[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, UNIVERSITY OF TORONTO AND UNIVERSITY OF SASKATCHEWAN]

OXYMERCURATION OF 2,6-DIMETHYLHEPTEN-5-OL-2

A. G. BROOK, A. RODGMAN, AND GEORGE F WRIGHT

Received March 10, 1952

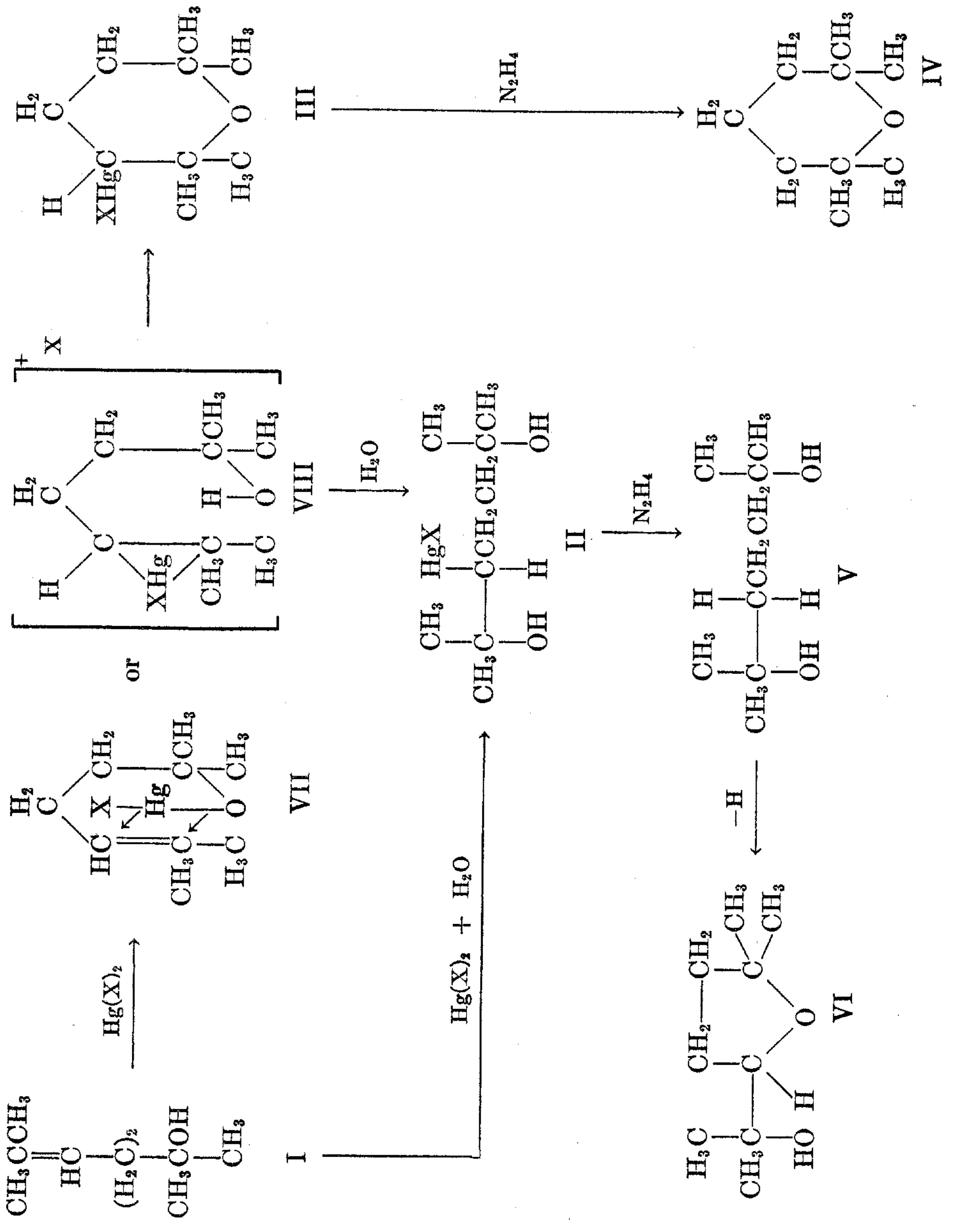
Positional isomers are usually not obtained when an alkene is oxymercurated, although several exceptions have been noted (1, 2, 3). However these exceptions do not occur unexpectedly. On the other hand Sand and Singer (4, 5) reported two pairs of isomers which were formed by oxymercuration of 2,6-dimethylhepten-5-ol-2. They implied by analogy with the oxymercuration products from α-terpineol that these were diastereomers, but this is obviously impossible since only one asymmetric carbon atom would be present in the products from dimethylheptenol.

The oxymercuration of 2,6-dimethylhepten-5-ol-2 was carried out by Sand and Singer with mercuric acetate in water, and potassium iodide was added subsequently. The pair of isomers with the composition $C_9H_{19}O_2HgI$ (II, X = iodide) was alkali-soluble and was represented as 2,6-dimethyl-3-iodomercuriheptanediol-2,6. The other pair, containing one molecule less of the elements of water, was designated by the structure 2,2,6,6-tetramethyl-3-iodomercuritetrahydropyrans. These structure designations were assumed solely by analogy with the three oxymercurials which Sand and Singer obtained from α-terpineol.

