[CONTRIBUTION FROM THE DEPT. OF CHEMISTRY, UNIVERSITY OF TORONTO]

OXYMERCURATION OF *cis*- AND *trans*-PROPENYLBENZENE

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Received March 3, 1954

Only one product, 2-chloromercuri-1-methoxy-1-phenylpropane (I), was isolated by Wright (1) when he methoxymercurated propenylbenzene, and the yield was only 21%. In view of the fact that oxymercuration has been shown to yield positional isomers (2, 3), and also that propenylbenzene is an equilibrium mixture of geometric isomers, it has seemed worthwhile to reinvestigate this oxymercuration, and to compare it with that of styrene (1) and 2-methyl-1-phenyl-2-propene (4).

The preparation of *cis*-propenylbenzene, by catalytic reduction of 1-phenyl-1-propyne, was first reported by Gredy (5), then by Campbell and O'Connor (6), and finally by Mixer, *et al.* (7). The latter workers also reported the isolation of *trans*-propenylbenzene by fractional distillation of a mixture of the geoisomers. In none of these reports were the melting points or freezing points utilized as criteria of geoisomeric purity.

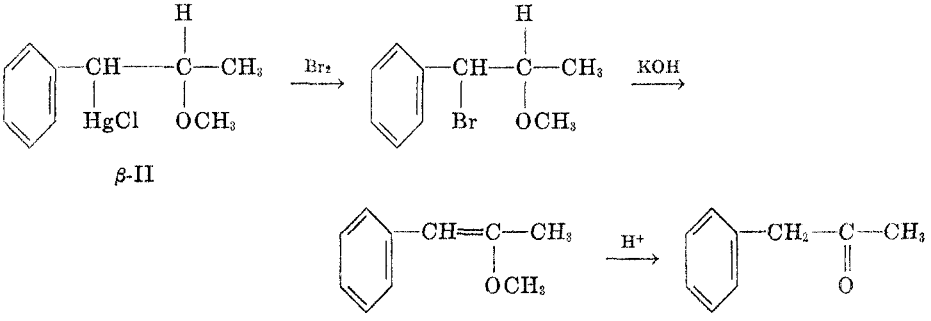
Consequently we have outlined here in detail our isolation of the two propenylbenzenes. The *trans* geoisomer used in our investigation was obtained from the equilibrium mixture (containing 14.2% *cis* geoisomer) firstly by fractional distillation and secondly by fractional crystallization of an ether solution at −80°. The pure *trans* geoisomer boils at 53.8–54° (8 mm.) and melts at −27.1° to −25.9°. Pure *cis*-propenylbenzene could not be obtained in this way. Instead it was obtained from 2-methyl-3-phenylpropenoic acid (8) by decarboxylation with copper chromite in quinoline followed by crystallization from dry ether at −80°. It boils at 52.1° (12 mm.) and melts at −60.5° to −59.0°. It forms a dibromide melting at 11.5–12.8° in contrast to the dibromide, m.p. 67°, obtained from the *trans* geoisomer (9).

When the pure *trans* geoisomer is treated with mercuric acetate in methanol the yield of the 2-chloromercuri-1-methoxy-1-phenylpropane (β-I) reported earlier (1) is 45–50%. Additionally a small amount (2.8%) of an isomer (β-II), melting at 30°, may be isolated from the mother liquor, but we have been unable to effect a further separation of mercurials. Both of the compounds obtained from *trans*-propenylbenzene should be classified as β-diastereomers since "α" and "β" designate mercurials derived, respectively, from *cis* and *trans* geometric isomers. The structure of the low-melting isomer (β-II) has been demonstrated in the manner used previously for the predominant product (β-I) melting at 95° (1). Thus the mercurial, β-II, is brominated, dehydrobrominated, and the resulting enol ether (III) hydrolyzed to 1-phenylpropanone-2 (IV), characterized as its 2,4-dinitrophenylhydrazone.

The low-melting isomer, β-II, may thus be designated as 1-chloromercuri-2-methoxy-1-phenylpropane, a positional isomer of β-I.

