminal olefins and active methylene compounds whose keto–enol equilibria are on the side of enol forms.

The possibilities of reaction 1 with β-alkoxyethylmercuric acetates in alcohols have been studied. In methanol, ethanol, and 2-propanol, the corresponding β-alkoxyethylmercuric acetates were prepared. To these solutions, perchloric acid (1.7 M) and then acetylacetone were added. After standing overnight at room temperature, the reaction mixtures were worked up in the same way as in the case of acetic acid solvent. The same product (VI) as with acetic acid solvent was obtained in all cases and the yields were almost the same.

Structure Proof for Mercurials VI–XIII.—The most convenient method of structure proof for the mercurials appears to be the replacement of mercury with hydrogen by sodium borohydride reduction in ethanol, because this reduction proceeded much faster than that of the β-diketo group. Unfortunately, the solubilities in this solvent are rather limited and the reduction rates were slow. In these cases, pyridine containing 10% water was used as the solvent. However, the reduction in this solvent was accompanied by side reactions involving the splitting of the β-diketo group and cyclopropane formation because of the basicity of pyridine. Alternative methods were required in several cases.

Borohydride reduction of VI in pyridine gave mercury (60%) and an organic mixture of 1,1-diacetylpropane and 1,1-diacetylcyclopropane (7:3) after 15-hr. reaction at 55–65°. The former was identified by gas chromatography using an authentic sample prepared from ethyl bromide and sodium acetylacetonate. The structure proof of the latter is described in a later section. The low yield of the organic products (16% on the basis of 60% demercuration) appears to be due to the loss of the material during the course of the isolation. As an additional proof, VI was decomposed with 3% aqueous sodium hydroxide to give the known 5-chloromercuripentan-2-one in 66% yield. All these results show that VI is 3,3-diacetylpropylmercuric chloride.

By the same method as in the case of VI, VII was reduced to a mixture (71% yield on the basis of 50% demercuration) of 1-acetyl-1-benzoylpropane and 1-acetyl-1-benzoylcyclopropane (4:1). The former product was identified by gas chromatography using an authentic sample. This shows that VII is 3-acetyl-3-benzoylpropylmercuric chloride. Further evidence was obtained by the following experiment. Reduction of VII with zinc dust and 10% sodium hydroxide gave a symmetrization product ($RHgCl \rightarrow RHgR + Hg$). Decomposition of this product with hydrochloric acid gave *n*-butyrophenone and 3-benzoylpropylmercuric chloride ($RHgR \rightarrow RHgCl + RH$). The former is the ketonic hydrolysis product of the expected 1-acetyl-1-benzoylpropane and the latter is that of the expected 3-acetyl-3-benzoylpropylmercuric chloride.

The reduction, ketonic hydrolysis, and other experiments with VIII were unsuccessful, because of the difficulties in the separation of the products. However, from the mercury content analysis and the analogy with the other cases, it is doubtless that VIII is 3,3-dibenzoylpropylmercuric chloride.

The structure of X was proved by the fact that the borohydride reduction of this compound in ethanol gave 1,1-diacetyl-2-methylpropane in 65% yield on the basis of 87% demercuration. Similarly, the reduction of XI gave expected 1,1-diacetyl-2-phenylpropane. By gas chromatography and infrared spectra,

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[4] K. Ichikawa, K. Fujita, and O. Itoh, *J. Am. Chem. Soc.*, **84**, 2632 (1962).

[5] K. Ichikawa, K. Fujita, and O. Itoh, *Bull. Inst. Chem. Res., Kyoto Univ.*, **42**, 221 (1964).

both reduction products were found to be identical with the authentic samples prepared by the reactions of sodium acetylacetonate with isopropyl and α-phenylethyl bromide, respectively.

Several attempts to prove the structures of XII and XIII by chemical methods, including reduction, were unsuccessful. However, the infrared spectra of XII and XIII were completely identical with those of 1-acetyl-1-benzoyl-2-phenylpropane and 1-benzoyl-1-ethoxycarbonyl-2-phenylpropane, respectively, except that the absorption maxima due to carbonyl groups in XII (1720 and 1670 cm.$^{-1}$) were shifted to slightly shorter wave lengths compared with those of the corresponding diacylpropane (1725 and 1675 cm.$^{-1}$).