Each of the pairs from dimethylheptenol comprised an oil and a crystalline solid. Furthermore the oil could be easily, or was spontaneously converted to the solid. In general, oxyalkanemercurials are reasonably stable except in acidic media (3, 6); furthermore an alkene of specific configuration has always been found to yield a single product of oxymercuration. In these circumstances it seemed worthwhile to reinvestigate the chemistry outlined by Sand and Singer. Such reexamination would also evaluate the possibility that positional isomerism might exist in this instance if easy elimination and re-addition could occur.

The hydroxymercuration of dimethylheptenol was repeated according to the directions of Sand and Singer. There was little evidence of oily iodomercuri compounds of type II or III (X = iodide). The precipitation of III from the reaction mixture failed to produce a "water-clear oil." Instead a curdy white precipitate was formed such as Sand and Singer obtained in their later experiments. This slightly sticky product, when purified as they describe by evaporation of its ether solution, did yield in addition to the crystals a small amount of oily material. However this eventually crystallized also, especially if some of the solid were ground into it. Similarly the isolation of the linear iodomercurial (II) by treatment of the alkaline reaction mixture with carbon dioxide yielded only a solid, and gave no evidence of an oily isomer.

The absence of isomers was again demonstrated when sodium chloride rather than iodide was added to the reaction system. The linear chloromercurial (II, X = Cl) was a highly crystalline substance. The cyclic chloromercurial (III, X = Cl) precipitated as a viscous gum which slowly crystallized completely


I
$Hg(X)_2$
VII
or
VIII
III
N_2H_4
IV
$Hg(X)_2 + H_2O$
H_2O
II
N_2H_4
V
$-H$
VI

when left in contact with aqueous sodium chloride. In short there was no evidence for the existence of positional isomers. It would seem that the "oily isomers" reported by Sand and Singer were merely supercooled liquids, possibly stabilized by traces of unchanged dimethylheptenol.

It was of interest to ascertain whether the cyclic compound was formed from the linear compound or independently of it. Several attempts to convert the linear compounds (II, X = iodide or chloride) to the cyclic analog (III) by the use of acetic anhydride either did not produce a change, or else caused reversion to the alkene. Indeed, evidence that the tetramethylhalomercuritetrahydropyran (III) was not necessarily formed from the dimethylhalomercuriheptanediol (II) was afforded by oxymercuration in absence of water.

Although mercuric acetate is not soluble, as such, in dimethylheptenol an equivalent of the salt disappeared into four equivalents of the alcohol (I) within an hour at 25–30°. A 91% yield of 2,2,6,6-tetramethyl-3-chloromercuritetrahydropyran could be isolated by treatment of the molecular distillation residue with aqueous sodium chloride and carbon dioxide. This 91% yield of III (X = Cl) should be compared with approximately equal 20% yields of II and III (X = Cl) which were obtained when dimethylheptenol was treated with mercuric acetate in water.

It is difficult to reconcile this behavior with the ionic mechanism involving an "alkenemercurinium salt" (VIII) postulated by some workers (7). Firstly, it would not be expected that a tertiary alcohol or its alkoxide ion (which, according to the postulation, would be required for the reaction with dimethylheptenolmercurinium ion) would possess activity comparable with that of water or an hydroxyl ion. Secondly one might expect that ionic species would be more prevalent in aqueous media than in dimethylheptenol, but yields are higher in the latter medium than in water. Finally it might be predicted on the basis of an ionic mechanism involving a salt like mercuric acetate (from a weak base and weak acid) that addition of acetic acid would initially increase the rate of the ionic reaction by reducing solvolysis. In actual fact the addition of acetic acid reduces the rate. Since it has been shown (8) that nominal amounts of acetic acid do not decompose the final product it is evident that the retarding effect of this acid must involve the intermediate stages of the reaction.

The kinetics of oxymercuration have been reported previously (1, 9) as second order over-all in an excess of the hydroxylated species. This designation of order did not take into account the formation of acetic acid during the course of the reaction, but it has now been considered in a kinetic examination of the oxymercuration of dimethylheptenol. A further change in the previous method of kinetic study was required because the hydroxyl and alkene functional groups are both present in dimethylheptenol. Therefore the concentration of alkene function relative to mercuric salt cannot be varied in a solvent containing the hydroxyl function because this latter function is integral with the dimethylheptenol.

Consequently we sought an inert solvent as the reaction medium for kinetic studies of this oxymercuration, and 1,2-dimethoxyethane was found to be suitable. After treatment with sodium chloride a 60% yield of 2,2,6,6-tetramethyl-3-chloromercuritetrahydrofuran was obtained from a suspension of mercuric acetate in a solution of dimethylheptenol in this solvent. The solubility of mercuric acetate in 1,2-dimethoxyethane is about 0.01 mole/liter; this is sufficient for kinetic studies at concentrations approximately 10^{-3} molar. Mercury at this concentration may be determined by the dithizone method (1) rapidly and conveniently if the analysis is carried out colorimetrically (10, 11).