The conversion of 2-chloromercuri-1-methoxy-1-phenylpropane (β-I) to the

2,4-dinitrophenylhydrazone of propiophenone has been repeated, and the over-all yield has been found to be approximately the same as that of 1-phenylpropanone-2 dinitrophenylhydrazone from 1-chloromercuri-2-methoxy-1-phenylpropane (β-II). Furthermore these dinitrophenylhydrazones can be separated by chromatography on a bentonite column. Therefore in order to ascertain the ratio of positional isomers which are formed in the methoxymercuration of *trans*-propenylbenzene the entire reaction system has been submitted to the reaction series II → IV. The dinitrophenylhydrazones are then separated, into 60% of that derived from propiophenone and 40% of that from 1-phenylpropanone-2, and this is believed to be the prevalent ratio of I to II.



β-II

III

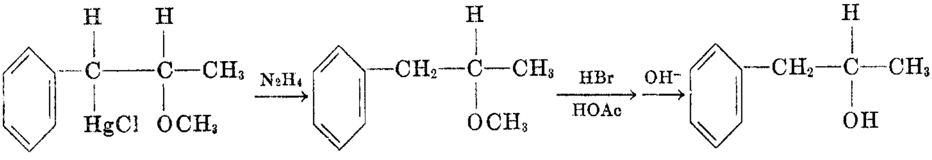
IV

We have not been able to shift this ratio to an extent that is observable within the precision of our determination. Mercuric benzoate in methanol behaves like mercuric acetate, and the latter salt gives minimal addition of mercury at the carbon to which phenyl is attached whether the alcoholic medium comprises methanol, cyclohexanol, or benzyl alcohol. Thus either steric effects are not involved or else the mercury atom is overwhelming in this respect.

In contrast to the methoxymercuration of *trans*-propenylbenzene the comparable reaction with the *cis* geoisomer is straight-forward. Two positional isomers can be separated cleanly by fractional crystallization. The one melting at 65° comprises 75–80% of the total and may be designated as α-1-chloromercuri-2-methoxy-1-phenylpropane (α-II) since it yields 1-phenylpropanone-2 (characterized as the semicarbazone) when it is subjected to the reactions shown in the formulation as β-II → IV. Only 5–10% of the product, m.p. 115°, has been isolated as α-2-chloromercuri-1-methoxy-1-phenylpropane (α-I). Its positional isomerism has been ascertained by the same series: bromination, dehydrobromination, and hydrolysis of the enol ether to propiophenone, identified as its semicarbazone.

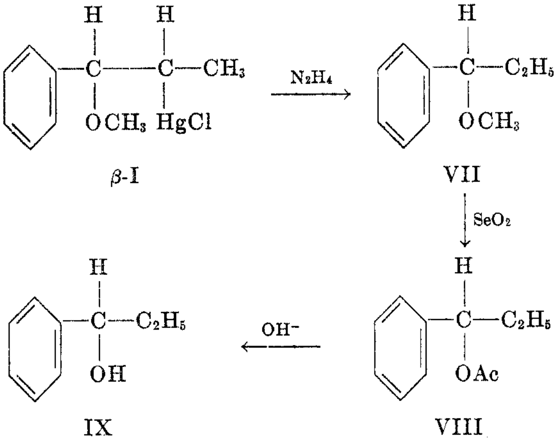
Further proof of these structures has been obtained by reduction of the mercuri linkage in each positional isomer. Thus α-1-chloromercuri-2-methoxy-1-phenylpropane (α-II) with excess hydrazine hydrate gives a 7% yield of 2-methoxy-1-phenylpropane (V).

V has been characterized as the phenylurethan of 1-phenyl-2-propanol (VI), obtained by hydrolysis of the 1-phenyl-2-bromopropane which is formed by ether splitting of V with hydrogen bromide. Reduction of β-2-chloromercuri-1-methoxy-1-phenylpropane (β-I) by hydrazine gives a 10% yield of 1-methoxy-1-phenylpropane (VII). Attempted conversion to 1-bromo-1-phenylpropane by hydrogen bromide leads largely to propenylbenzene, but the ether is split successfully by use of selenium dioxide in acetic anhydride.



