[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF TORONTO]

Methoxymercuration of Cyclohexene

BY JOAN ROMEYN AND GEORGE F. WRIGHT

The methoxymercuration of cyclohexene has been reported earlier[1] but an extensive study of the reaction and its products has been reserved until the present report.

The elements of *methoxy-* and *acetoxymercuri-* seem to add to an ethene as a single unit and not as individual radicals, since a single diastereomer is always characteristic of each geometric isomer of the ethene. The *cis* geometric isomer always reacts faster than its *trans* analog, and the rate is easy to follow, after removal of organomercurial by chloroform extraction, by titration of the residual inorganic mercury.

This reaction, which is strongly peroxide catalyzed, yields only one 1-chloromercuri-2-methoxycyclohexane with the non-geoisomeric cyclohexene. One might expect a second-order consumption of mercury, by analogy with other methoxymercurations, but the rates deviated badly until the reaction was followed in very pure methanol using mercuric acetate concentrations of 10^{-3} m.p.l. and pure, peroxide-free, cyclohexane regenerated by acid hydrolysis of 1-chloromercuri-2-methoxycyclohexane. This indicated that, when catalyst peroxide was present, it was destroyed during the reaction.

This peroxide effect is shown in Fig. 1, where (A) represents the consumption of dithizone (standardized against mercuric sulfate) *versus* time for a reaction mixture containing pure, peroxide-free reagents. The linearity of the reciprocal concentration plot (B) for this experiment shows that the reaction is strictly second-order with respect to cyclohexene and mercuric acetate. By contrast curve (C) represents similar reagents containing 2×10^{-4} m.p.l. of peracetic acid. The reciprocal concentration curve (D) shows the rapid change in rate as this peroxide is consumed. Mercurous salt is formed at the same time.

It may be expected that this destructible catalyst will be present in any of the reagents used in methoxymercuration. Thus Table I shows the reasonable rate constant obtained with pure, peroxide-free reagents, the decaying rate constant when peroxide is known to be present, and a similar deviation from constancy when mercuric lactate is employed instead of the acetate. This inconstancy was expected since mercuric lactate is an unstable salt which cannot be purified satisfactorily, and actually gives a titanous chloride test for peroxide. It is evident from this work that methoxymercuration rates are reliable only when peroxide catalyst is rigorously excluded.

TABLE I

RATE CONSTANTS, CYCLOHEXENE METHOXYMERCURATION

Pure reagents 10^{-3} m. p. l.		Pure reagents 2×10^{-3} m. p. l. plus 2×10^{-4} m. p. l. peracetic acid		Pure reagents 1.6×10^{-3} m. p. l. mercuric lactate instead of acetate	
Time, min.	$k \times 10^{-2}$	Time, min.	$k \times 10^{-2}$	Time, min.	$k \times 10^{-2}$
3.0	27	1.2	356	4.2	141
7.0	44	4.4	134	12.3	166
16.0	37	10.6	68	29.8	112
33.1	32	24.6	45	65.2	86
52.5	35	128.2	34		
82.0	32				
110.7	35				
183.7	32				

Earlier studies on methoxymercuration leave some doubt whether the reactions proceed to completion or to a measurable equilibrium. An answer to this question was obtained in the case of cyclohexene by synthesis of 1-acetoxymercuri-2-methoxycyclohexane. This initial product of methoxymercuration was then treated, 0.1 molar in methanol solution, with one equivalent of acetic acid. The system was not peroxide-free. No reversal was evident by titration for inorganic mercury after twelve days. Since the forward reaction at this concentration would have been complete in less than thirty minutes, it seems definite that cyclohexene methoxymercuration proceeds to completion.