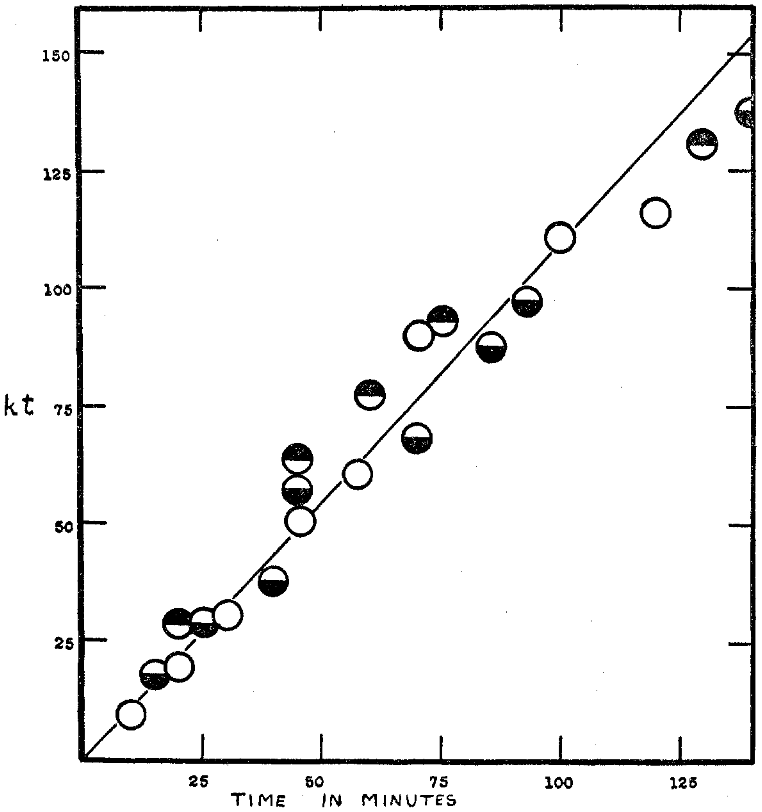


FIG. 1. THE REACTION BETWEEN MERCURIC ACETATE AND DIMETHYLHEPTENOL IN 1,2-DIMETHOXYETHANE AT 25.0° ± 0.1°

Legend:	Symbol	Mercuric Acetate (moles/liter)	Dimethylheptenol (moles/liter)
	○	4.0×10^{-3}	4.8×10^{-3}
	◓	2.0×10^{-3}	2.0×10^{-3}
	◒	4.0×10^{-3}	4.0×10^{-3}

A series of kinetic measurements were carried out over concentration ranges of 2.0–4.8 × 10^{-3} moles per liter for the dimethylheptenol (I) and 2.0–4.0 × 10^{-3} moles per liter for the mercuric acetate. The results shown in Fig. 1 indicate agreement with second order kinetics according to the relationship

1. $$kt = \left[\frac{2.303}{(a - b)} \log \frac{b}{a} \frac{(a - x)}{(b - x)}\right]$$

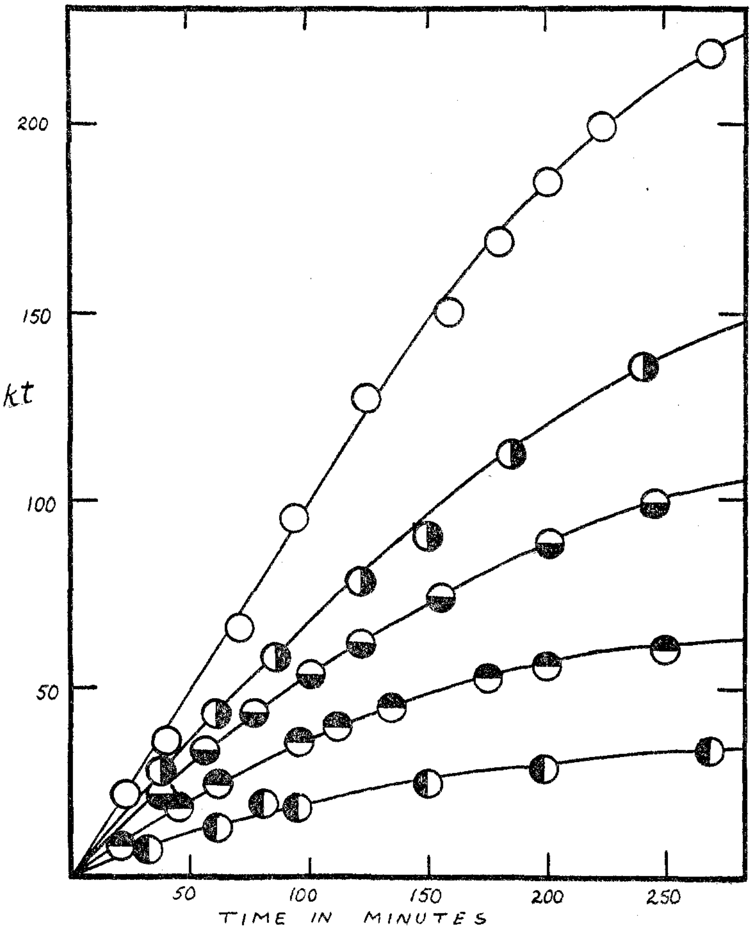


FIG. 2. THE REACTION BETWEEN MERCURIC ACETATE (4.0×10^{-3} moles/liter) AND DIMETHYLHEPTENOL (4.0×10^{-3} moles/liter) IN 1,2-DIMETHOXYETHANE WITH ADDED ACETIC ACID AT 25.0 ± 0.1°

Legend: *Acetic Acid* ○ *none;* ◑ *2.0×10^{-3} moles/liter;* ◒ *4.0×10^{-3} moles/liter;* ◓ *8.0×10^{-3};* ◐ 16.0×10^{-3} moles/liter

where "a" represents concentration of mercuric acetate and "b" the concentration of the dimethylheptenol, or

$$2. \qquad kt = \left(\frac{1}{a - x} - \frac{1}{a}\right)$$

when equal concentrations of the reagents are used initially.