α-II V VI

This novel scission probably is applicable only to benzyl ether types. The 1-acetoxy-1-phenylpropane (VIII) may be saponified to 1-phenyl-1-propanol (IX) which has been characterized as its α-naphthylurethan.

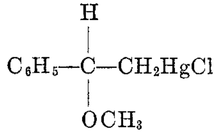
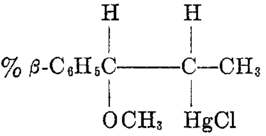
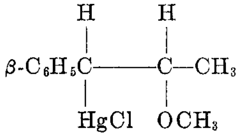
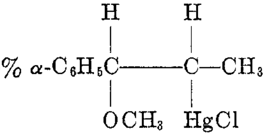
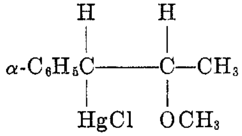
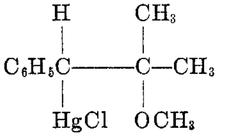


β-I VII VIII IX

The results of these methoxymercurations are shown in Table I together with those of styrene and 2-methyl-1-phenyl-2-propene. According to the ratio of positional isomers in this series of oxymercurations the large polar deformation of styrene is oppositely disposed to that of 2-methyl-1-phenylpropene, while *cis*-propenylbenzene resembles the latter compound most closely in this respect. On the other hand *trans*-propenylbenzene appears to be almost non-polar. These polar aspects derived on the basis of the orientation of the oxymercury addend are reflected in the rates of the several additions. These rates have been evaluated according to the relationship $kt = Ka\left[\frac{1}{a-x} - \frac{1}{a}\right] + (1 - K)\ln\frac{a}{a-x}$ previously derived (10), where x is concentration of the oxymercurial at time t in minutes, a is initial concentration of mercuric acetate in moles per liter, while K is an arbitrary constant dependent on the acetic acid formed in the reaction. Fig. 1 (plotting kt *versus* t) does not show the reaction rate of styrene, which is too fast to plot on this graph, but the rate of reaction of 2-methyl-1-phenyl-2-pro-

