[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

Rearrangement of Unsaturated 1,4-Glycols. II. *cis* and *trans* Forms of 2,5-Dimethyl-3-hexene-2,5-diol

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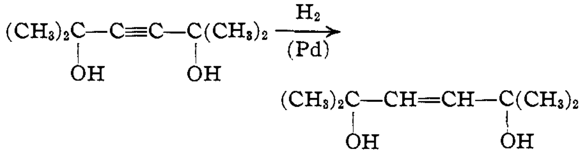
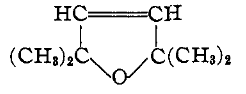
In an earlier investigation it was found that 2-methyl-2-butene-1,4-diol undergoes 1,4-dehydration readily under the influence of acidic reagents to give tiglic aldehyde.[1] This transformation of an unsaturated 1,4-diol is related to the well-known dehydration rearrangements of saturated 1,2-glycols and it seemed of interest in this connection to examine the behavior of 2,5-dimethyl-3-hexene-2,5-diol (I), which is a vinylene homolog (vinylog) of pinacol. Owing to the presence of the substituted ethylenic system in the unsaturated 1,4-diol, this example also affords an opportunity to observe the effect of differences in spatial configuration on the course of reaction.

2,5-Dimethyl-3-hexene-2,5-diol (I) was prepared first by Salkind[2] by partial hydrogenation of the corresponding acetylenic diol, obtained from acetylene-*bis*-magnesium bromide and acetone, using colloidal palladium as catalyst. By fractional crystallization the reduction product was separated into two isomeric glycols of the formula $C_8H_{16}O_2$: α-diol, m. p. 76.5–77°, and β-diol, m. p. 69–69.5°. On heating with dilute sulfuric acid, or with various dehydrating agents, either glycol gave the same product: a volatile liquid (b. p. 102°) of camphor-like odor, which corresponded to the formula $C_8H_{14}O$ and showed the reactions of an unsaturated compound. This substance was designated as the γ-oxide and formulated as 2,2,5,5-tetramethyl-2,5-dihydrofuran (II), although no definite evidence was presented to confirm this constitution. The possibility of forming an ethylene oxide (III) or of pinacolone rearrangement to give an unsaturated ketone (IV) was not considered.

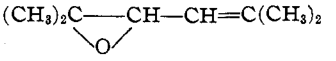


$$(CH_3)_2\underset{OH}{C}-C\equiv C-\underset{OH}{C}(CH_3)_2 \xrightarrow[(Pd)]{H_2} (CH_3)_2\underset{OH}{C}-CH=CH-\underset{OH}{C}(CH_3)_2$$

(I)



(II)



(III)

$(CH_3)_3C-CH=CH-COCH_3$

(IV)

Salkind observed that the α-diol seemed to undergo dehydration more rapidly than the β-diol, and on this basis assigned the *cis*-configuration to the α-diol and the *trans*-configuration to the β-diol. Subsequently Roth and Muller[3] determined the heats of combustion and found a higher value for the isomer of lower melting point (β-diol). Since the *cis*-isomer of this type of compound is usually found to have the lower melting point and greater heat of combustion, Salkind's assignment of configurations appeared to be of doubtful validity.

In 1928 Bourguel[4] reported the isolation of a new isomeric form of the ethylenic glycol (γ-diol, m. p. 101°), which he obtained by reducing 2,5-dimethyl-3-hexyne-2,5-diol with sodium and methanol. Bourguel considered the γ-diol to be the true *trans*-isomer and Salkind's β-diol to be the true *cis*-isomer; the α-diol of Salkind was found to be a solid solution of 83% β-diol and 17% γ-diol. By mixing the β- and γ-diols in the correct proportions he was able to prepare a solid solution corresponding to Salkind's α-diol, and showed that the α-diol underwent dehydration to the γ-oxide only to the extent of the β-diol content (83%). Bourguel's assignment of the *cis*-configuration to the β-diol was based upon its rapid and essentially quantitative conversion to the γ-oxide, but no additional evidence was brought forward to establish the structure of this dehydration product. The γ-diol was found to give on dehydration an unsaturated compound, b. p. 124–126°, which was believed to be 2,5-dimethyl-1,3,5-hexatriene (V) although no analysis was

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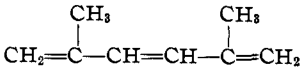
[1] Shepard and Johnson, THIS JOURNAL, **54**, 4386 (1932).