Fig. 1 shows that the specific rate constant 1.62×10^{-2} liters moles^{-1} sec.^{-1} does not deviate appreciably over the first 30% of the reaction. However Fig. 2 (upper curve) shows that it drops off badly after this time period.

Inspection of equations 3 and 4 which describe the formation of intermediate

VII in the reaction of dimethylheptenol (I) and mercuric acetate to form 2,2,6,6-tetramethyl-3-acetoxymercuritetrahydropyran (III)

3. $$\mathrm{I} + \mathrm{Hg(OAc)_2} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{VII} + \mathrm{HOAc}$$

4. $$\mathrm{VII} \xrightarrow{k_3} \mathrm{III}$$

shows that no account has been taken during the foregoing kinetic treatment of the acetic acid which is a product of the reaction. The rate of formation of VII (X = OAc), when this intermediate is considered, is expressed in the steady state according to equation 5.

5. $$\frac{d[\mathrm{VII}]}{dt} = k_1[\mathrm{I}][\mathrm{Hg(OAc)_2}] - k_2[\mathrm{VII}][\mathrm{HOAc}] - k_3[\mathrm{VII}]$$

or

6. $$[\mathrm{VII}] = \frac{k_1[\mathrm{I}][\mathrm{Hg(OAc)_2}]}{k_2[\mathrm{HOAc}] + k_3}$$

The observed rate may then be expressed

7. $$\frac{d[\mathrm{III}]}{dt} = -\frac{d[\mathrm{Hg(OAc)_2}]}{dt} = \frac{k_1[\mathrm{I}][\mathrm{Hg(OAc)_2}]}{k_2/k_3[\mathrm{HOAc}] + 1}$$

The concentrations of equimolar amounts of dimethylheptenol and mercuric acetate may again be designated as "a", initially, and as "a − x" at time t. The concentration of any acetic acid which may be deliberately added initially may be designated as c. Thus c + x represents the concentration of acetic acid at time t. The specific rate constant k_1 may then be expressed

8. $$k_1t = \left[\frac{k_2}{k_3}(a + c) + 1\right]\left(\frac{1}{a - x} - \frac{1}{a}\right) - \frac{k_2}{k_3}\ln\frac{a}{a - x}$$

When the experiment represented by the upper curve in Fig. 2 is reevaluated in this manner (C = O) the improved rate constancy is shown in Fig. 3. Furthermore co-linearity with the line in this figure was achieved with a series of experiments wherein the additional acetic acid was varied from 2.0 to 16.0 $\times 10^{-3}$ moles per liter. In these cases the ratio k_2/k_3 was determined as 25 liters moles^{-1} at 25° ± 0.1 by the method of trial and error.

These experiments show that the effect of retardation by acetic acid may be expressed adequately by equations 3 and 4 which specify that oxymercuration proceeds by addition of the solvolysis product, a basic mercuric salt, to the alkene. In order to rationalize the experimental results with the concept of an "alkanemercurinium ion" one must assume depression of ionization by the addition of acetic acid. However processes such as aromatic mercuration, in which ionic mercury seems to partake (12), are accelerated by addition of acid (13). This acceleration probably operates by suppression of solvolysis of the mercuric salt. The present results do not then seem to be in accord with an ionic mechanism for oxymercuration of an alkene.

Sand and Singer seem to have defined the structures of the oxymercuration products from dimethylheptenol essentially by analogy with the corresponding products from α-terpineol, which yielded *trans*-terpin and cineole upon reduction with sodium amalgam. The oxymercurials from dimethylheptenol yielded only the latter alkene (I) upon reduction with either sodium amalgam or hydrogen sulfide. However we have been able to reduce these oxymercurials (II and III) to the saturated analogs with hydrazine hydrate (14) and thus have confirmed the structures which Sand and Singer assumed.