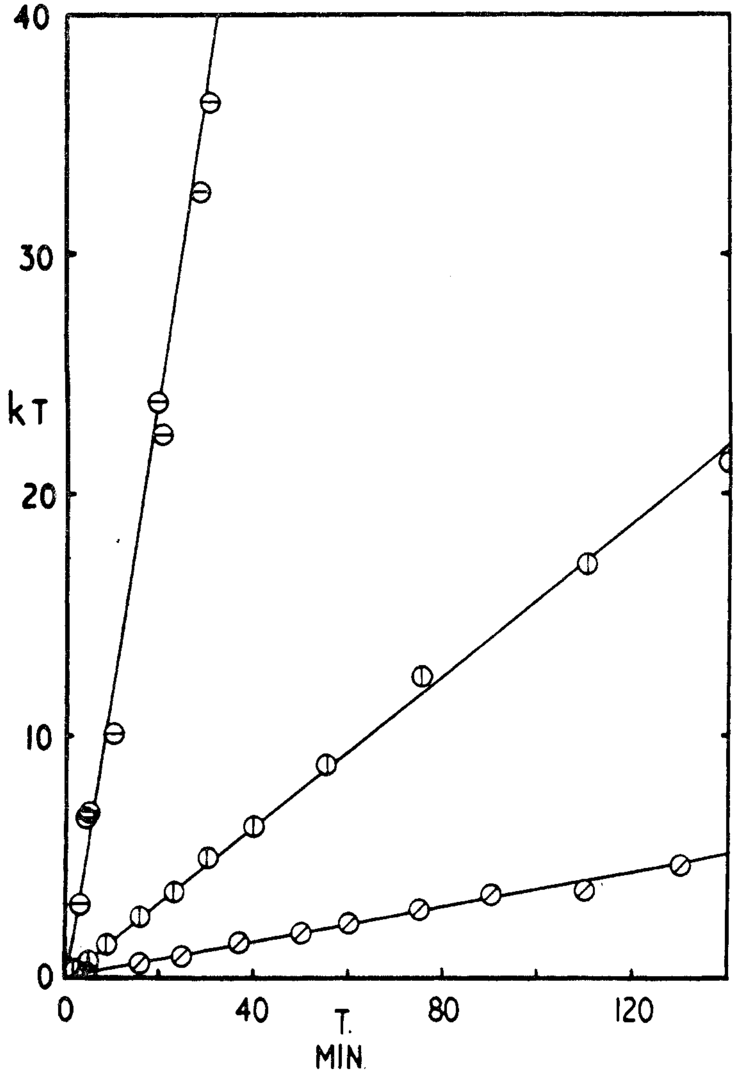
TABLE I

METHOXYMERCURATIONS OF STYRENES

Substance	Mercuration Products and Yields	
Styrene	100%  $C_6H_5\text{—}\overset{H}{\underset{OCH_3}{C}}\text{—}CH_2HgCl$	
trans-Propenylbenzene	60%  $\beta\text{-}C_6H_5\overset{H}{\underset{OCH_3}{C}}\text{———}\overset{H}{\underset{HgCl}{C}}\text{—}CH_3$	40%  $\beta\text{-}C_6H_5\overset{H}{\underset{HgCl}{C}}\text{———}\overset{H}{\underset{OCH_3}{C}}\text{—}CH_3$
cis-Propenylbenzene	15%  $\alpha\text{-}C_6H_5\overset{H}{\underset{OCH_3}{C}}\text{———}\overset{H}{\underset{HgCl}{C}}\text{—}CH_3$	85%  $\alpha\text{-}C_6H_5\overset{H}{\underset{HgCl}{C}}\text{———}\overset{H}{\underset{OCH_3}{C}}\text{—}CH_3$
2-Methyl-1-phenyl-2-propene		100%  $C_6H_5\overset{H}{\underset{HgCl}{C}}\text{———}\overset{CH_3}{\underset{OCH_3}{C}}\text{—}CH_3$

pene is closely comparable (k = 1.16 mole·liter·min.$^{-1}$). Since *cis*-propenylbenzene contains one less methyl group than 2-methyl-1-phenyl-2-propene its alkene linkage should be less subject to polar deformation. This greater orbital symmetry, reflected in the 85:15 ratio of 1-chloromercuri to 2-chloromercuri-1-phenylmethoxypropanes, seems also to be related to the lesser reaction rate of *cis*-propenylbenzene (k = 0.157 mole·liter·min.$^{-1}$) as compared with that of 2-methyl-1-phenyl-2-propene. This relationship continues to a yet-slower methoxymercuration rate of *trans*-propenylbenzene (k = 0.037 mole·liter·min.$^{-1}$). The 6:4 ratio in favor of 2-chloromercuri-1-methoxy-1-phenylpropane shows that polar deformation is slight in this *trans* geoisomer and thus completes the correlation between reaction rate and disposition of the adding groups.

Because of this correlation the addition of the elements of methoxymercuric acetate to an alkene such as propenylbenzene is more informative than the addition of hydrogen chloride. Both addends behave similarly in the sense that addition to propenylbenzene is slower than to styrene or to 2-methyl-1-phenyl-2-propene, but they differ in that positional isomers have not been discovered among the products from propenylbenzene obtained by addition of hydrogen chloride (11). This difference may be due to existence of an intermediate during the hydrogen chloride addition, but not during the oxymercuration.



RATE OF METHOXYMERCURATION

	K.	k.-MIN.$^{-1}$	CONC.
⊖ 1-PHENYL-2-METHYLPROPENE-1	10	1.16	0.1 M.
⦶ CIS-PROPENYLBENZENE	3.5	0.157	0.1 M.
⊘ TRANS-PROPENYLBENZENE	3.2	0.037	0.1 M.

