OXYMERCURATION OF THE METHYLCYCLOHEXENES[1]

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ABSTRACT

It has been found that, while hydroxymercuration of 2-methylcyclohexene leads to a single product, 3-methylcyclohexene gives a nonworkable mixture and 4-methylcyclohexene gives both positional and diastereoisomers of which three of the four have been isolated. The ratio of positional isomers is found to be 5:1 in favor of farthest distance of the methyl group from the mercury atom. The conversion of the chloromercuri-hydroxy-methylcyclohexanes to chloromercuri-methoxy-methylcyclohexanes by potassium *tert*-butoxide and dimethyl sulphate has been accomplished. Thus the products of hydroxymercuration have been related configurationally to two of the three products of 4-methylcyclohexene methoxymercuration. Among these products that one is most prevalent in which the mercury is most distant, positionally and configurationally, from the methyl group in the alkene.

Since oxymercuration of a single geometric form of an alkene containing no substituent possessing asymmetry always forms but one diastereomer (15) it has seemed worth while to oxymercurate alkenes in which one substituent contains an asymmetric center. Such an alkene might be expected to form either or both of positional and diastereoisomers. One such alkene has previously been oxymercurated, but in this circumstance the alkene (4, 11, 12), α-terpineol, contains an alcoholic function which may influence the oxymercuration or partake in it. For this reason the absence of diastereoisomers or positional isomers in the oxymercuration of α-terpineol may not define generally the behavior of alkenes containing an asymmetric substituent. Consequently we have chosen to examine simpler types, the methylcyclohexenes.

The hydroxymercuration of 2-methylcyclohexene (I) does not involve the possibility of diastereoisomerism although positional isomers are possible. However, the reaction yields only one compound, which is called* 1-↓-chloromercuri-1-↓-hydroxy-2-↑-methylcyclohexane (II) (where the symbols ↑ and ↓ signify 'upper' and 'lower' positions in a planar cyclohexane structure assumed to be the mean of the several conformational possibilities). This substance may be reduced by sodium amalgam in water to 1-methylcyclohexanol (III).

The oxymercuration of 3-methylcyclohexene (IV) (2) does not proceed so smoothly. No crystalline product can be isolated from the methoxymercuration (all attempts at separation by differences in density and by selective adsorption or ion-exchange techniques have thus far failed) and only a small amount of crystalline product has been segregated from the oily mixture obtained by hydroxymercuration of this alkene. This compound seems to be 1-↓-chloromercuri-2-↓-hydroxy-3-↑-methylcyclohexane (V) since it may be reduced by hydrazine to 2-↑-methyl-↓-cyclohexanol (VI). The latter is identified as its α-naphthylurethane (6). It is evident that either or both of diastereomers and positional isomers may be present in the oxymercuration product, but its intractability makes a decision about isomer type impossible until new techniques of separation are devised.

Although a multiplicity of products has also been obtained from the oxymercurations of 4-methylcyclohexene (VII) the separation has been more successful than that of the previous instance. However, quantitative isolation has not been effected. The crude