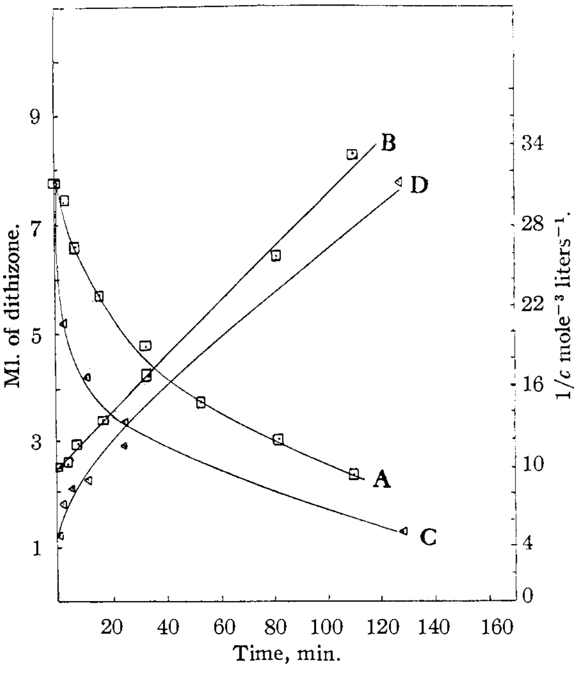

Fig. 1.

Although the reaction has always been assumed as the addition of methoxymercuric acetate to a

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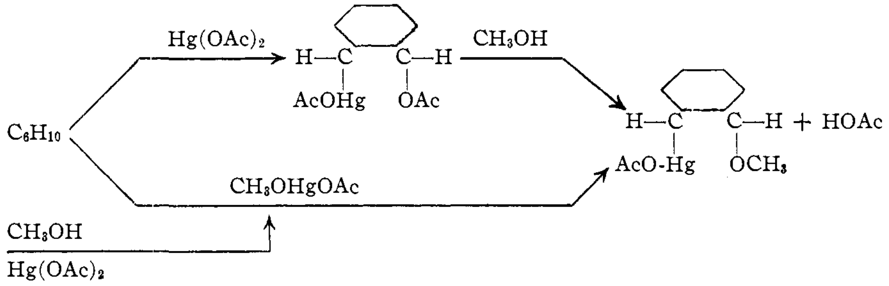
[1] G. F. Wright, THIS JOURNAL, **57**, 1993 (1935).

double bond, this hypothetical addendum has never been isolated as a chemical individual. Alternatively one might postulate that mercuric acetate added to the double bond, after which *acetoxy* and *methoxy* exchanged to give the final product. In such an event the addition reaction would have to be the slow step since the reaction rate is second-order in excess of methanol.



Actually we found that addition of mercuric acetate to cyclohexene does take place, but very slowly, over several days in contrast to the thirty minute addition in methanol medium. This great difference in rate indicates that the cyclohexene–mercuric acetate addition product is not the methoxymercuration intermediate. The low yields of methoxymercurial which may be obtained from it probably result by reversion of the complex to cyclohexene and mercuric acetate. No success has attended attempts to isolate the complex.

Since methoxymercuric acetate thus seems to add as a unit, and no measurable equilibrium can be discovered, it was interesting to find that the addition was asymmetric if *l*-mercuric lactate was used instead of mercuric acetate. The mixture of *ddl*-[1a] and *lll*-lactomercurials has been separated into a pure diastereomer melting at 115.6° and a fraction melting at 72–72.5°. The latter may be separable, but is more likely to be a diastereomeric complex of *ddl* and *lll*-isomers in 1:1 ratio. This ratio is established by conversion from the lactomercurial to the chloromercurial with dilute sodium chloride. This removal of the *l*-lactate radical evidently leaves an optically inactive *dd,ll* mixture because the melting point of the 1-chloromercuri-2-methoxycyclohexane is that of the inactive product and its rotation is zero. Diastereomeric complexes have been reported previously,[2] though the ratio has not been 1:1. Since the two fractions melting at 115.6° and 72–72.5° were obtained almost in equal amounts, the asymmetric synthesis evidently formed about two parts of one diastereomer to one of the other.

When the pure diastereomeric lactomercurial, m. p. 115.6°, was treated with sodium chloride a new, levorotatory, 1-chloromercuri-2-methoxycyclohexane was isolated. This *dd* enantiomer melted at 63°, which designates the inactive *dd, ll*-chloromercurial m. p. 116° as a racemic compound.