[2] Salkind, *Chem. Zentr.*, **85**, I, 1813 (1914); **94**, III, 1390 (1923); *Ber.*, **56**, 187 (1923).

[3] Roth and Muller, *ibid.*, **60**, 643 (1927).

[4] Bourguel and collaborators, *Compt. rend.*, **180**, 1753 (1925); **187**, 383, 663 (1928); *Bull. soc. chim.*, [4] **45**, 1084 (1929); [4] **47** 173 (1930).



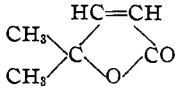
$$CH_2=\overset{\overset{CH_3}{|}}{C}-CH=CH-\overset{\overset{CH_3}{|}}{C}=CH_2$$

(V)

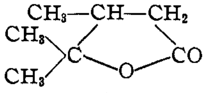
reported. In later work Salkind and Sabojev[5] reported the conversion of the α- and β-diols into stereoisomeric dibromides and investigated the behavior of the dibromides on hydrolysis. In spite of Bourguel's evidence to the contrary they maintained the view that the β-diol must have the *trans* configuration.

We have undertaken to establish the configurations of the isomeric 2,5-dimethyl-3-hexene-2,5-diols in an unequivocal manner, independent of relationship to the γ-oxide, by synthesis of an authentic *cis*- or *trans*-form from maleic or fumaric acid. For this purpose methyl maleate was allowed to react with an excess of methylmagnesium bromide at −30° and the products were not allowed to come into contact with acids at any point. From this reaction the pure β-diol, m. p. 69–70°, was obtained in 30–35% yields and no other ethylenic diol could be detected. This mode of synthesis indicates clearly that the β-diol is the *cis* form, in accord with Bourguel's assignment of configurations.

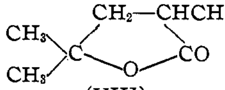
In the reaction of methyl maleate with methylmagnesium bromide there was formed, in addition to the β-diol, an accessory liquid product in an amount corresponding to about 50% of the original ester.[6] When the reaction was carried out at 25° instead of −30°, very little of the β-diol was obtained and a larger proportion of the ester was converted into the liquid product. The latter was found to contain about 15% of an unsaturated lactone which was shown definitely to be γ,γ-dimethylcrotonolactone (VI). The main portion of the liquid product consisted of a saturated compound of the formula $C_7H_{12}O_2$, which appears to be a trimethyl-γ-butyrolactone (VII or VIII) formed by 1,4-addition of one molecule of the Grignard reagent to the α,β-unsaturated carbonyl system and reaction of the other ester group in the normal way.



(VI)



(VII)



(VIII)

The reaction of methyl fumarate with methylmagnesium bromide was carried out at temperatures ranging from −40 to 0° but no ethylenic diol could be isolated from the reaction mixtures. A liquid product was obtained in amounts corresponding to as much as 85% of the fumaric ester, and this material was found to contain the same lactones that had been produced from methyl maleate.

Although the configuration of the *trans*-diol could not be established by synthesis from methyl fumarate, the experimental evidence now available indicates that the γ-diol, m. p. 101°, is the true *trans*-form. This view was tested further by preparing the γ-diol according to Bourguel's method and comparing the dielectric constants of the β- and γ-diols. In the *trans*-diol the moments of the individual hydroxyl groups are disposed so that they tend to offset each other; consequently the dielectric constant should be distinctly lower than that of the *cis*-diol. Measurements of the β- and γ-diols, using 1% solutions in benzene, showed that the γ-diol had a lower dielectric constant as had been anticipated.[7] All of the new experimental evidence from the present study refutes the conclusions of Salkind and confirms the configurations assigned by Bourguel: namely, that the β-diol (m. p. 69–69.5°) is the *cis*-form and the γ-diol (m. p. 101°) is the *trans*-form.