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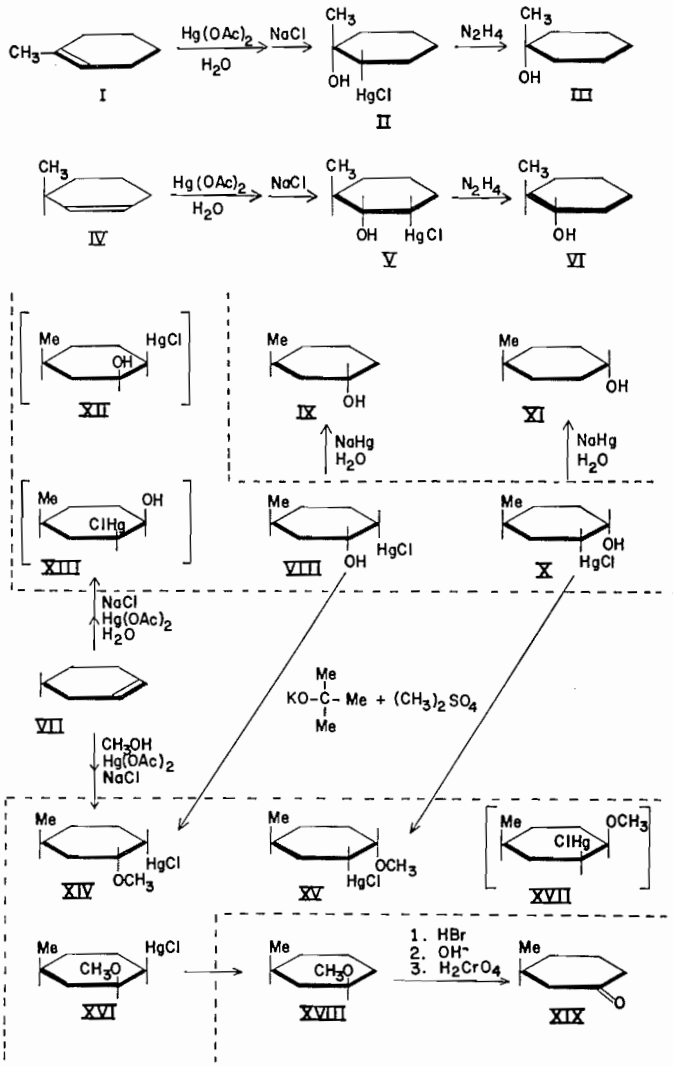
**The configuration of oxymercurials cannot yet be specified with certainty. The assignment used in this report is based on experimental results of Ref. 8 and the discussion of Ref. 16.*



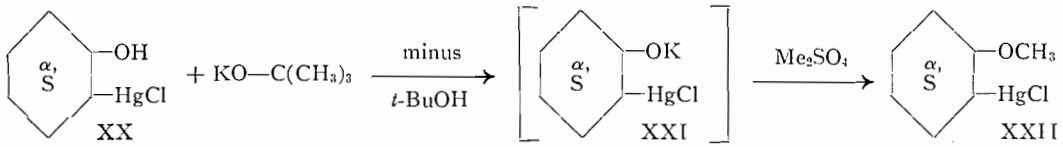
hydroxymercuration product melts at 100–120°, but not more than a 1% yield of 1-↓-chloromercuri-2-↓-hydroxy-4-↑-methylcyclohexane (VIII, m.p. 165°) has been isolated from this mixture. This structure has been demonstrated (assuming apex–apex addition during oxymercuration (8)) by sodium amalgam reduction to 3-↑-methyl-↓-cyclohexanol (IX) (1), identified by refractive index, by conversion to the α-naphthylurethane (m.p. 118°) or the *p*-nitrobenzoate (m.p. 68°), and by assuming that Angyal and Mills' correction of the structures assigned by Macbeth and Mills (7) is valid.

In addition to this component of the hydroxymercuration product of 4-methylcyclohexene, a second isomer, in 0.6% yield, has been isolated from the aqueous saline mother liquors. This substance, m.p. 143°, seems to be the positional isomer 1-↓-chloromercuri-2-↓-hydroxy-5-↑-methylcyclohexane (X) since reduction with sodium amalgam converts it to 4-↑-methyl-↓-cyclohexanol (XI) (1). The melting point – composition diagram of this mercurial (X) with respect to VIII has been determined, and a eutectic temperature of 108° has been found. Since many of the crystal crops obtained during the

separation of VIII melt below this binary eutectic temperature we assume that either or both of the diastereomers XII and XIII also are present in the hydroxymercuration product of 4-methylcyclohexene.

The ratio of the positional isomers 1-chloromercuri-2-hydroxy-4-methylcyclohexane (VIII and XII) versus 1-chloromercuri-2-hydroxy-5-methylcyclohexane (X and XIII) has been determined by sodium amalgam reduction of the entire hydroxymercuration product (aqueous-soluble and insoluble). This mixture of 3- and 4-methylcyclohexanols has been oxidized to the corresponding mixture of 3- and 4-methylcyclohexanones, which are converted to their 2,4-dinitrophenylhydrazones. Chromatographic separation of these derivatives on a bentonite column shows that the ratio of 3-methylcyclohexanone to 4-methylcyclohexanone is 5:1. It may be significant that the preponderant positional isomer is 1-chloromercuri-2-hydroxy-4-methylcyclohexane (VIII and perhaps XII), in which the mercury atom is situated as far as possible from the methyl group.