We shall re-designate the inactive *dd,ll* 1-chloromercuri-2-methoxycyclohexane as the α-diastereomer, whereas it was specified in the earlier report[1] as the labile isomer because it could be isomerized by boiling ethanol to a product melting at 86 °with the same elemental composition. Neither the isomerization nor the isomer is so simple as was assumed formerly.

Isomerization in boiling ethanol was extremely erratic. Although it was somewhat more reliable in butanol, the isomerization evidently depended on an impurity. It was found that this impurity could be supplied by addition of catalytic amounts of diphenylmercury, hydrazine hydrate, or benzoyl peroxide, but not by ascaridole or cyclohexene peroxide. This array of catalysts has in common the ability to convert RHgCl into R_2Hg. Diphenylmercury accomplishes this by simple radical interchange to give phenylmercuric chloride, which actually was found. Hydrazine hydrate has been used previously for preparation of R_2Hg types.[3] The free phenyl radical which benzoyl peroxide produces on decomposition may be expected to release mercurous chloride from RHgCl according to the transformation.

$$\begin{aligned} R^{\cdot} + R'{:}Hg{:}Cl &\longrightarrow R'{:}Hg^{\cdot} + R{:}Cl \\ R'{:}Hg^{\cdot} + R'{:}Hg{:}Cl &\longrightarrow R'{:}Hg{:}R' + {\cdot}Hg{:}Cl \end{aligned}$$

Mercurous chloride was produced when benzoyl peroxide, the preferred catalyst, was employed. The isomerization process thus becomes an exchange reaction where the $C_7H_{13}O$ radical may racemize from the *dd* to

$$2C_7H_{13}OHgCl \rightleftharpoons (C_7H_{13}O)_2Hg + HgCl_2$$

the *dl* configuration.

We believe that the diastereomeric equilibrium lies far in the direction of the *dl*, or β isomer, since none of the α isomer results when the pure β form is treated in ethanol with benzoyl peroxide. This cannot be demonstrated more rigorously because considerable decomposition accompanies the isomerization, as might be expected if the R_2Hg compound were involved. All attempts to isolate R_2Hg derivatives of methoxymercurials have failed heretofore because of their instabilities. The isomerization must therefore be stopped short of complete destruction, and this usually gives a product melting at 86° which cannot easily be separated by crystallization.

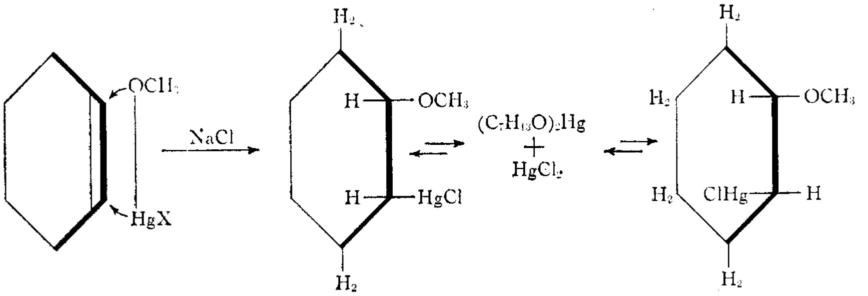
(1a) The configuration designations of the two asymmetric centers in the methoxycyclohexylmercuric radical are entirely arbitrary.

(2) R. C. Hockett and C. S. Hudson, THIS JOURNAL, **53**, 4454–4455 (1931).

(3) H. Gilman and G. F. Wright, THIS JOURNAL, **55**, 3302–3314 (1933); H. Gilman and M. B. Barnett, *Rec. trav. chim.*, **55**, 563 (1936).

This product, which formerly was called the stable isomer, is actually a diastereomeric mixture from which the β isomer can be isolated because it is more stable to acidic media than the α form. When the mixture is dissolved in acetic acid and aqueous sodium chloride is added, the evolution of cyclohexene is observed. The impure β isomer can further be purified by solution in alkali and reprecipitation with dilute hydrochloric acid, and when finally pure, melts about two degrees lower than the α isomer.