On warming with 15% sulfuric acid the *cis*-diol was converted almost quantitatively into an unsaturated liquid of the formula $C_8H_{14}O$, which agreed in all respects with the γ-oxide described by Salkind and may be represented by formula II, III or IV. Treatment of the *cis*-diol with concentrated hydrochloric acid at −10°, and subsequent neutralization with pyridine, likewise gave the γ-oxide. The constitution of the γ-oxide was shown definitely to be 2,2,5,5-tetramethyl-2,5-dihydrofuran (II) in the following manner. On hydrogenation at 25° in the presence of Raney nickel, the γ-oxide took up two atoms of hydrogen to give a saturated compound (2,2,5,5-tetramethyltetrahydrofuran) which was transformed by

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(5) Salkind and Sabojev, *Ber.*, **62**, 2169 (1929).

(6) The reaction of methyl maleate and methyl fumarate with methylmagnesium iodide was reported by Purdie and Arup, *J. Chem. Soc.*, **97**, 1537 (1910). Operating at about 50° and using the customary treatment with acid, they obtained only liquid products from which no definite compound could be isolated. Using phenylmagnesium bromide they obtained from methyl maleate a 10% yield of 2,2,5,5-tetraphenyl-2,5-dihydrofuran, but from methyl fumarate no definite product was secured.

(7) We are indebted to Mr. L. G. Joyner for measurements of the dielectric constants.

hydrogen bromide into 2,5-dibromo-2,5-dimethylhexane, m. p. 67.5–68.5°. The latter showed no depression of the melting point when mixed with an authentic specimen of the dibromide prepared from synthetic 2,2,5,5-tetramethyltetrahydrofuran, which was obtained from the known 2,5-dimethylhexane-2,5-diol.[8]

The *trans*-diol behaved quite differently from the *cis*-diol toward acids. On boiling for three minutes with 15% sulfuric acid (containing some acetic acid to dissolve the diol), the *trans*-isomer gave no trace of the γ-oxide but was converted completely to a mixture of unsaturated hydrocarbons. About half of the product was a liquid of the formula C_8H_{12}, b. p. 128°, which reacted with maleic anhydride to give a crystalline addition product, m. p. 135–136°, and polymerized with great rapidity. The constitution of this unsaturated hydrocarbon was not definitely established but from its mode of formation it is presumably the *trans*-form of 2,5-dimethyl-1,3,5-hexatriene (V). The remainder of the dehydration product consisted of a high-boiling fraction (b. p. 145–147° (18 mm.)) corresponding to the formula $C_{16}H_{24}$, which is evidently a dimer of the triene.

When a solution of the *trans*-diol in the 15% sulfuric acid reagent was allowed to stand at 25° for two days, about 50% was recovered unchanged and the portion that had reacted was converted mainly into the hydrocarbon C_8H_{12}. This was accompanied by a small fraction which may have been the intermediate dehydration product, 2,5-dimethyl-3,5-hexadiene-2-ol, reported by Bourguel. The material decomposed on heating to give the hydrocarbon C_8H_{12} and polymers.

Treatment of the *trans*-diol with concentrated hydrochloric acid at −10° for a long period, followed by neutralization with pyridine, produced neither the γ-oxide nor unsaturated hydrocarbons. The product was a liquid (b. p. 175–180°) having the composition $C_8H_{14}Cl_2$, which corresponds to the replacement of both hydroxyls of the diol by chlorine.

The behavior of the *cis*- and *trans*-diols toward sulfuric and hydrochloric acids shows that the spatial configuration of these unsaturated glycols exerts a very marked and clear cut influence on their chemical reactivity and on the course of reaction. The differences observed in these open-chain structures are no less marked than those observed in the dehydration of the *cis*- and *trans*-forms of 1,2-dimethylcyclohexane-1,2-diol, and in other cycloalkane derivatives.[9]