The products (VIII and X) obtained from 4-methylcyclohexane have been methylated in order, for the first time, to correlate the disposition of addends in hydroxymercuration with that in methoxymercuration; also it was expected that the methylated mercurials would be useful as seeds to induce crystallization of the products from methoxymercuration. The reliability of the methylation technique has been demonstrated with α-1-chloromercuri-2-hydroxycyclohexane (XX) (3). When this compound is treated with potassium *tert*-butoxide, the potassium salt (XXI) is obtained (no precipitation of potassium chloride occurs). Aqueous acidification regenerates XX showing that inversion has not occurred. Alternatively if XXI is treated with dimethyl sulphate a 90% yield of α-1-chloromercuri-2-methoxycyclohexane (XXII) is obtained.

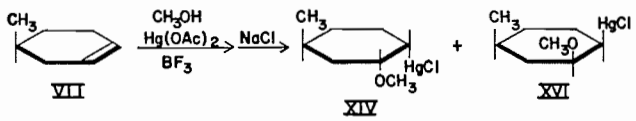


Since inversion is not expected during the methylation step it would seem that configuration of the hydroxymercurial from cyclohexene is identical with that of the methoxymercurial. The same technique has been employed in conversion of the hydroxymercurial (VIII) to 1-↓-chloromercuri-2-↓-methoxy-4-↑-methylcyclohexane (XIV) and of the hydroxymercurial X to 1-↓-chloromercuri-2-↓-methoxy-5-↑-methylcyclohexane (XV).

Three of the four possible isomers have been isolated as pure compounds in small amount from the 94% of crude product, m.p. 53–62°, obtained by methoxymercuration of 4-methylcyclohexane. The isomer obtained in largest amount has been found to be XIV, m.p. 108–109°, the methylation product of 1-↓-chloromercuri-2-↓-hydroxy-4-↑-methylcyclohexane, VIII, which also was found in greatest quantity among the hydroxymercuration products by crystallization. The second product was isolated in 3% yield by fractional precipitation from the mother liquors, and evidently is 1-↑-chloromercuri-2-↑-methoxy-4-↑-methylcyclohexane (XVI), the diastereomer of the first product, XIV. This structure has been demonstrated by sodium amalgam reduction to 1-↑-methoxy-3-↑-methylcyclohexane which has been degraded by ether fission, hydrolysis of the resultant bromide to the alcohol, and oxidation of the latter to 3-methylcyclohexanone (XIX). The third isomer, 1-↓-chloromercuri-2-↓-methoxy-5-↑-methylcyclohexane (XV) was obtained in 0.3% yield by seeding of the rediluted crystallization liquors with the same substance obtained by methylation of the hydroxymercurial, X.

The fourth possible isomer, 1-↑-chloromercuri-2-↑-methoxy-5-↑-methylcyclohexane (XVII), which would be diastereomeric with XV was not isolated, though it is probably present in small amount. However, it would seem that the methoxymercuration which disposes the mercuri group on position 4 with respect to the methyl group is more rapid than that which disposes it on position 3, either from steric or polar influences or both. If this opinion is valid then acceleration of the methoxymercuration ought to accentuate this difference.

This has been found to be the fact. When the accelerator, boron trifluoride etherate, is included in the system, neither of the positional isomers XV or XVII is detectable. Their absence has been demonstrated by treating the entire product through the reaction sequence of reduction, ether fission, hydrolysis, and oxidation (XVI → XIX), whereby only 3-methylcyclohexanone is found. The actual products, XIV and XVI, have been isolated in better yield than obtains in the uncatalyzed reaction. Since none of the fractions encountered during separation of XIV and XVI by crystallization melted below 54°, the eutectic temperature of a mixture of the two, it is reasonable to assign a composition to the crude methoxymercuration product, m.p. 54–74°. Since the melting point of this crude product is depressed by admixture of a small amount of 1-↑-chloromercuri-2-↑-methoxy-4-↑-methylcyclohexane (XVI) it is evident from the temperature–composition diagram that the catalyzed methoxymercuration product of 4-methylcyclohexene comprises about 80% of 1-↓-chloromercuri-2-↓-methoxy-4-↑-methylcyclohexane, XIV. Thus the methoxymercuration, like the hydroxymercuration, yields predominantly the isomer in which the mercuri linkage is farthest removed from the methyl group in 4-methylcyclohexene.