Demercuration of 3,3-Diacylpropylmercuric Chlorides with Base.—Usual organomercurials are stable to base. So far in the literature, it appears that no reaction of the carbon–mercury bond with base under mild conditions has been reported. 3,3-Diacylpropylmercuric chlorides, which are the products of the reaction between β-diketones and oxymercurials as mentioned above, showed interesting behavior toward base.

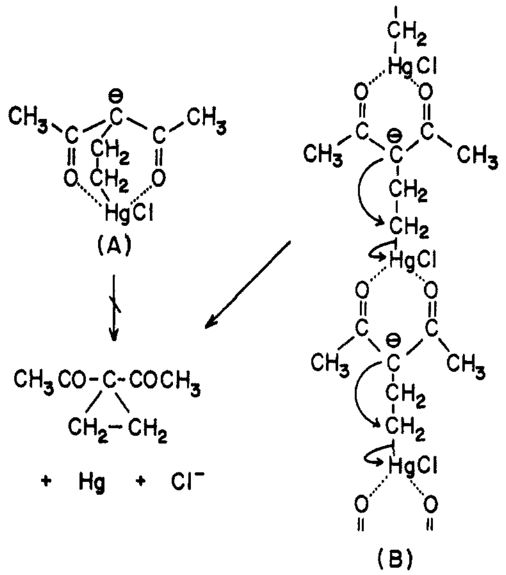
When VI was treated with aqueous potassium hydroxide (10%) at room temperature, instantaneous formation of metallic mercury was observed, and 1,1-diacylcyclopropane (XIV) was obtained as the only detectable organic product. Considering the reaction conditions and the structure of the product, this demercuration should be a kind of nucleophilic substitution on the carbon (bonded to mercury) by the carbanion formed from the active methylene with base. This unusual demercuration appears to be facilitated by the presence of the β-diketo group, because no other reason can be found for it. Since the β-diketo group has a strong chelating power for metal ions, the same kind of interaction could be expected between this group and the mercury bonded to carbon. Assuming that this is the case, both intermolecular and intramolecular interaction could be possible. The intramolecular one appears to be unlikely, because the attack of the carbanion to form cyclopropane appears to be difficult stereochemically. Therefore, the intermolecular one (B in Scheme I) is more likely. Scheme I shows the most probable mechanism of the demercuration with potassium hydroxide.

VII reacted very slowly with 10% potassium hydroxide even at steam bath temperature. However, when acetylacetone was added to the suspension of VII in alcoholic potash, the demercuration proceeded even at 50°. The extent of the demercuration was about 30% after 10-hr. reaction at 70°. The product was 1-acetyl-1-benzoylcyclopropane (XV), and no other product could be detected. It is not clear whether the effect of the acetylacetone added is due to the increase of the solubility of VII or its chelation with VII.

3,3-Diacetyl-2-methylpropylmercuric chloride (X) reacted similarly in the presence of added acetylacetone at 50–80° to give 1,1-diacetyl-2-methylcyclopropane (XVI).

Scheme I

Mechanism of the Demercuration of 3,3-Diacetylpropylmercuric Chloride with Aqueous Potassium Hydroxide



The structures of the cyclopropanes XIV–XVI have been assigned on the basis of analyses, chemical behavior, and spectral data. All these compounds gave negative results for bromine, permanganate, and ferric chloride tests and did not form copper salts, showing that no double bond including enol exists. Since bis-2,4-dinitrophenylhydrazones could be prepared, these compounds have two carbonyl groups. No other structures than cyclopropanes can satisfy the requirements of the chemical behavior mentioned above and the results of elementary analyses. Attempts to oxidize these compounds to the known diacid were unsuccessful, because the product was extremely soluble in water and extraction was impossible. The n.m.r. spectra of XIV at 60 Mc./sec. showed signals at τ 7.80 (six hydrogens of the two CH$_3$CO groups, intensity 6) and 8.53 (four hydrogens attached to cyclopropane ring, intensity 4). No other signal was observed and no coupling was recognized because of the symmetry of the structure. Similarly, the n.m.r. data of XV and XVI (given in the Experimental Section) can be explained reasonably in terms of the assigned structures. Infrared absorptions due to carbonyl groups are shifted to 1670–1700 cm.$^{-1}$ with shoulders because of the conjugation of this group with the cyclopropane ring. Ultraviolet spectra support these structures also. Detailed discussion of the spectral data will be reported in a separate paper.