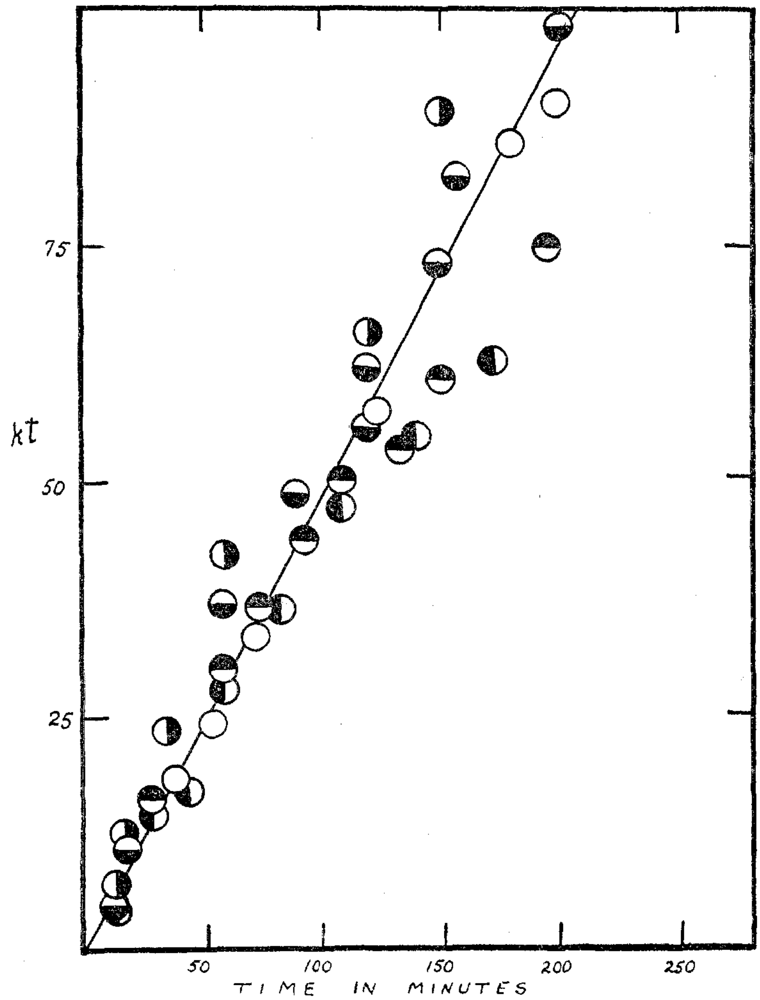


FIG. 3. THE REACTION BETWEEN MERCURIC ACETATE (4.0×10^{-3} moles/liter) AND DIMETHYLHEPTENOL (4.0×10^{-3} moles/liter) IN 1,2-DIMETHOXYETHANE WITH ADDED ACETIC ACID AT 25.0 ± 0.1°

Legend: Acetic Acid added ○ none; ◑ 2.0×10^{-3} moles/liter; ◒ 4.0×10^{-3} moles/liter; ◓ 8.0×10^{-3} moles/liter; ◐ 16.0×10^{-3} moles/liter

When the compound which was assumed to be 2,2,6,6-tetramethyl-3-chloromercuritetrahydropyran (III) was boiled with hydrazine hydrate a volatile oil could be separated from a residue which was probably the mercuri-*bis* derivative. The volatile oil was identified as 2,2,6,6-tetramethyltetrahydropyran by preparation of its hydrogen bromide addition product, which was identical with that obtained from the authentic material (15).

The reduction product obtained by treatment of 2,6-dimethyl-3-iodomercuriheptanediol-2,6 (II, X = iodide) with hydrazine hydrate is not a known substance. However we consider it to be 2-[2,2-dimethyltetrahydrofuryl]propanol-2 (VI). Slow oxidation with periodic acid yields acetone which must have been formed from the hydroxyisopropylidene group. Infrared spectra indicate absence of alkene and carbonyl linkages, but presence of an hydroxyl and probably of an ether linkage. The hydroxyl group is evidently tertiary, because it will not react with phenyl isocyanate or with dinitrobenzoyl chloride, although it yields a chloro derivative upon treatment with acetyl chloride. The reduction product (VI) is not an unexpected product from II if the intermediate free radical (V) is assumed to be stabilized by loss of a hydrogen atom (14, 16). The isolation of VI, like that of IV, thus seems to confirm the structure designation by Sand and Singer of compounds II and III.

EXPERIMENTAL

All melting points have been corrected against known standards.

2,2,6,6-Tetramethyl-3-halogenomercuritetrahydropyrans

A. From mercuric acetate without water. A suspension of 1 g. (0.00314 mole) of mercuric acetate in 2 ml. (0.012 mole) of 2,6-dimethylhepten-2-ol-6 (b.p. 178°/751 mm.); d_{25}^{25} 0.845; n_D^{20} 1.44832) was shaken vigorously. The solid dissolved during one hour. After three hours the excess of dimethylheptenol was distilled molecularly at 35–50° (10^{-3} mm.). The residue was dissolved in a total of 15 ml. of 10% aqueous sodium hydroxide. This solution was filtered to remove traces of mercurous oxide and the filtrate was divided into two equal parts.

One-half of the solution was treated with 1 g. of potassium iodide in 3 ml. of water. The crystalline solid (0.46 g., 63%) melted at 107–108°. Recrystallization from ethanol raised this melting point to 108–110°. A mixture melting point with 2,2,6,6-tetramethyl-3-iodomercuritetrahydropyran (III, X = iodide) prepared by Sand and Singer's method was not lowered.

The other half of the alkaline solution was treated with 10 ml. of saturated sodium chloride and then with an excess of gaseous carbon dioxide. The crystalline 2,2,6,6-tetramethyl-3-chloromercuritetrahydropyran (III, X = Cl) weighed 0.54 g. (91%), m.p. 97–98°. The melting point was unchanged by crystallization from 2:1 ethanol-water (7 ml. per g.).

Anal. Calc'd for $C_9H_{17}ClHgO$: C, 28.7; H, 4.51.

Found: C, 28.5; H, 4.65.

When the iodomercurial was treated with silver acetate in water-ethanol and this acetoxymercurial was treated with sodium chloride the chloromercurial was obtained in 75% yield.

B. From mercuric acetate and water. To a solution of 38.1 (0.12 mole) of mercuric acetate in 150 ml. of water was added 16.5 g. (0.117 mole) of dimethylheptenol. This mixture was shaken 100 times as rapidly as possible in a separatory-funnel and then 250 ml. of 10% aqueous potassium hydroxide was added. The mercurous and mercuric oxides were filtered off, and the solution was divided into two parts.