FIGURE 1

EXPERIMENTAL

Melting points have been corrected against reliable standards. X-Ray diffraction patterns have been recorded in relative intensities [I/I₁] at d spacings in Å using Cu, Kα radiation, Ni filtered.

trans-Propenylbenzene. The dehydration of 1-phenyl-1-propanol was effected (12) in 77% yield, b.p. 52.0–53.5° (8 mm.), n_D^{20} 1.5495, m.p. −33° to −28°. This geoisomeric mixture may be purified by 13 crystallizations from dry ether (0.2 ml./g.) at −70°, leaving 15% as the *trans* isomer, n_D^{20} 1.55072, d_D^{20} 0.902, m.p. −27.1° to −25.9°, b.p. 53.0° (8 mm.); dibromide melts sharply at 67°. Alternatively fractional distillation under reduced pressure from a 50-plate column at 100:1 reflux ratio gives material having the same constants.

Methoxymercuration of trans-propenylbenzene. To a solution of 47.7 g. (0.15 mole) of mercuric acetate in 375 ml. of methanol was added 17.7 g. (0.15 mole) of pure *trans*-propenylbenzene. After nine hours the clear solution was poured into 1200 ml. of 2% aqueous sodium chloride. The precipitated gum was dissolved in 250 ml. of hot absolute ethanol. The cooled solution yielded 22.1 g. (38%) of crude β-2-chloromercuri-1-methoxy-1-phenylpropane, m.p. 86–96°. Crystallization from 150 ml. of hot ethanol raised this m.p. to 93–95°. The combined ethanolic liquors, by partial evaporation, could be made to yield 7–12% more of this product; alternatively the liquors are a source of β-1-chloromercuri-2-methoxy-1-phenylpropane if they are diluted to 500 ml. with absolute alcohol and seeded with this compound. The seeds may be obtained by diluting a portion of the liquors with methanol, then adding petroleum ether as a second phase, chilling to −80° and allowing to warm to 0° during three days.

Two days after seeding the ethanolic liquors at −80° the cold system was filtered to remove 15.3 g. (26%), m.p. 6–12°. After five low-temperature crystallizations from absolute ethanol (10 ml./g.) there remained 1.5 g. (2.8%) of β-1-chloromercuri-2-methoxy-1-phenylpropane, m.p. 29.5–30.9°.

Anal. Calc'd for $C_{10}H_{13}ClHgO$: C, 31.2; H, 3.40.
Found: C, 31.0; H, 3.42.

This satisfactory analysis of a mercurial is typical of those carried out using a modification of the Pregl micro carbon-hydrogen determination (13) and is in contrast to the penultimate analysis reported in this paper. This latter analysis was carried out in the ordinary Pregl tube. High hydrogen values are usually obtained when mercurials are analyzed by the unmodified procedure.

Phenylpropanone 2,4-dinitrophenylhydrazone. A solution of 0.50 g. (0.0013 mole) of β-1-chloromercuri-2-methoxy-1-phenylpropane in 5 ml. of absolute ethanol was treated with 0.21 g. (0.0013 mole) of bromine. After 30 minutes the colorless solution was poured into water and the whole extracted thrice with 5-ml. portions of ether. The extract, washed with 5 ml. of saturated aqueous sodium chloride and then with 5 ml. of water, was vacuum-evaporated (0.25 ml.). This residue was boiled for seven hours under reflux with 10 ml. of 25% methanolic potassium hydroxide, then poured into 60 ml. of water and extracted with four 5-ml. portions of ether. The extract, water-washed and dried with magnesium sulfate, was evaporated and the residue was dissolved in 1 ml. of methanol. To this solution was added 15 ml. of 2,4-dinitrophenylhydrazine reagent (14) and 0.32 g. (79%) of propiophenone 2,4-dinitrophenylhydrazone (m.p. 145–150°) precipitated. Crystallized from 7:3 ethanol-acetic acid to recover 0.27 g., it melted at 150–152° and was not depressed by a mixture melting point with an authentic sample, m.p. 152°.