During the course of the analysis of XVI by gas chromatography, a puzzling phenomena was observed. When a column packed with silicone SE-30 (5% on Celite) was used, a sharp single peak was observed at any analysis temperature up to 230°. With another column packed with polyethylene glycol 20M (5% on Celite) and at 90–230°, however, two peaks appeared and their relative ratio changed with the analysis temperature. The first one increased and the second decreased with the increase of temperature. This indicates that isomerization occurred during the course of the analysis. This was confirmed by the following experiment. When XVI was treated with the packing material at 200° by flow method, 4,4-diacyl-1-butene (XVII) was obtained, and its retention time was the same as that of the first peak mentioned above. Similar results with substituted cyclopropanes have been reported recently.[6]

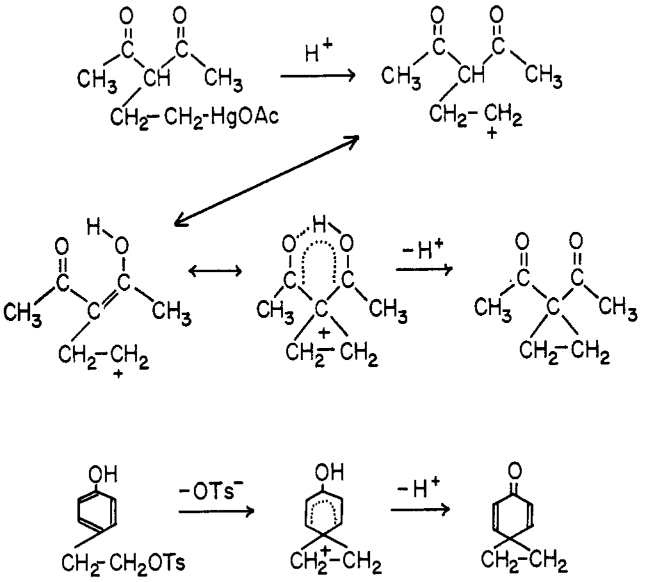
Demercuration of 3,3-Diacetylpropylmercuric Acetate with Acid.—When the reaction mixtures from the preparation of VI in methanol and 2-propanol containing 1.7 *M* perchloric acid (see earlier part of this paper) were allowed to stand at 15–20° for 3 days, formation of metallic mercury was observed. The extents of the demercuration were 46% in methanol and 30% in 2-propanol. The major product (more than 95%) was the cyclopropane XIV. At a higher temperature (30°) and in methanol, a mixture of XIV and 3,3-diacetylpropyl methyl ether (XVIII) (1:2) was obtained after 2 days reaction, and the extent of the demercuration was 60%. In ethanol solution, the demercuration was much slower than in the cases above, and no formation of mercury was observed at 20° even after 3 days reaction. At 30° and after 3 days, however, the extent of the demercuration reached about 80%. The product was a mixture of XIV and 3,3-diacetylpropyl ethyl ether (XIX) (1:3.3). The demercuration in water also gave XIV at 25° after 4 days reaction, although the yield was only about 10%.

In acetic acid solution the demercuration proceeded with much lower perchloric acid concentration because of the stronger acidity of the acetic acid–perchloric acid system. With 1.0 *M* perchloric acid, pentan-1-ol-4-one acetate (XX), which is thought to be formed by the splitting of an acetyl group from the expected 3,3-diacetylpropyl acetate, was obtained as the main product (more than 95%) in 65% yield on the basis of 73% demercuration. With higher perchloric acid concentration (1.7 *M*), a mixture of XX and 3-acetyl-2-methyl-4,5-dihydrofuran (XXI) (45:40) was obtained in 54% yield after 24-hr. reaction at 20–25°.

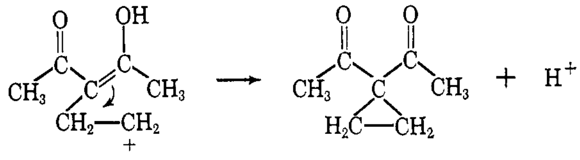
The structures, of XVIII and XIX were assigned on the basis of analytical data, ultraviolet and infrared spectra, and several chemical tests described in the Experimental Section. The structural proof of XXI will be reported in a separate paper, since the same compound was obtained as a main product in the reaction of the ethylene–thallium triacetate adduct with acetylacetone in acetic acid containing perchloric acid.