Two-thirds of this solution was treated with 13.2 g. (0.08 mole) of potassium iodide dissolved in 25 ml. of water. The addition of this salt caused the immediate precipitation of a gummy solid. This solid suspension was filtered to remove solution A. The solid was dissolved in 50 ml. of diethyl ether and dried with sodium sulfate. The dried solution was evaporated in a dish under a vacuum. The slightly gummy crystalline residue was ground in 5 ml. of absolute ethanol and this solution was filtered to remove 6.0 g. (16%) of 2,2,6,6-tetramethyl-3-iodomercuritetrahydropyran, m.p. 106–108°. This light-sensitive compound was purified by crystallization from 25 ml. of absolute ethanol, m.p. 108–110°. The ethanolic filtrates upon evaporation yielded 2 g. (5%) of the same compound. There was no evidence of residual oily product.

The other one-third of the alkaline solution was treated with 50 ml. of saturated aqueous sodium chloride and then at 0° with gaseous carbon dioxide. The precipitate was separated from the aqueous medium (B). The precipitate was only partially crystalline but re-treatment in water-ethanol and sodium chloride yielded a solid, m.p. 50–55° which was crystallized from water-ethanol. The purified chloromercurial (III) melted at 96–97° and weighed 4 g. (25%).

C. From mercuric acetate and 1,2-dimethoxyethane. To a suspension of 3.18 g. of mercuric acetate in 10 ml. of 1,2-dimethoxyethane (peroxide-free, purified by boiling and distilling from sodium under nitrogen) was added 1.45 g. (0.01 mole) of dimethylheptenol. After 6.5 hours of agitation the original solid had disappeared. The liquid was filtered and then evaporated, finally at 60–65° (10^{-3} mm.). The residue dissolved in 30 ml. of warm 10% aqueous potassium hydroxide. This solution, with 25 ml. of saturated aqueous sodium chloride and then with gaseous carbon dioxide, precipitated a 60% yield of 2,2,6,6-tetramethyl-3-chloromercuritetrahydropyran, m.p. 97.7–98.5°. This was identified by conversion to the analogous iodomercurial, m.p. 108–110°.

2,6-Dimethyl-3-halogenomercuriheptanediol-2,6

A. From solution "A", above. The filtrate "A" was saturated with gaseous carbon dioxide. A slightly gummy solid precipitated, which rapidly became entirely crystalline, wt. 10.0 g. (25%), m.p. 128–130° (decomp.). Crystallization from 160 ml. of hot benzene raised this melting point to 134.5–135° (decomp.). Although this melting point is 10° higher than that reported by Sand and Singer, the analysis is indicative of the same 2,6-dimethyl-3-iodomercuriheptanediol-2,6 reported by them.

Anal. Calc'd for $C_9H_{19}HgIO_2$: C, 22.2; H, 3.91.
Found: C, 22.4; H, 3.99.

B. From solution "B" above. After several days, solution "B" deposited a white crystalline solid, m.p. 127–129° weighing 2.7 g. (17%). Crystallization from 2:1 benzene-acetone (8 ml. per g.) raised this melting point to 135.5–136°.

Anal. Calc'd for $C_9H_{19}ClHgO_2$: C, 27.3; H, 4.81.
Found: C, 27.4; H, 4.89.

This 2,6-dimethyl-3-chloromercuriheptanediol-2,6 could be converted to the iodomercuri analog by solution of 0.2 g. (0.0005 mole) in 3 ml. of 10% alkali to which solution 0.1 g. of potassium iodide (in 2 ml. of water) and then gaseous carbon dioxide was added. The white precipitate (0.2 g., 82%) melted at 131–132° (decomp.). Crystallization from 5 ml. of benzene raised this melting point to 134–135°. A mixture melting point with the iodomercuri compound (from solution "A") was not lowered.

2,2,6,6-Tetramethyltetrahydropyran. To a refluxing solution of 2,2,6,6-tetramethyl-3-chloromercuritetrahydropyran (m.p. 95–97°; 11.9 g. or 0.0316 mole) in 150 ml. of 25% aqueous sodium hydroxide was added 5 ml. (0.085 mole) of 85% hydrazine hydrate during a period of two hours. The mixture was cooled and extracted with ether. The third phase, metallic mercury, weighed 5.2 g. (82%). The etherous extract was dried with sodium sulfate and distilled, finally at 45–65° (20 mm.), leaving residual *bis*-mercurialkane. The oil was redistilled at 140–142° (720 mm.) n_D^{20} 1.427.

Anal. Calc'd for $C_9H_{18}O$: C, 76.0; H, 12.7.
Found: C, 75.9; H, 12.6.

The infrared absorption spectrum showed no band characteristic of the hydroxyl group but a broad band at 9.92 μ may be characteristic of the ether linkage. The product did not react with bromine or acidic 2,4-dinitrophenylhydrazine. When it was added to a saturated solution of hydrogen bromide in glacial acetic acid an addition compound, m.p. 65–66° was formed. This melting point was not depressed upon admixture with the hydrogen bromide addition complex formed from authentic 2,2,6,6-tetramethyltetrahydropyran prepared from 2,6-dimethylheptanediol-2,6 (15).