The properties of the two diastereomers are not very different. They are both thermally quite stable and can be distilled under reduced pressure. The α isomer is more soluble in acetic acid than is the β form. The α chloromercurial also dissolves more rapidly than the β analog in alkali, although each is regenerated unchanged upon careful acidification, and Miss Underhill in this Laboratory has found the base strength of both soluble cations to be approximately equal. This difference in rate of solution is even more pronounced in the case of the two bromomercurials. Since the methoxymercurials differ from other mercurials chiefly in the attribute of easy alkali solubility and anion lability, we consider that the methoxyl linkage in the α diastereomer must be closer to the mercury atom than it is in the β diastereomer. It follows then that the addends in methoxymercuration must be introduced in the *cis* sense, that is, at apex and apex of the ethylenic carbons (or base and base) since the product of methoxymercuration is the α isomer.



Since the isomerization involves only the carbon atom attached to the mercury atom, one might expect the configuration at the adjacent asymmetric carbon atom to be unaffected, and therefore that isomerization would occur without complete racemization. This was found to be the case; the β diastereomer produced from the levorotatory α diastereomer was found to have a significant rotation, although the sign of optical activity was reversed.

Experimental[3a]

Reagents for Rate Studies.—Methanol (n^{14} 1.3312) was purified by the method of Bjerrum and Lund[4] except that the reduction was carried out completely in a nitrogen atmosphere. This precaution assured the absence of formaldehyde or of peroxide in the solvent. Dithizone (1 g.) was dissolved in 50 cc. of chloroform and extracted thrice with 100-cc. portions of 1% aqueous ammonia. The combined aqueous extracts were acidified with 2.5 cc. of concentrated nitric acid and extracted with 50 cc. of chloroform. The dithizone was recovered in 90% yield by evaporation of the solvent. Its 0.25% solution in carbon tetrachloride was not stable for more than one day, and was therefore prepared freshly for each series of titrations.

The impurities in cyclohexene (benzene, cyclohexadiene and peroxide) were avoided most conveniently by boiling an alkaline solution of pure 1-chloromercuri-2-methoxycyclohexane in a distillation flask under a carbon dioxide atmosphere while 16% hydrochloric acid was added slowly from a dropping funnel. The wet distillate was washed with aqueous alkali, dried by freezing and distilled and stored under oxygen-free atmosphere. Mallinckrodt mercuric acetate from one lot was used throughout this work.

Kinetic Measurements.—In order to slow down the reaction to a measurable rate, the concentrations of cyclohexene and mercuric acetate were each initially in the order of 10^{-3} mole per liter in methanol. At this concentration it was necessary to use the dithizone method of mercury analysis outlined recently.[5] It may be seen from Table I that good rate constancy prevails when pure reagents are used, but that inclusion of a little peracetic acid causes a marked acceleration which, however, decays rapidly with time. The reciprocal concentration curve (D), Fig. 1, for this determination is characteristic of reaction mixtures containing peroxide as an impurity. The *l*-mercuric lactate, used instead of mercuric acetate in the third experiment, thus demonstrates its small peroxide content in the decreasing rate constant more certainly than by the slight qualitative peroxide test it gave with titanous chloride.

Preparation of α,1-Acetoxymercuri-2-methoxycyclohexane.—A suspension of 31.8 g. (0.1 mole) of mercuric acetate in 300 cc. of methanol containing 10.1 g. (0.12 mole) of cyclohexene was shaken until the mercuric salt had dissolved. After a delay of eight days, the mixture was evaporated at 35° *in vacuo* to a volume of 50 cc. Crystallization finally occurred after a dry air stream was passed over the surface of this residue. This crude product (m. p. 54–60°) was wastefully crystallized repeatedly from hot petroleum ether (b. p. 60–70°, 4 cc. per gram) until a melting point of 63–64° was obtained.

Anal. Calcd. for $C_9H_{16}O_3Hg$: C, 29.1; H, 4.31. Found: C, 29.0; H, 4.31.