If this tendency toward farthest disposition of the mercuri linkage with respect to the methyl group is a steric one then it must be related to the mercury substituent itself rather than to its acyl substituent. When mercuric benzoate or mercuric stearate is used instead of mercuric acetate in the methoxymercuration of 4-methylcyclohexene and the initial products are converted to the mixture of methoxychloromercurials, the melting point of the crude products is not essentially different from that obtained when mercuric acetate is used.

EXPERIMENTAL*

1-↓-Chloromercuri-2-↓-hydroxy-2-↑-methylcyclohexane (II)

A mixture of 4.8 g. (0.05 mole) of 2-methylcyclohexene (14), b.p. 108.5–109.5° (760 mm.), n_D^{20} 1.4507, with 15.9 g. (0.05 mole) of mercuric acetate dissolved in 125 ml. of water was shaken for 45 minutes, then filtered from mercurous salt into 80 ml. of saturated aqueous sodium chloride. The precipitate, vacuum-dried, weighed 10.8 g. (62%), m.p. 115–118°. Two crystallizations from benzene (4 ml. per g.) left 5.5 g. (51% recovery), m.p. 128.0–129.5°. Calc. for $C_7H_{13}OHgCl$: C, 24.1; H, 3.75. Found: C, 24.2; H, 3.71. Sodium amalgam reduction (described below) gave a 51% yield of 1-methylcyclohexanol, m.p. and m.m.p. 25–26°.

**Melting points have been corrected against reliable standards. X-Ray patterns are recorded as relative intensities [I/I_1] at d spacings in Å using Cu K_α (Ni filtered) radiation, for strongest lines.*

1-↓-Chloromercuri-2-↓-hydroxy-3-↑-methylcyclohexane (*V*)

The 3-methylcyclohexene (b.p. 100.8–101.5° at 760 mm., n_D^{20} 1.4452), 9.6 g. (0.10 mole), was shaken with a solution of 31.8 g. (0.10 mole) of mercuric acetate in 300 ml. of water for 50 minutes, then the whole was poured into 1500 ml. of 4% aqueous sodium chloride. The gummy precipitate (15.3 g., 44%) was filtered off, m.p. 74–80°. We have not yet been able to separate this mixture.

The aqueous liquors, vacuum-evaporated to a volume of 300 ml., yielded 3.40 g. (10%) of product, m.p. 110–115°. After six crystallizations from methanol (5–10 ml. per g.) a pure product, 0.83 g., m.p. 175.0–175.6°, was obtained. Calc. for $C_7H_{13}OHgCl$: C, 24.1; H, 3.75. Found: C, 23.9; H, 3.64.

2-↑-Methyl-↓-cyclohexanol (*VI*)

To a mixture of 0.85 g. (0.0024 mole) of 1-↓-chloromercuri-2-↓-hydroxy-3-↑-methylcyclohexane and 35 g. of 3% sodium amalgam was added 6 ml. of ice-cold water. After 2 days at 0° the system was extracted with four 5-ml. portions of diethyl ether. The extract, water-washed and magnesium sulphate-dried, was distilled, 0.19 g. (68%), b.p. 60–62° (10 mm.). The melting point of the α-naphthylurethane, 158.5–159.5°, was not lowered by mixture with the authentic material.

Preparation and Purification of 4-Methylcyclohexene (*VII*)

A mixture of 171.5 g. of 4-methylcyclohexanol (E.K.) and 90 g. of 85% phosphoric acid was heated in a fractionating still at a rate such that the head temperature did not exceed 105°. When no more would distill the organic layer of the residue was separated, dried with magnesium sulphate, and distilled, b.p. 102–104°, 116 g. (81%). Distillation through a 50-plate column (r.r. 50:1) gave 67% as pure 4-methylcyclohexene, b.p. 103–103.2° (760 mm.), n_D^{20} 1.4420, d_4^{20} 0.800, identical with that reported previously (9).