Experimental

Methyl Maleate and Methylmagnesium Bromide: *cis*-2,5-Dimethyl-3-hexene-2,5-diol (I).—A solution of 72 g. (0.5 mole) of methyl maleate in 150 cc. of anhydrous ether was added slowly with stirring to a solution of 3 moles of methylmagnesium bromide in 1500 cc. of anhydrous ether, while the temperature of the reaction mixture was kept at −30 to −35°. The mixture was allowed to stand with stirring until the temperature had risen to +10° and then poured with stirring into 2 liters of an ice-cold saturated solution of ammonium chloride. The use of acids at this point was found to be objectionable. The ether layer was separated and the aqueous solution extracted three times with a total of 1200 cc. of ether. The combined ether solutions were dried and the solvent was removed by distillation from a steam-bath. The residual oily liquid was dissolved in 100 cc. of petroleum ether (60–70°) and cooled to −10° in a freezing mixture. The diol crystallized on standing and was separated by filtration. After recrystallization from petroleum ether the yield was 26 g. (35% of the theoretical); m. p. 69–70°. This product is identical with the lower melting diol obtained by Salkind (β-diol, m. p. 69°) and from the method of preparation must be the *cis*-isomer.

Examination of Accessory Products.—The petroleum ether filtrates from the crystallizations of the *cis*-diol were distilled under reduced pressure and gave 45 g. of a liquid which was thought at first to be a pure individual: b. p. 85° (6 mm.), 103° (18 mm.), 207° (750 mm.); d^{25}_4 0.980; n^{25}_D 1.4368. The liquid took up bromine in carbon tetrachloride solution and decolorized alkaline permanganate solution, but failed to react with carbonyl reagents. The compound could be saponified with hot alkali but no alcohol was produced. On the basis of these observations and the method of formation, the compound appeared to be γ,γ-dimethylcrotonolactone (VI) but the elementary analysis disclosed that the material corresponded more closely to a trimethylbutyrolactone (VII).

Anal. Calcd. for $C_6H_8O_2$ (VI): C, 64.30; H, 7.14. Calcd. for $C_7H_{12}O_2$ (VII): C, 65.62; H, 9.23. Found: C, 65.09, 65.23; H, 9.53, 9.32.

On hydrogenation with Raney nickel catalyst at 25° and 6.5 atmospheres the liquid took up only about 0.15 mole of hydrogen, and the resulting product differed but slightly from the original material in physical properties: m. p. 0–5°, b. p. 207° (745 mm.), d^{25}_4 0.9928, n^{25}_D 1.4343. The specific refraction of the hydrogenated product (r_D 2.66) agreed with that calculated for a trimethylbutyrolactone, and was higher than the value calculated for the dimethylbutyrolactone (r_D 2.59) that would be formed by hydrogenation of VI.

The product of hydrogenation on treatment with alcoholic ammonia gave a crystalline material melting at 88–104°, which obviously was not a pure individual. After repeated fractional crystallizations from benzene this was separated into two amides: A, m. p. 98.5–99.5°; B, m. p.

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[8] Pogorzelsky, *Chem. Zentr.*, **70**, I, 773 (1899); **75**, I, 578 (1904).

[9] Bartlett and Pockel, THIS JOURNAL, **59**, 820 (1937).

104–106°. The lower melting amide, A, was shown to be γ-hydroxyisocaproic amide by comparison with an authentic specimen obtained by the action of ammonia on synthetic γ,γ-dimethylbutyrolactone. The authentic γ-hydroxyisocaproamide (see below) melted at 98–99°, and when mixed with an equal amount of the amide A melted at 98.5–99°. The amide B showed a marked depression of the melting point (m. p. 85–102°) when mixed with the synthetic amide.

We have not established the constitution of the amide B or of the trimethylbutyrolactone from which it is derived. Considerations based on the mechanism of formation of the saturated lactone lead us to believe that it is β,γ,γ-trimethylbutyrolactone (VII), which could be formed either by 1,4-addition of methylmagnesium bromide to γ,γ-dimethylcrotonolactone (VI) *or* by 1,4-addition of the Grignard reagent to methyl maleate followed by reaction of only one of the ester functions. Since the same trimethylbutyrolactone was obtained from methyl fumarate it appears that a *trans* configuration of the original ester is not an obstacle to the ultimate formation of a cyclic product.