The acetoxymercurial can be made in better yield and greater quantity by stirring equimolar quantities of silver acetate and 1-α-chloromercuri-2-methoxycyclohexane in water for twelve hours. The filtrate is concentrated *in vacuo* after removal of silver chloride.

Attempted Reversal of Methoxymercuration.—A solution of 0.1 m. p. l. of 1-acetoxymercuri-2-methoxycyclohexane and 0.1 m. p. l. of acetic acid in methanol containing peroxide was analyzed by thiocyanate titration, after three-fold extraction with chloroform of an aliquot diluted into water. Titration after twelve days showed that less than 0.1% of inorganic mercury was present.

Cyclohexene–Mercuric Acetate Complex.—When 1.96 g. (0.024 mole) of cyclohexene and 3.19 g. (0.01 mole) of mercuric acetate were let stand eleven days, a residue remained after one hour of evaporation under 12 mm. This gummy residue was dissolved in 25 cc. of methanol. After three days, the solution was poured into dilute sodium chloride to yield 1.32 of α-1-chloromercuri-2-methoxycyclohexane (38% of theoretical).

[3a] All melting points are corrected.

[4] J. Bjerrum and H. Lund, *Ber.*, **64**, 210 (1931).

[5] T. Connor and G. F. Wright, THIS JOURNAL, **68**, 256–258 (1946).

The half-life of a methoxymercuration of 10^{-3} m. p. l. of mercuric acetate and cyclohexene in methanol is about thirty minutes. When the medium is changed to 1:1 methanol–dioxane the half-life is about four thousand minutes. This half-life is nearly six thousand minutes when 10^{-3} m. p. l. of methanol and of mercuric acetate are dissolved in 1:1 cyclohexene–dioxane.

Preparation of *l*-Mercuric Lactate.—A suspension of 216 g. (1 mole) of yellow mercuric oxide and 1 mole of a *l*(+)-lactic acid (85% solution, enantiomerically 96% pure) was shaken in the dark for thirty minutes to complete solution. After filtration the water was removed *in vacuo* at a temperature under 60°. The residue was treated with 1 liter of ethanol. After twelve hours, the crystalline mass was filtered off and crystallized from ethanol containing 1–2% lactic acid. The inactive salt is less soluble than the active one (1 g. of *l* per 2 cc. ethanol); (1 g. of *d,l* per 10 cc. ethanol), so fractional crystallization will purify the enantiomeric salt. We used a product melting at 126–128°, $[\alpha]_D$ +15° for a 5% solution in water. The yield was over 80% of the theoretical but losses occur, accompanied by precipitation of mercurous salt, if the preparation is exposed to much light. The *d,l*-mercuric lactate prepared in the same manner melted at 142–144°.

Asymmetric Synthesis of α-*l*-1-Lactomercuri-2-methoxycyclohexane.—The preparation of the crude product was identical with that reported previously for the corresponding inactive mercurial.[1] The mixture (3.58 g., m. p. 78–82°) was dissolved in 11 cc. of acetone, filtered and chilled to −10.6°, filtered and washed with cold acetone to leave 0.96 g. melting at 105–108°. This was crystallized from benzene–petroleum ether (b. p. 60–70°) to melt at 11.5.5°, $[\alpha]_D$ +46° as 5% solution in benzene; yield 1.3 g.

Anal. Calcd. for $C_{10}H_{18}O_4Hg$: C, 29.8; H, 4.56. Found: C, 29.8; H, 4.47.

The acetone filtrate from which the crude 115.5° diastereomer was separated was evaporated to dryness *in vacuo*, then redissolved in 4 cc. acetone and chilled to −5°. This yielded 1.62 g. melting at 72.5–73°. This was not analyzed but a 90% yield of *dd,ll*-1-chloromercuri-2-methoxycyclohexane could be isolated by dissolving it in water and treating with aqueous sodium chloride. The melting point of the chloromercurial was 113–115.5°, indicating that the fraction melting 72.5–73° is almost entirely a 1:1 mixture of *ddl* and *lll* diastereomers. It is probably a diastereomeric complex.