2-[2,2-Dimethyltetrahydrofuryl]propanol-2. To a boiling solution of 19.9 g. (0.041 mole) of 2,6-dimethyl-3-iodomercuriheptanediol-2,6 in 100 ml. of 10% aqueous potassium hydroxide was added 6 ml. (0.1 mole) of 85% hydrazine hydrate. An oil and metallic mercury (7.0 g., 85%) separated from the aqueous phase. The etherous extract was dried and distilled. The principal fraction weighed 4.2 g. (65%), b.p. 79–80° (32 mm.). This was redistilled, b.p. 172–173° (720 mm.), n_D^{15} 1.4378.

Anal. Calc'd for $C_9H_{18}O_2$: C, 68.5; H, 11.4.
Found: C, 68.4; H, 11.5.

This product reacted neither with acidic dinitrophenylhydrazine nor with bromine. Reaction of 2.5 g. with a slight molar excess of acetyl chloride gave 2.0 g. of a chloride, b.p. 108–110° (30 mm.), n_D^{20} 1.439 which decomposed before it could be analyzed. Further evidence of the tertiary alcohol structure was afforded by failure of the reduction product to form a urethan or a dinitrobenzoate. The presence of the isopropylidene group was demonstrated by agitation of 0.95 g. (0.006 mole) of the reduction product in 45 ml. of 1:1 methanol-water containing 1.50 g. (0.0065 mole) of paraperiodic acid for two days. Only 20% of the material was oxidized, but acetone (isolated as its 2,4-dinitrophenylhydrazone and authenticated by mixture melting point) was obtained in a yield of 60% on the 1:1 basis. Examination of the infrared absorption spectrum of the reduction product showed a strong hydroxyl band at 2.86 μ and a large broad band at 8.66 μ which may represent an ether linkage. No absorption characteristic of alkene or carbonyl linkages was found.

Attempted cyclization of 2,6-dimethyl-3-halogenomercuriheptanediol-2,6 (II) *with acetic anhydride.* When 1 g. of II (X = iodide) was either stirred at 25° or was heated to 135° with acetic anhydride, it decomposed and only dimethylheptenol was recovered. The more stable chloromercurial, II (X = Cl) was recovered unchanged when it was treated with acetic anhydride at 25°. When it was heated for 30 minutes at 100°, it decomposed, and only dimethylheptenol and mercuric chloride were recovered.

Kinetic measurements. The concentrations of peroxide-free 2,6-dimethylheptenol and vacuum-dried mercuric acetate (purified by crystallization from dilute acetic acid) in peroxide-free 1,2-dimethoxyethane in the experiments without additional acetic acid ranged from $2.0–4.0 \times 10^{-3}$ moles per liter for the salt and $2.0–4.8 \times 10^{-3}$ moles per liter for the alkenol. The concentrations of the alkenol and mercuric acetate in 1,2-dimethoxyethane in the experiments with added acetic acid were each 4.0×10^{-3} moles per liter. The acetic acid concentration was varied from $0–16 \times 10^{-3}$ moles per liter. The measurements were carried out at a temperature of 25.0 ± 0.1°.

Analytical method. The analytical procedure (1) for determination of mercury with dithizone [purified as described previously (8)] was modified so that a colorimetric rather than a titrimetric procedure was possible. A Klett-Summerson photoelectric colorimeter, equipped with a No. 66 (red) filter, was used.

The colorimeter was calibrated in terms of a standard (0.001 molar) solution of mercuric acetate in methanol. A 1-ml. aliquot of this solution was diluted to 100 ml. with distilled water. To 1 ml. of this diluate in a separatory-funnel was added 10 ml. of 0.1 *N* hydrochloric acid. The solution was thrice-extracted with three 3-ml. portions of chloroform (which had previously been purified by three-fold extractions with 200-ml. portions of 0.1 *N* hydrochloric acid and then with 200-ml. portions of distilled water per liter of chloroform). To the chloroform-extracted aqueous layer was added 5.0 ml. of dithizone solution (0.01 mg. of dithizone per ml. carbon tetrachloride) and the phases were mixed vigorously for 30 seconds. The dithizone solution was drawn off into the colorimeter tube and the color intensity was determined, using distilled water as a blank. Figure 4 shows the plots of colorimetric readings (R) *versus* mercuric acetate concentrations for two different initial concentrations of the dithizone solution in carbon tetrachloride. The colorimeter response is linear from 0–7 gamma of mercuric acetate in a solution containing 4 × 10^{-5} moles dithizone per liter. This linearity is maintained for higher mercuric acetate concentrations by increasing the dithizone concentration to 10^{-4} moles per liter (upper plot, Fig. 4). No solvent effect was observed when 1,2-dimethoxyethane replaced the methanol as the medium for the standard solution.