γ,γ-Dimethylbutyrolactone.—A solution of one equivalent of methylmagnesium bromide was added slowly with efficient stirring to a solution of 107 g. of *n*-butyl levulinate in 100 cc. of anhydrous ether, maintained at −35°. After hydrolysis with cold ammonium chloride solution, the ether layer was separated and the aqueous layer extracted with two 100-cc. portions of ether. The combined ether solutions were dried with anhydrous magnesium sulfate, and the ether removed by distillation on a steam-bath. To the oily residue (crude *n*-butyl γ-hydroxyisocaproate) was added 250 cc. of a 15% solution of potassium hydroxide in 95% ethanol. The mixture was refluxed for two hours, cooled to 25°, and diluted with 200 cc. of water. The alkaline solution was extracted twice with 100-cc. portions of ether to remove non-acidic products, then sulfuric acid was added cautiously with cooling until the solution was slightly acidic to litmus. The free γ-hydroxyisocaproic acid spontaneously forms the lactone, which was removed by extracting the mixture three times with 150-cc. portions of ether. Distillation gave 20 g. (30% yield) of pure γ,γ-dimethylbutyrolactone (γ-isocaprolactone): colorless liquid, b. p. 87° (14 mm.), 207° (750 mm.), n^{25}_{4} 1.4320, m. p. 9–9.5°.

A sample of 2.0 g. of the lactone was treated with a mixture of 10 cc. of concd. aqueous ammonia and 10 cc. of ethanol. The solution was allowed to evaporate almost to dryness at room temperature, and treated again with aqueous ammonia and ethanol. Evaporation gave white crystals of γ-hydroxyisocaproamide, which were recrystallized from benzene. The purified product weighed 1.2 g. and melted at 98–99°. The recorded m. p. of this amide is 101°.[10]

Methyl Fumarate and Methylmagnesium Bromide.—This reaction was carried out by adding the solid methyl fumarate (m. p. 102–103°) to about 6 equivalents of methylmagnesium bromide, using various temperatures of reaction between −40 and 0°. Although the conditions of reaction and the method of working up the mixture were varied in several ways, none of the desired *trans*-diol could be isolated and we believe that none was formed. The reaction mixtures invariably contained unchanged methyl fumarate, unidentified complex products (presumably polymeric substances), and a liquid boiling at 103° (18 mm.). This liquid had the same physical constants, chemical reactions, and composition as the mixture of lactones obtained from methyl maleate. Hydrogenation of the liquid product and subsequent treatment with ammonia gave the same amides, A and B, described above.

***trans*-2,5-Dimethyl-3-hexene-2,5-diol** (I).—The γ-diol was prepared by reduction of the acetylenic glycol, 2,5-dimethyl-3-hexyne-2,5-diol, which was obtained by the reaction of acetylene-*bis*-magnesium bromide with acetone. Slight modifications of the reduction procedure of Bourguel increased the yield of the γ-diol from 30 to 65%. The purified product formed monoclinic crystals from toluene; m. p. 101.5–102.5°.

Dielectric Constants of the *cis*- and *trans*-Diols.[7]—Solutions of 4.937 g. of each isomer in 500 cc. of thiophene-free benzene were used for the measurements. Accurate results were not sought, since reasonably good values were considered to be sufficient. The results were as follows:

Benzene alone (reported previously 2.28)	2.27
Solution of *trans* diol	2.31
Solution of *cis* diol	2.33

The difference in dielectric constant between the solutions of the *cis* and *trans* isomers was much greater than experimental error, and is quite significant in view of the fact that the solutions were quite dilute (about 1%) and that a highly sensitive apparatus was not used. These results confirm the previous assignment of configuration.

Dehydration of the *cis*-Diol. (a) **With Sulfuric Acid.**—To 80 cc. of 15% sulfuric acid was added 5.0 g. of the *cis*-diol, m. p. 69–70°, and the whole was refluxed for two hours. An equal volume of water was added, the mixture was distilled, and the organic products were extracted from the distillate with two 100-cc. portions of ether. The ether extracts were dried over anhydrous calcium chloride and the ether removed by fractional distillation. The product (4.0 g.) was a colorless liquid with camphor-like odor; b. p. 100–102° (747 mm.), n^{25}_{D} 1.4078, $n^{17.5}_{D}$ 1.4101. This corresponds to the γ-oxide obtained by Salkind, which he describes as follows: b. p. 102–103°, $d^{17.5}_{4}$ 0.8093, $n^{17.5}_{D}$ 1.4093, MR_D 38.55, calcd. for $C_8H_{14}O$.