Preparation of Active α-1-Chloromercuri-2-methoxycyclohexane.—To a solution of 0.18 g. of the lactomercurial (m. p. 115.5°) in methanol was added a 5% potassium chloride solution. The precipitate weighed 0.14 g. and melted at 62–63°. Crystallization from 1 cc. of petroleum ether (b. p. 60–70°) raised this melting point to 63.5°. Rotation of a 5% solution in ethanol was $[\alpha]_D$ −40.00°.

Anal. Calcd. for $C_7H_{13}HgCl$: C, 24.1; H, 3.72. Found: C, 24.3; H, 3.93.

Preparation of Inactive β-1-Chloromercuri-2-methoxycyclohexane. A. Isomerization with Diphenylmercury.—A solution of 3.48 g. of α-1-chloromercuri-2-methoxycyclohexane in 25 cc. 95% ethanol containing 0.35 g. of diphenylmercury (0.001 mole) was refluxed for nineteen hours, then filtered hot to remove an insoluble precipitate which was principally phenylmercuric chloride (m. p. 248°, wt. 0.2 g.). The unchanged α-isomer (wt. 2.73 g., m. p. 104–105°) was filtered off and the filtrate treated with saturated aqueous mercuric chloride solution. The precipitated mixture weighed 0.44 g. and melted at 79–80°. This was dissolved in 3.9 cc. of acetic acid at 45°, filtered and diluted with 8 cc. of 5% sodium chloride. After three hours, this was filtered (wt. 0.20 g., m. p. 106–111°). Re-solution in alkali followed by acidification of *p*H 3 yielded the β diastereomer melting at 112°. Its identity was demonstrated by mixed melting point.

B. Isomerization with Hydrazine Hydrate.—A turbidity appeared when a solution of 4.11 g. (0.012 mole) of α 1-chloromercuri-2-methoxycyclohexane in 30 cc. ethanol was heated with 0.1 cc. of 100% hydrazine hydrate. After nine hours' reflux, the mixture was filtered to remove 0.74 g. of mercurous salt. Precipitation of the filtrate with dilute aqueous sodium chloride yielded 2.2 g. melting about 87°. When this was dissolved in 17 cc. of acetic acid and then treated with 17 cc. of 5% aqueous sodium chloride for seven hours, a 0.67-g. yield of β-chloromercurial, m. p. 110–111° resulted. Further purification by solution in alkali and acidification to *p*H 3 yielded, after two hours, 0.62 g., m. p. 114.1°.

A similar isomerization of the α bromomercurial gave a yield even poorer than that obtained with the chloromercurial.

C. Isomerization with Benzoyl Peroxide.—This catalyst is the most satisfactory of the three but the yields are sometimes as low as 10% and sometimes as high as 60%. This seems to be dependent on the rate of benzoyl peroxide decomposition.

Since the conversion was so unpredictable, a repetitive process for production of β isomer was used as follows: a solution of 8.91 g. (0.023 mole) of α-chloromercurial in 57 cc. of ethanol containing 0.010 g. benzoyl peroxide was refluxed for eight hours. The ethanol solution was decanted from the unchanged α isomer after cooling had induced crystallization. This supernatant solution, together with subsequent portions obtained in the same manner was poured into a flask containing 3 g. of mercuric chloride. After six repetitions of this process (5 cc. less ethanol being used in each cycle) the reaction mixture was filtered hot to remove suspended by-product and cooled to yield 1.78 g. of unchanged α isomer, m. p. 105–107°. The combined ethanol solution was precipitated by addition of 150 cc. of 5% aqueous sodium chloride solution. The precipitate weighed 3.76 g. and melted at 70.5–71°. It was dissolved in 30 cc. of acetic acid at 40°, filtered and diluted with 30 cc. of 5% aqueous sodium chloride. This yielded 2.06 g. of material melting at 100°. Subsequent experiments demonstrate that this melting point would have been higher (with consequent diminution in yield) if the aqueous suspension had stood longer than two hours. This was demonstrated by solution of 0.1 g. α isomer in 1 cc. of cold acetic acid and dilution with 1 cc. 2.5% sodium chloride solution after fifteen minutes. The voluminous precipitate which first appeared did not entirely disappear until three hours had elapsed. Another method, less efficient than the acetic acid purification, but undoubtedly owing to the same principle, involves crystallization from 6:4 water–ethylene chlorohydrin.