SCHEME II

MECHANISM OF CYCLOPROPANE FORMATION FROM 3,3-DIACETYLPROPYLMERCURIC ACETATE BY A NONCLASSICAL CARBONIUM ION MECHANISM



By Jensen and co-workers[7] and ourselves,[8] it has been established that the demercuration of RHgOAc in acidic media is a kind of solvolysis: $RHgOAc + H^+ \rightarrow RHg^+ + HOAc$, $RHg^+ \rightarrow R^+ + Hg$, $R^+ \rightarrow$ products. The formation of XVIII, XIX, and XX from VI can be explained by this mechanism. In order to explain the formation of XIV from the same VI, an additional mechanistic consideration is required. One of the possibilities is the assumption of the formation of a nonclassical carbonium ion as in the case of cyclopropane formation from β-(*p*-hydroxyphenyl)-ethyl tosylate which was proposed by Winstein and co-workers[9] and illustrated in Scheme II for reference. If this is the case, the nonclassical carbonium ion XXII in Scheme II (including its other resonance formulae) should be a common reaction intermediate leading to the formation of XIX, XX, and XIV. The protonation to the carbonyl group of XIV should also result in the formation of this intermediate, and this process is considered to be very fast. Therefore, the transformation of XIV to XX or XIX should be very fast in acidic media. This was disproved by the following experiment. A solution of XIV (3 g.) in methanol (75 ml.) containing 1.7 *M* perchloric acid was kept at 30° for 24 hr. Analysis of the product by gas chromatography showed that only 33% of XIV was solvolyzed to give XVIII and 4-oxopentyl methyl ether (23:10). The latter is thought to be formed by the splitting of the acetyl group from the former. It is concluded that the nonclassical carbonium ion mechanism in this case cannot be applied. Intramolecular alkylation of the classical carbonium ion (shown below) is the most probable mechanism.



The reason why the products are different at lower and higher temperature is not clear. XVIII and XIX could be the solvolysis products from XIV which is formed as the primary product. However, the possibility of direct formation by the reaction of the carbonium ion with the solvents cannot be excluded; also, the mechanism of the formation of XXI should be studied by further experiments. These are under investigation and will be reported shortly.

Experimental Section

Reaction of Oxymercurials with Active Methylenes.—The following example shows the typical experimental procedure for the preparation of VI–XIII. Into a mixture of mercuric acetate (64 g., 0.2 mole) and acetic acid (60 g.), ethylene was introduced with stirring until the mixture became clear and no

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(6) D. E. McGreer, N. W. K. Chiu, and R. S. McDaniel, *Proc. Chem. Soc.*, 415 (1964).

(7) F. R. Jensen and R. T. Quellette, *J. Am. Chem. Soc.*, **83**, 4477, 4478 (1961).

(8) K. Ichikawa and H. Ouchi, *ibid.*, **82**, 3876 (1960).

(9) S. Winstein and R. Baird, *ibid.*, **79**, 756 (1957); R. Baird and S. Winstein, *ibid.*, **79**, 4238 (1957); **85**, 567 (1963); R. Heck and S. Winstein, *ibid.*, **79**, 3105 (1957); R. Baird and S. Winstein, *ibid.*, **84**, 798 (1962).

formation of a yellow precipitate of mercuric oxide was observed upon adding the sample to 10% sodium hydroxide solution. Into this solution, acetylacetone (40 g., 0.4 mole) and then perchloric acid (15 g., 70%) were added at room temperature. After standing overnight, 10% aqueous sodium chloride solution was added. The resulting white crystals were separated and recrystallized from ethanol to give pure VI, m.p. 132–133°, 63.5 g., 87% yield. The mercury content was analyzed by the zinc powder–sodium hydroxide method.[10] The other mercurials were synthesized and analyzed similarly. The results of mercury analyses are shown in Table I.

TABLE I

Compd.	M.p., °C.	Formula	Hg, % Calcd.	Hg, % Found
VI	132–133	$C_7H_{11}ClHgO_2$	55.26	55.44
VII	103.5–104	$C_{12}H_{13}ClHgO_2$	47.21	46.72
VIII	133.5–134.5	$C_{17}H_{15}ClHgO_2$	41.16	41.26
IX	143–143.5	$C_{10}H_{11}ClHgO_2$	52.33	51.97
X	101–101.4	$C_8H_{13}ClHgO_2$	53.4	52.4
XI	94.8–95.9	$C_{13}H_{15}ClHgO_2$	45.66	45.36
XII	155.7–156.7	$C_{18}H_{17}ClHgO_2$	40.01	39.12
XIII	115–125	$C_{19}H_{19}ClHgO_3$	37.75	36.81
VIII′	144–145	$C_{19}H_{17}ClHgO_3$	37.89	37.64