2,4-Dinitrophenylhydrazones of phenylpropanone and propiophenone from trans-propenylbenzene methoxymercuration. Approximately the same yield (72%) of propiophenone dinitrophenylhydrazone was obtained by an identical procedure starting with β-I. Therefore the original gum obtained from methoxymercuration of *trans*-propenylbenzene was treated in the same manner as were the pure mercurials to give a mixture of dinitrophenylhydrazones, m.p. 141–165°. A solution of 20 mg. in 1 ml. of benzene was placed on "Volclay" bentonite (activated for 12 hours at 170°) in a column 16 x 350 mm. wet with benzene and was developed by 250 ml. of benzene into two bands which were separated mechanically. Elution of the top band with ethanol yielded 12 mg. of propiophenone dinitrophenylhydrazone, m.p. 189–191° upon evaporation. Similar treatment of the lower band yielded 8 mg. of phenylpropanone dinitrophenylhydrazone, m.p. 149–151°. The identity of each substance was authenticated by a mixture melting point.

cis-Propenylbenzene. A solution of 180 g. (1.11 moles) *trans*-2-methyl-3-phenylpropenic acid (8) in 600 ml. of dry quinoline and 5 g. of a copper chromite catalyst (15) was stirred under reflux while four more 5-g. portions of catalyst were added at hourly intervals. After five hours of subsequent reflux the system was acidified with dilute hydrochloric acid and the whole was filtered. Filter and filtrate were extracted with four 200-ml. portions of ether The combined extract was washed with three 500-ml. portions of 10% aqueous alkali, then with 200 ml. of water. The etherous layer, evaporated and then distilled, yielded 74.6 g. (57%) of crude *cis*-propenylbenzene, b.p. 50–52° (9 mm.), m.p. −65.0° to −62.8°. Redistillation through a 50-plate column yielded the pure *cis* geoisomer (80% recovery), b.p. 52.1° (12 mm.), m.p. −60.5° to −59.0°, n_D^{20} 1.5430, d_D^{20} 0.902. Comparison of the refractive index with that of *trans*-propenylbenzene shows that the equilibrium mixture contains 14.2% of the *cis* geoisomer.

1,2-Dibromo-1-phenylpropane from cis-propenylbenzene. A chilled solution of *cis*-propenylbenzene (0.50 g., 0.0042 mole) in 5 ml. of absolute ethanol was treated with 0.68 g. (0.0042 mole) of bromine. After the color had faded rapidly the solution was chilled to −80° and 1.02 g. (86%) of the dibromide separated out, m.p. 0–4°. After two recrystallizations from ethanol (3 ml./g.) at −80° the dibromide (0.5 g., 43% recovery) melted at 11.5–12.8°.

Anal. Calc'd for $C_9H_{10}Br_2$: C, 38.9; H, 3.63.
Found: C, 39.5; H, 3.88.

Methoxymercuration of cis-propenylbenzene. To a solution of 52.3 g. (0.164 mole) of mercuric acetate in 400 ml. of methanol was added 19.4 g. (0.164 mole) of *cis*-propenylbenzene. After seven hours the turbid system was filtered into 1200 ml. of 2% aqueous sodium chloride. After two days at 8° the crude crystalline product (56.8 g., 90%) melted at 45–55°. This product was dissolved in methanol (9 ml./g.), chilled to −80°, and seeded with crystals obtained as described in the oxymercuration of the *trans* geoisomer. The yield of α-1-chloromercuri-2-methoxy-1-phenylpropane, m.p. 62–63°, obtained in this way weighed 43 g. (76%). X-ray pattern: [10] 12.99; [4] 6.28; [3] 5.23, 4.72, 4.12, 3.87, 3.81, 3.10.

Anal. Calc'd for $C_{10}H_{13}ClHgO$: C, 31.2; H, 3.40.
Found: C, 31.1; H, 3.32.