Hydroxymercuration of 4-Methylcyclohexene

A solution of 159 g. (0.50 mole) of mercuric acetate in 1850 ml. of water was shaken with 48 g. (0.50 mole) of 4-methylcyclohexene for 1 hour, then poured into 5.5 liters of 4% aqueous sodium chloride at 35°. The precipitate was filtered and the aqueous filtrate was vacuum-evaporated, leaving a residue which was water-washed to remove sodium chloride. The remainder (6.6 g., 3.8%), m.p. 68–102°, was crystallized seven times from benzene (10 ml. per g.) leaving 0.96 g. (0.5%) of 1-↓-chloromercuri-2-↓-hydroxy-5-↑-methylcyclohexane (X), m.p. 142–143°. Calc. for $C_7H_{13}OHgCl$: C, 24.1; H, 3.75. Found: C, 24.3; H, 3.84. X-Ray diffraction: [10] 15.63, 13.48, 7.89; [8] 2.82; [7] 6.70, 5.94, 5.37.

The crude saline-insoluble mercurial (134 g., 77%), m.p. 116–129°, was boiled with 1500 ml. of benzene. The cooled mixture was filtered to remove 113 g., m.p. 126–137°. Crystallization from 1300 ml. of benzene raised this melting point to 135–160°. Four more crystallizations from 10:1 benzene:methanol (9 ml. per g.) left 1.9 g. (1.7%) of 1-↓-chloromercuri-2-↓-hydroxy-4-↑-methylcyclohexane (VIII), m.p. 164–164.8°. Calc. for $C_7H_{13}OHgCl$: C, 24.1; H, 3.75. Found: C, 24.0; H, 3.95. X-Ray diffraction: [10] 11.2; [9] 11.9; [8] 9.93; [7] 3.72; [6] 5.43, 4.98, 4.52, 4.17.

The high hydrogen value is typical of analyses of mercurials using the ordinary Pregl micro carbon–hydrogen tube filling. The more precise hydrogen values reported here were obtained by a modification of the tube filling (5).

4-↑-Methyl-↓-cyclohexanol (*XI*)

Sodium amalgam reduction of X as described above gave 85% as 4-↑-methyl-↓-cyclohexanol, b.p. 80–82° (22 mm.). The α-naphthylurethane melted at 158.5–159°.

3-↑-Methyl-↓-cyclohexanol (IX)

A similar reaction with 1-↓-chloromercuri-2-↓-hydroxy-4-↑-methylcyclohexane gave 80% as IX, b.p. 75–77° (18 mm.), n_D^{20} 1.5479. The α-naphthylurethane melted at 116–118°. The *p*-nitrobenzoate melted at 68–69°.

Melting Point – Composition Diagram, Binary System of VIII and X

Weighed portions of VIII and X were dissolved in 0.25 ml. of methanol and vacuum-evaporated, and the melting point was taken. The final mixture, defining the eutectic mixture, was examined in the thaw-point apparatus (10). Both softening point and disappearance of last crystal are recorded.

Mg. VIII	Mg. X	% VIII	Shrink	Melt
5.5	1.7	76	140	149
6.7	0.8	89	151	156
1.6	1.5	52	117	132
1.3	4.7	22	111	130
3.0	3.2	48	117	125
1.3	1.9	41	110	120
1.8	4.5	29	109	118
1.3	2.4	35	109	119
1.711	3.183	34.8	106.5	119.5

Ratio of 1-Chloromercuri-2-hydroxy-4-methylcyclohexanes to 1-Chloromercuri-2-hydroxy-5-methylcyclohexanes Obtained by Hydroxymercuration of 4-Methylcyclohexene