Further purification of the β isomer can be effected by solution in acetic acid (minimum 0.8 g. per cc. at 50°), followed by filtration and dilution with an equal volume of 5% aqueous sodium chloride. The recovery of material melting at 112.1° was 78%. Further purification either by this method or by direct crystallization from acetic acid (solution at 50°) is ineffective, but the melting point can be raised to a maximum of 113.7° by crystallization from boiling nitromethane (1 g. in 4 cc.). A mixed melting point with the α isomer was lowered to 85–86°.

Anal. Calcd. for $C_7H_{13}OHgCl$: C, 24.07; H, 3.75. Found: C, 24.06; H, 3.79.

Distillation of α and β 1-Chloromercuri-2-methoxycyclohexane.—Sublimation of mercurous salt accompanied the distillation of 3.48 g. of α-chloromercurial at 187° (8 mm.). The distillate weighed 2.8 g. and melted at 103–108°. A single crystallization from ethanol raised this to 115°, and a mixed melting point with the starting material was not lowered.

The β isomer distilled at approximately the same temperature and pressure. Recovery from 2.28 g. was 1.10 g., m. p. 107°. Crystallization from ethanol raised this to 113.6°.

Base Strength and Reactivity of α and β Methoxycyclohexylmercuric Ion.—To 0.1396 g. (4 × 10^{-4} mole) of each 1-chloromercuri-2-methoxycyclohexane was added 2 × 10^{-4} mole of aqueous alkali and the suspensions made up to 1 liter with conductivity water. Solution was complete in one week. The *p*H of the solution containing the β isomer was 5.2 according to Accutint paper, while that of the α isomer was 5.5. This slight difference in acidity could be checked against glass–calomel electrode, but potentiometric titration showed no difference.

When equimolar solutions of the α and β chloromercurials in ethanol were treated with ethanol solutions of iodine, the disappearance of color was about 5 times faster for the α than for the β isomer.

Preparation of Inactive β-1-Bromomercuri-2-methoxycyclohexane.—A solution of 3.48 g. (0.01 mole) of β-1-chloromercuri-2-methoxycyclohexane in 4 cc. of 10% aqueous sodium hydroxide was filtered and acidified with dilute hydrobromic acid to yield 3.56 g. of bromomercurial, m. p. 115-116.1°. This would not completely redissolve in 75 cc. of 2% aqueous sodium hydroxide. It was re-acidified with hydrobromic acid and filtered, m. p. 116.1°. Two crystallizations from 11 parts of ethanol failed to raise this melting point.

Anal. Calcd. for $C_7H_{13}OHgBr$: C, 21.37; H, 3.33. Found: C, 21.24; H, 3.25.

Preparation of Inactive α-1-Bromomercuri-2-methoxycyclohexane.—Great care was necessary in acidifying the alkaline solution of α-1-chloromercuri-2-methoxycyclohexane with hydrobromic acid since over-acidification would lead to decomposition. The 3.5 g. of bromomercurial re-dissolved easily in 75 cc. of 2% alkali. Re-acidification with hydrobromic acid yielded the crude bromomercurial, m. p. 112.6°. This was twice crystallized from 11 parts of boiling ethanol to melt at 114.2°.

Anal. Calcd. for $C_7H_{13}OHgBr$: C, 21.37; H, 3.33. Found: C, 21.6; H, 3.39.