Conversion of VI to 5-Chloromercuripentan-2-one.—Into 200 ml. of 3% aqueous sodium hydroxide, 43 g. of VI was added gradually. After these had reacted for 2 hr. at 20°, metallic mercury (7 g.) was filtered off. The filtrate was combined with 2 g. of sodium hydroxide and kept on a steam bath for 30 min. After cooling to room temperature, a small amount of mercury was removed. Upon acidifying the filtrate with hydrochloric acid, 26 g. of white crystals was obtained. Recrystallization from water gave 5-chloromercuripentan-2-one, m.p. 74.5–75.5° (lit.[2] m.p. 74.5–75°). The yield was 66%.

Borohydride Reduction of VI.—Into 50 ml. of pyridine containing 10% water, 36.3 g. (0.1 mole) of VI was dissolved. Another 50 ml. of the same solvent containing 0.975 g. (0.026 mole) of sodium borohydride was added to the above solution at 55–65°. The reaction mixture was kept at this temperature for 15 hr. After removing 12 g. of mercury which had formed, pyridine was distilled off under reduced pressure, until the volume of the mixture became about 30 ml. The residue was acidified with 0.1 *N* hydrochloric acid, and the white precipitates which had formed were filtered off. The filtrate was extracted with ether and dried over potassium carbonate. Distillation gave 1.2 g. of liquid product, b.p. 72–76° (22.5 mm.). Analysis by gas chromatography showed that this was a mixture of XIV and 1,1-diacetylpropane in a ratio of 3:7. The authentic sample of the latter was prepared by a usual method from ethyl bromide and sodium acetylacetonate.

Borohydride Reduction of VII.—VII (4.29 g.) was reduced with 0.11 g. of sodium borohydride as described for reduction of VI. After 9-hr. reaction, 0.96 g. of mercury was formed. After removing most of the pyridine, ether was added to precipitate 1 g. of crystals of unreacted VII. The ether extract was dried and distilled to give 0.65 g. of liquid product, b.p. 138–143° (13 mm.). By gas chromatography, this was identified as a mixture of XV and 1-acetyl-1-benzoylpropane in a ratio of 1:4. An authentic sample of the latter was prepared by the reaction of ethyl bromide with sodium benzoylacetonate.

Symmetrization of VII and Decomposition of the Product with Hydrochloric Acid.—Into 130 ml. of 5% aqueous sodium hydroxide, 32 g. of VII was added. This mixture was heated to 60° and treated with 15 g. of zinc powder in five portions in 1 hr. with stirring. The reaction was continued for an additional 1 hr. at 70–75°. The solution was separated from the amalgam formed and acidified with hydrochloric acid. There were obtained 4 ml. of oily product and 1 g. of benzoic acid. The oil was combined with the ether extract of the water layer and dried over sodium sulfate. After removing ether, the symmetrization product thus obtained was treated with 3 ml. of concentrated hydrochloric acid at 60–70° for 10 min. The reaction mixture was cooled to room temperature and then treated with 50 ml. of water. The white crystals formed were filtered, recrystallized from ethanol and identified as 3-benzoylpropylmercuric chloride, m.p. 143–143.5° (lit.[2] m.p. 143–143.5°), the yield being 5 g. The filtrate separated from the crystals was extracted with ether. Distillation gave 3 g. of *n*-butyrophenone, b.p. 105–110° (9 mm.), semicarbazone m.p. 180.5–184° (m.m.p. 181.5–182.5° with an authentic sample).

Borohydride Reduction of X.—Into 300 ml. of ethanol containing 4 g. of sodium hydroxide and 8 ml. of water, 3.8 g. of sodium borohydride was dissolved. This solution was added to a suspension of 75.5 g. of X in 300 ml. of ethanol at steam-bath temperature with stirring in 1 hr. After continuing the reaction for additional 3.5 hr., 34.7 g. of mercury formed was removed. Ethanol was distilled off, and the inorganic precipitates formed were filtered off. Distillation gave 18.5 g. of liquid product, b.p. 77.7–82° (19 mm.), which gave a correct analysis for 1,1-diacetyl-2-methylpropane and was found to be identical with an authentic sample (prepared from isopropyl bromide and sodium acetylacetonate) by gas chromatography and infrared spectra.