A mixture of 4.2 g. (0.05 mole) of 4-methylcyclohexene and 15.9 g. (0.05 mole) of mercuric acetate in 125 ml. of water was shaken for 80 minutes, then poured into 100 ml. of saturated aqueous sodium chloride. The precipitate (12.4 g., 71%) was combined with 0.33 g. obtained by chloroform extraction of the saline filtrate, and this 0.036 mole was treated in 100 ml. of water for 15 days at 25° with a 2.5% amalgam containing 8.4 g. (0.364 atom) of sodium. The system was extracted with four 15-ml. portions of diethyl ether and this extract, distilled, gave 1.32 g., 0.0115 mole (32%), of 3- and 4-methylcyclohexanols, b.p. 74–76° (15 mm.). This mixture was dissolved in 2.494 g. (0.075 mole) of cold 70% aqueous sulphuric acid and stirred at 0° while a solution of 1.16 g. (0.004 mole) of sodium dichromate in the same amount of sulphuric acid was added during 75 minutes. Subsequently, after 15 minutes at 70°, the cooled system was extracted with four 3-ml. portions of diethyl ether. The extracts, dried and distilled, gave 0.89 g. (69%) of the cyclohexanones, b.p. 59–61° (14 mm.), n_D^{20} 1.4465. This mixture (0.20 g., 0.0018 mole) was treated with 20 ml. of 2,4-dinitrophenylhydrazine reagent (13). The precipitate, 0.39 g. (75%), melted at 99–108°. A solution of 15 mg. in 1 ml. of benzene was placed on a column (18 by 360 mm.) containing 65 g. of tightly-packed Volclay bentonite. This column was eluted (under 500 mm. gauge pressure) first with 300 ml. of 7.5: 92.5 diethyl ether – petroleum ether (b.p. 60–70°) and then with 600 ml. of these solvents in 12: 88 mixture. The two bands were removed separately and each was eluted with three 50-ml. portions of methanol. The upper band gave 2 mg. of 4-methylcyclohexanone dinitrophenylhydrazone, m.p. 130–132°, while the bottom band gave 10 mg. of 3-methylcyclohexanone, m.p. 143–145°. Both samples were identified by mixture melting point. The ratio of isomers is thus 17: 83.

Methylation of α-1-Chloromercuri-2-hydroxycyclohexane

From a 200 ml. modified Claisen flask containing 80 ml. of sulphur-free toluene was

distilled 15 ml. to remove residual water. To the remainder under nitrogen was added 0.59 g. (0.015 atom) of potassium and 10 ml. of dry *tert*-butyl alcohol. After stirring and refluxing had caused the metal to dissolve, the excess of the alcohol was removed by fractional distillation. The remaining suspension was cooled, treated with 1.68 g. (0.005 mole) of α-1-chloromercuri-2-hydroxycyclohexane, and stirred until after 20 minutes the mercurial had dissolved. After 15 minutes the whole was vacuum-distilled for the same time (large ebullition tube containing nitrogen) until 15 ml. of distillate was obtained. The remainder was stirred vigorously for 90 minutes with 1.89 g. (0.015 mole) of dimethyl sulphate. Then 20 ml. of 10% aqueous sodium hydroxide was added and, after 10 minutes of stirring, the toluene was vacuum-distilled. The remainder was filtered, diluted with 90 ml. of 1.5% aqueous sodium chloride, and saturated with carbon dioxide. The α-1-chloromercuri-2-methoxycyclohexane (1.57 g., 90%) melted at 109–112°. After crystallization from 8 ml. of methanol, the remaining 1.1 g. melted at 113.5–115.5° and was identified by mixture melting point.

1-↓-Chloromercuri-2-↓-methoxy-5-↑-methylcyclohexane (*XV*)

A similar methylation of 1-↓-chloromercuri-2-↓-hydroxy-5-↑-methylcyclohexane (X) gave a 77% yield of XV, m.p. 82–88°. Crystallized twice from methanol (80% recovery), it melted at 88–89°. Calc. for $C_8H_{15}OHgCl$: C, 26.4; H, 4.16; Found: C, 26.4; H, 4.32. X-Ray diffraction: [10] 11.70; [9] 5.84, 3.90, 3.49; [7] 3.66, 3.62, 3.25, 2.91.

1-↓-Chloromercuri-2-↓-methoxy-4-↑-methylcyclohexane (*XIV*)

Methylation of 1-↓-chloromercuri-2-↓-hydroxy-4-↑-methylcyclohexane (VIII) by the same procedure gave an 83% yield of XIV, m.p. 100–106°. Crystallization from methanol (3.3 ml. per g., 33% recovery) raised the melting point to 108.0–109.2°. Calc. for $C_8H_{15}OHgCl$: C, 26.4; H, 4.16. Found: C, 26.5; H, 4.39. X-Ray diffraction: [10] 2.40; [9] 13.8, 2.85; [8] 10.97, 10.39; [7] 2.097; [6] 2.47.