Preparation of Active β-1-Chloromercuri-2-methoxycyclohexane.—A solution of 7.6×10^{-4} mole of active α-1-chloromercuri-2-methoxycyclohexane (0.265 g.) in 5 cc. ethanol containing 1×10^{-5} mole (3 mg.) of benzoyl peroxide was refluxed for one hundred and forty-five minutes, then cooled and filtered to remove 40 mg. of mercurous salt. The filtrate was treated with 5×10^{-4} mole of mercuric chloride (0.135 g.) in 15% aqueous sodium chloride solution. The ethanol was evaporated under reduced pressure and the remaining solid filtered off. It weighed 0.18 g. and melted at 64-66°. This 68% yield was dissolved in alkali, filtered and acidified to *p*H 1 with hydrochloric acid. After two hours 0.105 g. was filtered off and crystallized from 1.2 cc. of petroleum ether (b. p. 60–70°). The 0.084 g. thus purified melted at 65.5–66°; repetition of this crystallization raised the melting point to 66.2°. Its mixed melting point with the active α diastereomer was 52–53°. The rotation of a 6% solution of this active β isomer in ethanol was $[\alpha]_D$ +12.82°.

Anal. Calcd. for $C_7H_{13}OHgCl$: C, 24.05; H, 3.76. Found: C, 24.03; H, 3.82 (av.).

Summary

1. The rate of methoxymercuration decreases with time when the peroxide catalyst is present, because the peroxide is consumed by side-reaction.

2. Methoxymercuric acetate and not mercuric acetate is the substance that adds to cyclohexane during methoxymercuration, and the reaction is not reversible.

3. The labile and stable isomers of 1-chloromercuri-2-methoxycyclohexane have been redesignated α and β, respectively, and have been shown to be diastereoisomers.

4. The α diastereomer is presumed to hold its added substituents adjacent to each other, and methoxymercuration therefore occurs in the *cis* sense.

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A Method of Calculating the Boiling Points of Silicon Compounds

BY RICHARD N. LEWIS AND ARTHUR E. NEWKIRK

Several attempts have been made to find a method of correlating boiling points and molecular structure.[1] That of C. R. Kinney[2] is applicable to a wide variety of organic compounds. He developed the formula, B.p. (deg. C.) = $230.14 \sqrt[3]{\text{B.P.N.}} - 543$, where B.P.N. is "the sum of the individual atomic and group boiling point numbers expressing the structure of the molecule." The equation was derived from the known boiling points of the normal paraffin hydrocarbons. The atomic boiling point numbers for carbon and hydrogen were chosen as 0.8 and 1.0.

It is possible to extend this equation to most of the simple compounds of silicon. In applying it to the silicon hydrides it was necessary to assume that hydrogen attached to silicon had a value other than 1.0 as a constant value for silicon could not be obtained otherwise. The values which best fit the observed boiling points of the four known hydrides are 0.60 for hydrogen and 4.20 for silicon (Table IV).

Boiling point numbers for atoms and groups attached to silicon are obtained from the substituted monosilanes. The b.p.n. of a polysubstituted silane is in general an additive function of the group b.p.n.'s except that these must be modified according to the degree of substitution. Thus, the b. p. n. of a methyl group decreases in the series methylsilane (3.43), dimethylsilane (3.17), trimethylsilane (3.02), tetramethylsilane (2.74), and the b.p.n. of chlorine decreases in the series chlorosilane (5.05), dichlorosilane (4.17), trichlorosilane (3.59), silicon tetrachloride (3.39). However, alkyl groups and halogens in the same molecule do not seem to have much effect on each other. It is possible, therefore, to calculate the boiling points of the methylchlorosilanes (Table I).

The discrepancy in the case of trimethylchlorosilane, although small, seems large enough to warrant a special value for chlorine in the general

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[1] F. Klages, *Ber.*, **76**, 788 (1943); A. W. Francis, *Ind. Eng. Chem.*, **33**, 554 (1941); see discussion by G. Egloff, J. Sherman and R. B. Dull, *J. Phys. Chem.*, **44**, 730 (1940).

[2] C. R. Kinney, THIS JOURNAL, **60**, 3032 (1938); *Ind. Eng. Chem.*, **32**, 559 (1940); **33**, 791 (1941); *J. Org. Chem.*, **6**, 220, 224 (1941); **7**, 111 (1942).