Anal. Calcd. for $C_8H_{12}O_2$: C, 67.57; H, 9.93. Found: C, 67.46; H, 9.88.

The bis-2,4-dinitrophenylhydrazone melted at 278.5–279°.

Anal. Calcd. for $C_{20}H_{20}N_8O_8$: C, 47.81; H, 4.41; N, 22.30. Found: C, 48.24; H, 4.46; N, 22.30.

Borohydride Reduction of XI.—By the same method as used for X above, 43.9 g. of XI was reduced with 0.50 g. of sodium borohydride to give 15 g. of mercury. Steam distillation of the reaction mixture gave 3.3 g. of organic crystals, m.p. 42–47°, and 0.9 g. of liquid product. By gas chromatography and infrared spectra, it was confirmed that the crystalline product was identical with an authentic sample of 1,1-diacetyl-2-phenylpropane, which was prepared from α-phenylethyl bromide and sodium acetylacetonate in acetone, b.p. 111–114° (2 mm.), m.p. 48.2–48.8°, the yield being 28%.

Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.93; H, 7.93.

The bis-2,4-dinitrophenylhydrazone melted at 267–269.2°.

The oily product was estimated to be 4-phenylpentan-2-one by gas chromatography. The residue of the steam distillation was treated with concentrated hydrochloric acid and steam distilled again to give 5.4 g. of oily product. This was analyzed to be a mixture of 1,1-diacetyl-2-phenylpropane and an unidentified product in a ratio of 45:65 by gas chromatography. The latter appears to be formed during the course of treatment with hydrochloric acid, because it was not detected in the product of the first steam distillation, and is thought to be a rearranged product.

The infrared spectra of XII (Nujol) had absorption maxima at 1720 (s), 1670 (s), 1592 (w), 1578 (w), 1495 (w), 1410 (w), 1370 (m), 1338 (w), 1295 (m), 1270 (sh), 1260 (m), 1218 (s), 1200 (s), 1178 (w), 1165 (w), 1150 (w), 1120 (w), 1030 (w, sh), 1025 (m), 1010 (w), 995 (w), 975 (m), 770 (w), 750 (m), and 690 (m) cm.$^{-1}$.

The infrared spectra of XIII (Nujol) had absorption maxima at 1680 (m), 1658 (s), 1588 (m), 1575 (m), 1550 (w), 1500 (w), 1490 (w), 1410 (w), 1350 (s), 1332 (m), 1300 (m), 1280 (w), 1238 (w), 1210 (m), 1188 (w), 1168 (w), 1155 (w), 1138 (m), 1120 (w), 1065 (w), 1040 (w), 1020 (w), 1065 (w), 1040 (w), 1020 (w), 975 (w), 770 (s), and 700 (s) cm.$^{-1}$.

Formation of XIV by Demercuration of VI with Aqueous Potassium Hydroxide.—Into 70 ml. of aqueous potassium hydroxide (0.14 mole), 50.9 g. (0.14 mole) of VI was added at room temperature. An exothermic reaction occurred and metallic mercury was formed. After standing for 2 hr., 21 g. of mercury was separated by decantation. The reaction mixture was extracted with ether, dried over sodium sulfate, and distilled to give 6.3 g. of XIV, b.p. 74–74.5° (8 mm.), n^{30}_{D} 1.4522, d^{30}_{4} 1.0253, mol. wt. 127.

Anal. Calcd. for $C_7H_{10}O_2$: C, 66.64; H, 7.99. Found: C, 67.05; H, 7.97.

Infrared absorption maxima were at 3060 (w), 2980 (w), 2970 (sh), 1710 (m), 1690 (s), 1430 (m), 1370 (s), 1330 (m), 1290 (m), 1230 (w), 1110 (m), 1070 (m), 1026 (w), 1005 (w), 970 (w), and 930 (m) cm.$^{-1}$. Ultraviolet absorptions, ϵ_{max}, were 153 at 215 mμ, 49 at 285 mμ in hexane; 1610 at 206 mμ, 220 at 275–276 mμ in ethanol. These were determined with JASCO Model IR-S and HITACHI ESP-2U spectrometers, respectively. The n.m.r. spectra were determined in deuteriochloroform with tetramethylsilane as internal standard using a

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[10] K. Ichikawa, S. Fukushima, H. Ouchi, and M. Tsuchida, *J. Am. Chem. Soc.*, **80**, 6005 (1958).