Methoxymercuration of 4-Methylcyclohexene

A. Uncatalyzed

A solution of 9.6 g. (0.10 mole) of 4-methylcyclohexene and 31.8 g. (0.10 mole) of mercuric acetate in 250 ml. of methanol was poured into 700 ml. of 2% aqueous sodium chloride after 30 minutes. After 2 hours the precipitate, 34.1 g. (94%), was filtered off, m.p. 53–62°. After 14 crystallizations from methanol the remainder (1.1 g., 3.2%) melted at 108–109°. A mixture melting point with 1-↓-chloromercuri-2-↓-methoxy-4-↑-methylcyclohexane (XIV) was not lowered.

The filtrate from the first methanolic crystallization (80 ml.) was evaporated to a volume of 65 ml. and then cooled at 0° for 3 days. The crystal crop, 3.4 g., m.p. 62–76°, was largely XIV. The filtrate was again evaporated to a volume of 50 ml. and cooled 5 days at 0° while 4.42 g., m.p. 50–60°, separated. Eight crystallizations from methanol (2–5 ml. per g.) left 1.07 g. (m.p. 89°) (2.9%) of 1-↑-chloromercuri-2-↑-methoxy-4-↑-methylcyclohexane (XVI). The X-ray powder pattern of XVI was: [10] 10.16, 3.45, 4.09; [9] 5.18, 5.75; [8] 3.72, 2.55, 3.08; [7] 2.11, 2.52, 3.08, 10.16; [6] 2.81, 2.94. Calc. for $C_8H_{15}OHgCl$: C, 26.4; H, 4.16. Found: C, 26.7; H, 4.12. Electrical polarization in dioxane at 20° is 387 cc.: Calc. R_D is 55.4 so dipole moment is 3.97 D.

The filtrate from the 4.42 g. portion was diluted with methanol to a volume of 120 ml., and chilled to −70°, and a layer of petroleum ether (b.p. 60–70°) was added. When this system was seeded with 1-↓-chloromercuri-2-↓-methoxy-5-↑-methylcyclohexane (XV), precipitation of 0.52 g., m.p. 43–60°, occurred during 3 days. When this crop was

crystallized four times from methanol (3 ml. per g.) there remained 0.10 g. (0.3%) of XV, m.p. 86–88°, identified by mixture melting point.

B. Catalyzed

To a solution of 3.18 g. (0.01 mole) of mercuric acetate in 100 ml. of methanol at 1° was added a solution of 0.96 g. (0.01 mole) of 4-methylcyclohexene and 0.14 g. (0.001 mole) of boron fluoride etherate in 50 ml. of methanol at 1°. After 30 minutes the system was poured into 400 ml. of 1% aqueous sodium chloride solution. After 12 hours the precipitate was filtered, 2.64 g. (73%), m.p. 54–74°.

When this product was submitted to the reactions described below the sole product was the 2,4-dinitrophenylhydrazone of 3-methylcyclohexanone, m.p. 143–145°.

Alternatively the 2.64 g. portion was crystallized six times from methanol (4 ml. per g.), leaving 0.31 g. (12%) of 1-↓-chloromercuri-2-↓-methoxy-4-↑-methylcyclohexane (XIV), m.p. 102–105°. A further crop (0.6 g.) was obtained by evaporation of 3 ml. of methanol from the 10 ml. filtrate from the first crystallization. Further evaporation of 2 ml. from the final 7 ml. filtrate caused separation of 0.27 g., m.p. 68–75°. Crystallization from 2 ml. of methanol gave 0.18 g. (7%) of 1-↑-chloromercuri-2-↑-methoxy-4-↑-methylcyclohexane (XVI), m.p. 84–86°, authenticated by mixture melting point. The crystalline nature of subsequent fractions indicated that not more than these two compounds were present (no fraction melted below 54°).

Thaw Point – Composition Diagram, Binary System of XIV and XVI

The mixtures were prepared by evaporation of solutions of weighed samples in 0.25 ml. of methanol. All determinations were made in the thaw-point apparatus (10). Disappearance of the last crystal in this determination is called the melting point.