When the combined mother liquors were evaporated to a 50-ml. volume and chilled, crude α-2-chloromercuri-1-methoxy-1-phenylpropane, m.p. 50–83° (10.2 g., 18%) was obtained. Four crystallizations from methanol (3 ml./g.) left 5.5 g. (10%), m.p. 114–115°.

Anal. Calc'd for $C_{10}H_{13}ClHgO$: C, 31.2; H, 3.40.
Found: C, 31.2; H, 3.44.

Each of these α-mercurials was subjected to the same reaction series: bromination, dehydrobromination, and acid hydrolysis which yielded phenylpropanone and propiophenone from the β-mercurials. These ketones were converted to the semicarbazones in 25 and 65% yield respectively and identified by their mixture melting points, 192° and 177°.

Reduction by hydrazine of β-2-chloromercuri-1-methoxy-1-phenylpropane. A mixture of 13 g. (0.034 mole) of β-2-chloromercuri-1-methoxy-1-phenylpropane and 300 ml. of 10% aqueous sodium hydroxide was boiled under reflux for four hours while 6.0 ml. (0.1 mole) of 85% hydrazine hydrate was added gradually. After 36 hours of subsequent reflux 50 ml. of steam-distillate was obtained from this system and treated with 25 ml. of ethanol and 1 g. of Raney nickel catalyst. This mixture absorbed 0.003 mole of hydrogen during a six-hour period. The reaction system was filtered into 100 ml. of water and this diluted filtrate was extracted with five 8-ml. portions of diethyl ether. The extract, washed with 20 ml. of water and dried with magnesium sulfate, was distilled, b.p. 61–66° (8 mm.), n_D^{20} 1.4888, 0.55 g. (11%).

This 1-methoxy-1-phenylpropane (16) (0.50 g., 0.0033 mole) was boiled four hours under reflux with 0.37 g. (0.0033 mole) of selenium dioxide and 1.0 ml. of acetic anhydride (b.p. 139–140°). The system was filtered to remove 0.21 g. (80%) of elemental selenium and the filtrate was neutralized with strong alkali and steam-distilled until 20 ml. had been collected. This distillate was boiled under reflux with 20 ml. of methanol and 1 g. of potassium hydroxide, then diluted with 80 ml. of water and extracted with four 10-ml. portions of diethyl ether. The dried extract, distilled, gave 0.27 g. (60%) of 1-phenylpropanol-1, b.p. *ca.* 95° (8 mm.). The α-naphthylurethane, m.p. 96.5–98°, was identical with an authentic sample according to mixture melting point. Identical results were obtained when authentic 1-methoxy-1-phenylpropane was subjected to this entire procedure.

Reduction by hydrazine of α-1-chloromercuri-2-methoxy-1-phenylpropane. A mixture of 15 g. (0.039 mole) of α-1-chloromercuri-2-methoxy-1-phenylpropane, 100 ml. of 5% aqueous sodium hydroxide, and 5.9 ml. (0.10 mole) of 85% hydrazine hydrate was boiled under reflux for seven hours, then 50 ml. was steam-distilled from it. After addition of 50 ml. of methanol and 1 g. of Raney nickel catalyst to this distillate it was found to absorb 0.0025 mole of hydrogen. After filtration from the nickel the system, diluted with 150 ml. of water, was extracted with five 10-ml. portions of diethyl ether. This extract, water-washed, dried and distilled, gave 0.44 g. (7.5%) of 2-methoxy-1-phenylpropane, b.p. 69–75° (11 mm.), n_{D}^{20} 1.4931.

This 2-methoxy-1-phenylpropane (0.40 g., 0.0027 mole) was heated for six hours at 90–100° with 1.76 ml. (0.012 mole) of 40% hydrobromic acid and 10 ml. of acetic acid, then neutralized and steam-distilled. After 0.5 g. of sodium hydroxide had been added to the 20 ml. of steam-distillate, the system was refluxed for two hours, then cooled and extracted with five 7-ml. portions of diethyl ether. The extract, water-washed, dried, and distilled gave 0.25 g. (68%) of 1-phenyl-2-propanol, b.p. *ca.* 98° (8 mm.). The melting point of its phenylurethan (86.5–87.5°) was not depressed by admixture with an authentic sample (m.p. 88°). Identical results were obtained when authentic 1-phenyl-2-propanol (17) was subjected to this procedure.