Varian 60. By the usual method, the bis-2,4-dinitrophenylhydrazone was obtained, m.p. 258–260° (from chlorobenzene).

Anal. Calcd. for $C_{19}H_{18}N_8O_8$: C, 46.92; H, 3.73; N, 23.04. Found: C, 46.77; H, 3.57; N, 23.03.

Formation of XV by Demercuration of VII with Potassium Hydroxide in the Presence of Acetylacetone.—Into a solution containing 2.5 g. of potassium hydroxide, 10 ml. of water, 15 g. of ethanol, and 25 g. of acetylacetone, 21.3 g. of XII was added and allowed to react at room temperature (10–20°) overnight. No formation of mercury was observed. When this mixture was heated to 40–60°, VII dissolved in the solution and the formation of mercury was observed. After 4 hr., 1 g. of potassium hydroxide in 3 ml. of water was added and the reaction was continued for an additional 2 hr. After removing the 5.2 g. of mercury formed, the reaction mixture was steam distilled, extracted with ether, dried over magnesium sulfate, and distilled. There was obtained 1.8 g. of XV, b.p. 112–113.5° (4 mm.), $n^{30}D$ 1.5485. Analysis by gas chromatography showed that this purity was more than 98%.

Anal. Calcd. for $C_{12}H_{12}O_2$: C, 76.57; H, 6.95. Found: C, 76.35; H, 6.76.

Infrared absorption maxima were at 3060 (m), 3045 (w), 3010 (m), 2995 (w), 2975 (w), 2928 (w), 1690 (sh), 1670 (s), 1595 (m), 1580 (m), 1450 (m), 1417 (m), 1362 (m), 1325 (s), 1305 (s), 1285 (sh), 1205 (m), 1172 (m), 1155 (w), 1132 (m), 1120 (w), 1070 (w), 1033 (m), 1023 (w), 1000 (m), 975 (m), 948 (s), 790 (s), and 715 (s) cm.$^{-1}$. Ultraviolet absorptions, log ϵ_{max}, were 3.67 at 214 mμ, 4.09 at 244 mμ, 2.49 at 310 mμ in hexane; 4.32 at 203.5 mμ, 4.03 at 246 mμ, 2.46 at 287 mμ in ethanol. N.m.r. spectra showed signals at τ 1.82–2.57 (multiplet), 7.95 (singlet), and 8.47 (sextet) with relative intensity 5:3:4.

Formation of XVI by Demercuration of X with Potassium Hydroxide in the Presence of Acetylacetone.—Into a solution containing 20 ml. of ethanol and 36 g. of acetylacetone, 45 g. of X was added and kept at 55–65° for 0.5 hr. To this mixture, 34 g. of potassium hydroxide in 130 ml. of water was added and the reaction was continued for 4.5 hr. The mercury formed, 19.9 g., was removed. The reaction mixture was acidified with hydrochloric acid, extracted with petroleum ether (b.p. 75–90°), dried over sodium carbonate, and distilled. X was obtained in 7 g. yield, b.p. 98–98.5° (23 mm.), $n^{25}D$ 1.4577, $d^{25}{}_4$ 1.0065.

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.54: H, 8.63. Found: C, 68.78; H, 8.74.

Infrared absorption maxima were at 3030 (m, sh), 3000 (s), 2970 (s), 2920 (m), 1710 (s), 1700 (s), 1642 (sh), 1625 (w), 1600 (w), 1470 (sh), 1450 (m), 1430 (m), 1398 (m), 1368 (s), 1315 (sh), 1305 (m), 1270 (m), 1260 (m), 1250 (w), 1220 (w), 1210 (w), 1200 (w), 1170 (w), 1110 (w), 1090 (w), 1020 (m), 965 (w), 895 (w), and 870 (w) cm.$^{-1}$. Ultraviolet absorptions, log ϵ_{max}, were 3.67 at 195 mμ, 2.80 at 268 mμ in hexane; 3.55 at 203 mμ, 2.08 ± 0.05 at 279 ± 1 mμ in ethanol. The n.m.r. spectra at 60 Mc./sec. showed signals at τ 7.68 (singlet), 7.90 (singlet), 8.40–8.65 (sextet), and 8.90–9.00 (doublet) with relative intensity 3:3:3:3. The bis-2,4-dinitrophenylhydrazone was prepared by the usual method and recrystallized from an ethanol–chlorobenzene mixture: m.p. 218–221°.