Mg. XVI	Mg. XIV	% XVI	Eutectic	M.p.
0.802	2.198	26.7	57.0	94.9
0.749	0.897	45.5	55.5	85.8
1.333	0.329	80.3	54.2	73.8
1.359	0.536	71.8	53.9	56.6
1.586	1.030	60.7	54.8	71.8
1.577	0.858	64.8	54.0	70.2

3-Methylcyclohexanone

A mixture of 1.30 g. (0.0036 mole) of α-1-↑-chloromercuri-2-↑-methoxy-4-↑-methylcyclohexane (XVI), 33 g. of 3% sodium amalgam, and 6 ml. of water reacted at 0° for 1 day and was ether-extracted. After evaporation of the ether the residue (*ca.* 0.5 ml.) with 1.03 g. (0.007 mole) of 40% hydrobromic acid and 10 ml. of acetic acid was heated at 90–100° for 11 hours, then made alkaline with 65 ml. of 15% alkali and boiled under reflux for 8 hours. Ether extraction gave 0.21 g. (52%) of 3-methylcyclohexanol, b.p. 65–70° (13 mm.). This distillate was dissolved in 0.332 g. (0.001 mole) of 30% aqueous sulphuric acid. The solution was stirred at 0° while 0.16 g. (0.0005 mole) of sodium dichromate in the same amount of sulphuric acid was added during 10 minutes. After 25 minutes more at 0° and 20 minutes at 70° the system was cooled and ether-extracted. The extract, water-washed and evaporated, left 0.15 ml., which was treated with 5 ml. of 2,4-dinitrophenylhydrazine reagent (13). The 0.110 g. of precipitate, m.p. 120–130°, was crystallized from 5 ml. of methanol, 0.065 g., m.p. 142–145°. A mixture melting point with an authentic sample was not lowered.

1-↓-Chloromercuri-2-↓-methoxy-2-↑-methylcyclohexane

A solution of 3.18 g. (0.01 mole) of mercuric acetate in 50 ml. of methanol was treated with 0.96 g. (0.01 mole) of 2-methylcyclohexene. After 5 minutes, a test with sodium hydroxide gave no yellow precipitate so the system was poured into 100 ml. of 3% aqueous sodium hydroxide with stirring. The solid chloromercurial (2.17 g., m.p. 79–82°, 75%) was four times crystallized from commercial hexane plus methanol, m.p. 83–84°. Diffraction pattern is [10] 9.82; [9] 4.29; [8] 6.06; [7] 3.26; [6] 6.41; [5] 4.92; [4] 5.64, 5.21; [3] 4.44, 3.65. Electric polarization in dioxane at 20° is 446.7 cc.; calc. R_D 55.0; dipole moment 4.31 D. Anal. calc. for $C_8H_{15}OHgCl$: C, 26.5; H, 4.16. Found: C, 26.1; H, 4.14.

REFERENCES

1. Angyal, S. J. and Mills, J. A. Rev. Pure Appl. Chem. (Australia), **2**, 185 (1952).
2. Berlande, A. Bull soc. chim. **9**, 642 (1942).
3. Brook, A. G. and Wright, G. F. Can. J. Research, B, **28**, 623 (1950).
4. Brook, A. G. and Wright, G. F. To be published.
5. Cross, C. K. and Wright, G. F. Anal. Chem. **26**, 886 (1954).
6. Jackman, L. N., Macbeth, A. K., and Mills, J. A. J. Chem. Soc. 1717 (1949).
7. Macbeth, A. K. and Mills, J. A. J. Chem. Soc. 709 (1945).
8. McNeely, K. H., Rodgman, A., and Wright, G. F. J. Org. Chem. **20**, 714 (1955).
9. Nametkin, S. and Brussow, L. Ber. **56**, 1807 (1923).
10. Rheinboldt, H. and Kircheisen, M. J. prakt. Chem. **113**, 348 (1926).
11. Sand, J. and Singer, F. Ann. **329**, 166 (1903).
12. Sand, J. and Singer, F. Ber. **35**, 3170 (1902).
13. Shriner, R. L. and Fuson, R. C. Identification of organic compounds. 3rd ed. John Wiley & Sons, Inc., New York. 1948. p. 97.
14. Wallach, O. Ann. **359**, 298 (1908).
15. Wright, G. F. J. Am. Chem. Soc. **57**, 1993 (1935).
16. Wright, G. F. Ann. N. Y. Acad. Sci. **65**, 436 (1957).