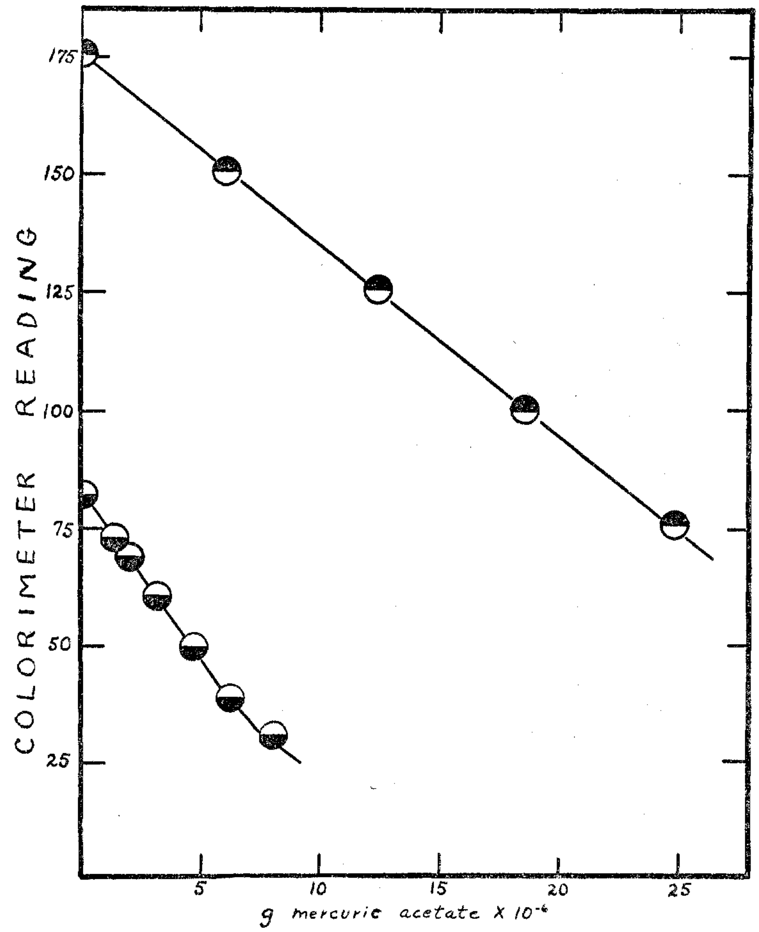


FIG. 4. CALIBRATION CURVES FOR DETERMINATION OF MERCURY USING DITHIZONE

During the kinetic studies aliquots were removed from the reaction mixture at various time intervals and analyzed according to this procedure. There was no indication that the 0.1 *N* hydrochloric acid was decomposing the organomercurial for the brief period of agitation during the chloroform extraction. Freedom from this difficulty (which has been encountered during the kinetic analysis of certain hydroxymercurations) was demonstrated by replacement of the 0.1 *N* hydrochloric acid with dilute sodium chloride. When the hydrochloric acid was then added subsequent to removal of the organochloromercurial by chloroform, the results with comparable aliquots of the reaction mixture were identical within experimental error.

SUMMARY

1. The supposed isomeric pairs which Sand and Singer reported as products of the oxymercuration of 2,6-dimethylhepten-5-ol-2 in water have been shown to be single compounds which are solids, or sometimes oils which slowly crystallize to the identical solids.

2. Since the two individuals are respectively linear and cyclic oxymercurials of dimethylheptenol there are also no positional isomers.

3. The positional structures of the cyclic and linear oxymercurials have been determined by reduction with hydrazine hydrate.

4. The oxymercuration of dimethylheptenol with mercuric acetate has been found to give a better yield of 2,2,6,6-tetramethyl-3-halogenomercuritetrahydropyran in absence of water than the total yield of this compound plus 2,6-dimethyl-3-halogenomercuriheptanediol-2,6 which are both obtained in aqueous medium.

5. The rate of oxymercuration is retarded by addition of acetic acid and this retardation has been considered in a kinetic study. It is suggested that addition of acetic acid should retard a nonionic coordination reaction but should accelerate a reaction proceeding by an ionic mechanism.

TORONTO, CANADA

REFERENCES

(1) CONNOR AND WRIGHT, *J. Am. Chem. Soc.*, **68**, 256 (1946).
(2) PEARSON, SIGAL, AND KRUG, *J. Org. Chem.*, **15**, 1048–1054 (1950).
(3) WRIGHT, *Chemistry in Canada*, **2**, 149–154 (1950).
(4) SAND AND SINGER, *Ber.*, **35**, 3170 (1902).
(5) SAND AND SINGER, *Ann.*, **329**, 166 (1903).
(6) CHATT, *Chem. Revs.*, **48**, 7–43 (1951).
(7) LUCAS, HEPNER, AND WINSTEIN, *J. Am. Chem. Soc.*, **61**, 3102 (1939).
(8) ROMEYN AND WRIGHT, *J. Am. Chem. Soc.*, **69**, 697 (1947).
(9) WRIGHT, *J. Am. Chem. Soc.*, **57**, 1993 (1935).
(10) KOLTHOFF AND SANDELL, *J. Am. Chem. Soc.*, **63**, 1906 (1941).
(11) WICHMANN, *Ind. Eng. Chem., Anal. Ed.*, **11**, 66 (1939).
(12) KLAPROTH AND WESTHEIMER, *J. Am. Chem. Soc.*, **72**, 4461 (1950).
(13) WESTHEIMER, SEGEL, AND SCHRAMM, *J. Am. Chem. Soc.*, **69**, 773 (1947).
(14) WRIGHT, *Can. J. Chem.*, **30**, 268 (1952).
(15) RUPE AND SCHLOCHOFF, *Ber.*, **38**, 1498 (1905).
(16) BERMAN, HALL, PYKE, AND WRIGHT, *Can. J. Chem.*, **30**, June (1952).