Anal. Calcd. for $C_{20}H_{20}O_8N_8$: C, 48.02; H, 4.02; N, 22.39. Found: C, 48.02; H, 4.26; N, 22.18.

Isomerization of XVI to XVII.—Through polyethylene glycol 20M (5% on Celite), packed in a glass tubing (8 × 400 mm.) and kept at 200° in an electric furnace, 2 g. of XVI was passed in 30 min. After 2 hr., the adsorbed material was purged out by nitrogen stream. In the Dry Ice–acetone trap 1.7 g. of liquid was obtained. Gas chromatographic analysis and infrared spectra showed that this was identical with the authentic sample of 4,4-diacetylbutene-1 prepared by the method reported by English.[11] From 25 g. of allyl bromide, 16.5 g. of acetylacetone, and 3.8 g. of sodium in 100 ml. of anhydrous ethanol, 11 g. of XVII was obtained, b.p. 190–225°. Infrared absorption maxima were at 3070 (w), 2980 (w), 2930 (w), 1725 (s), 1705 (s), 1635 (s), 1620–1585 (broad, s), 1425 (s), 1360 (s), 1280 (w), 1255 (w), 1220 (w), 1180 (w), 1160 (w), 1125 (w), 1020 (w), 1000 (m), 950 (m), 925 (m), 760 (w), 625 (w), and 570 (w) cm.$^{-1}$.

Acid Demercuration of VI.—The experimental procedure is the same as for the preparation of VI–XIII. The reaction mixture was separated from the mercury formed, combined with 10% aqueous sodium chloride to precipitate the unreacted mercurial, and neutralized with potassium hydroxide. This mixture was extracted with ether and then with benzene and distilled after drying over magnesium sulfate. The products were analyzed by gas chromatography and infrared spectra. An authentic sample of 3,3-diacetylpropyl ethyl ether was prepared by the following procedure. Into 60 g. of dioxane, 32 g. of β-ethoxyethyl iodide (0.16 mole) was added and heated to 70°. Into this solution, 18.3 g. of sodium acetylacetonate (0.15 mole) was added in several portions during the course of 1 hr., and the reaction mixture was heated on a steam bath for 12 hr. From the reaction mixture, sodium iodide was removed and then dioxane was removed under reduced pressure. The residue was extracted with benzene, washed with water twice, dried, and distilled to give 13 g. of the ether, b.p. 53–123° (13 mm.). Redistillation gave the ether in a purity of more than 95%, b.p. 101–105° (11 mm.), $n^{30}D$ 1.4442. Addition of the sample into copper acetate gave the copper salt, m.p. 180–182° dec. (lit.[12] m.p. 183°). Infrared absorption maxima of the ether were at 2960 (m), 2910 (m), 1740 (s), 1715 (s), 1630–1620 (broad, w), 1430 (m), 1360 (s), 1280 (w), 1250 (w), 1160 (m), 1132 (sh), and 1115 (s) cm.$^{-1}$.

3,3-Diacetylpropyl methyl ether was prepared similarly, b.p. 117–122° (29 mm.). Infrared absorption maxima were at 2960 (m), 2910 (m), 1740 (s), 1715 (s), 1630–1620 (broad, w), 1430 (m), 1360 (s), 1320 (w), 1280 (w), 1250 (w), 1190 (sh), 1160 (m), and 1120 (s) cm.$^{-1}$.

Pentan-1-ol-4-one Acetate.—The reaction of β-iodoethyl alcohol with sodium acetylacetonate gave pentan-1-ol-4-one acetate instead of the expected 3,3-diacetylpropyl alcohol. Into 150 g. of dioxane, 80 g. (0.5 mole) of β-iodoethyl alcohol was dissolved. This solution was heated to 50° and combined with 52 g. (0.42 mole) of sodium acetylacetonate. After 3-hr. reaction at 100°, the reaction mixture was filtered to remove sodium iodide formed and distilled. The main product was 40 g. of pentan-1-ol-4-one acetate, b.p. 79–83° (3 mm.), $n^{20}D$ 1.4270. The semicarbazone melted at 125–127° (lit.[13] 125–126°). The 2,4-dinitrophenylhydrazone melted at 87.8–88.5° and gave a correct analysis.

Anal. Calcd. for $C_{13}H_{16}N_4O_6$: C, 48.15; H, 4.97; N, 17.28. Found: C, 48.19; H, 4.99; N, 17.29.

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