Kinetic studies of methoxymercuration. All the experiments were carried out at 25 ± 0.1° at concentrations 0.1 *molar* in alkene and in mercuric acetate. The methanol was purified by Lund and Bjerrum's method (18). Mercuric acetate was twice crystallized from acetic acid, washed with dry peroxide-free diethyl ether, and vacuum-dried. Pure 2-methyl-1-phenyl-1-propene was obtained by steam-distillation of a dilute hydrochloric acid solution of 1-chloromercuri-2-methoxy-2-methylpropane, b.p. 62–63° (8 mm.), m.p. −50.5° to −49.2° (also −57.8° to −56.8°), n_{D}^{20} 1.5391, d_{D}^{20} 0.896. Styrene was obtained by distillation of the best grade of the Eastman Kodak chemical. The analytical technique followed than described previously (1) and satisfactory rate constants were obtained for each alkene except styrene, the methoxymercuration of which was complete in three minutes.

β-4-Chloromercuri-1-benzyloxy-1-phenylpropane. A suspension of 1.59 g. (0.005 mole) of mercuric acetate and 1.18 g. of *trans*-propenylbenzene in 6 ml. of benzyl alcohol (m.p. −15.3° to −14.2°) became almost clear during 18 hours. The excess of benzyl alcohol was distilled, b.p. below 60° (0.005 mm.); the residue was dissolved in methanol and poured into 35 ml. of 3% aqueous sodium chloride. After three days the gum partially crystallized; when it was dissolved in 40 ml. of hot methanol, 0.54 g. (23%) of crystalline solid, m.p. 127–130°, separated upon cooling. Two more crystallizations from methanol (40 ml./g.) gave 0.4 g., m.p. 128.5–130°.

Anal. Calc'd for $C_{16}H_{17}ClHgO$: C, 42.2; H, 3.68.
Found: C, 41.8; H, 3.91.

When this product was brominated, dehydrobrominated, and hydrolyzed as described previously it yielded exclusively propiophenone, identified as its semicarbazone.

β-2-Chloromercuri-1-cyclohexyloxy-1-phenylpropane. A mixture of 1.59 g. (0.005 mole) of mercuric acetate, 1.18 g. (0.01 mole) of *trans*-propenylbenzene, and 0.1 ml. of boron fluoride etherate in 12 ml. of cyclohexanol was shaken for four hours, then filtered from 0.18 g. of mercurous salt. The volatile materials were evaporated at 50° (0.3 mm.) leaving a residue which was dissolved in methanol. This solution, filtered into 35 ml. of 3% aqueous sodium chloride precipitated a gum which was dissolved in 35 ml. of methanol. Chilling of this solution to −80° during two days precipitated 0.32 g. (14%) of crystals, m.p. 86–89°. After two crystallizations from ethanol (30 ml./g.) 0.24 g. was recovered, m.p. 88.6–89.6°.

Anal. Calc'd for $C_{15}H_{21}ClHgO$: C, 39.7; H, 4.67.

Found: C, 40.1; H, 4.66.

Propiophenone was obtained from this compound when it was carried through the bromination—dehydrobromination—hydrolysis technique.

SUMMARY

1. Both *cis*- and *trans*-propenylbenzene have been found, upon methoxymercuration, to give mixtures of positional isomers.

2. It is believed that the ratio of isomers reflects the polar deformation in these geometric alkenes, especially since the rate of oxymercuration is slowest for *trans*-propenylbenzene which seems to be the most symmetrical of the series styrene:propenylbenzenes:2-methyl-1-phenyl-2-propene.

TORONTO 5, CANADA

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