Anal. Calcd. for $C_8H_{14}O$: C, 76.12; H, 11.45. Found: C, 76.00; H, 11.32.

(b) **With Hydrochloric Acid.**—To 20 cc. of concentrated hydrochloric acid cooled to −10° was added 5.0 g. of the *cis* diol and the flask well shaken. After the mixture had been allowed to stand at −10° for three days, 20 cc. of pyridine was added slowly with cooling. The mixture was adjusted to slight acidity with dilute hydrochloric acid and extracted with three 25-cc. portions of ether. The combined extracts were dried over anhydrous calcium chloride and fractionally distilled. The product (2.8 g.) was a colorless liquid with the characteristic camphor-like odor; b. p. 99–102°, n^{25}_{D} 1.4074. This liquid is the γ-oxide and is identical with that from the sulfuric acid dehydration.

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(10) Strom, *J. prakt. Chem.*, [2] **48**, 220 (1893).

The liquid dehydration product (γ-oxide) reacted with bromine in carbon tetrachloride solution and with alkaline permanganate solution. It failed to react with phenylhydrazine, 2,4-dinitrophenylhydrazine, semicarbazide, hydroxylamine, ammonia, or 10% sodium hydroxide solution. These tests are in agreement with the 2,2,5,5-tetramethyl-2,5-dihydrofuran structure (II) assigned by Salkind, and the observed molecular refraction (38.5) accords reasonably well with the value calculated for this structure (38.1).

On hydrogenation at 6.5 atmospheres and 25°, with Raney nickel catalyst, the γ-oxide was converted to a saturated liquid product which retained the camphor-like odor: b. p. 125–128°, n^{25}_D 1.4131, d^{25}_4 0.8241. The reduced product was shown definitely to be 2,2,5,5-tetramethyltetrahydrofuran (2,5-dimethyl-2,5-epoxyhexane) by conversion to the solid derivative, 2,5-dibromo-2,5-dimethylhexane.

The reduction product from the γ-oxide was dissolved in petroleum ether (30–60°) and dry hydrogen bromide was bubbled into the solution. A crystalline solid, reported to be the bromohydrin, soon separated from the solution; this material was not suitable as a solid derivative for identification since it decomposed rapidly on standing. Continued action of hydrogen bromide (twelve hours) converted the crystalline solid to a heavy oil, most of which finally dissolved. The petroleum ether was decanted from the remaining heavy oil and allowed to evaporate at room temperature. The dark, solid residue was mixed with a little potassium carbonate, water was added, and the crystalline product washed with water. The crude dibromide was recrystallized from petroleum ether (60–70°) and finally sublimed in vacuum; m. p. 67.5–68.5°. The melting point was not depressed by admixture with authentic 2,5-dibromo-2,5-dimethylhexane, m. p. 68–69°, obtained by a similar procedure from synthetic 2,5-dimethylhexane-2,5-diol and 2,2,5,5-dimethyltetrahydrofuran.

2,5-Dibromo-2,5-dimethylhexane.—A sample of authentic 2,5-dimethylhexane-2,5-diol was prepared by adding diethyl succinate (0.7 mole) to an excess of methylmagnesium bromide (2.9 moles) at −20°. The reaction mixture was poured onto ice-cold ammonium chloride solution and the product was finally crystallized from petroleum ether (90–100°). The purified material weighed 58 g. (55% yield) and melted at 88.5–89.5° (previously reported, 88.5–89°).

A sample of 30 g. of the diol and 125 cc. of 85% phosphoric acid were placed in a Claisen flask and heated to 140° in an oil-bath. The diol was dehydrated rapidly and gave 21 g. of 2,2,5,5-tetramethyltetrahydrofuran, b. p. 117–122°. Treatment of this product with hydrogen bromide, as described above, gave a sample of 2,5-dibromo-2,5-dimethylhexane melting at 68–69°. The diol also gave this dibromide directly, by treatment with hydrogen bromide.

Reaction of the *trans*-Diol with Hydrochloric Acid.—To 60 cc. of concd. hydrochloric acid cooled to −10° was added 5.0 g. of the *trans*-diol and the mixture shaken thoroughly. The mixture was allowed to stand at −10° for eight days and then neutralized by cooling and slowly adding pyridine. The barely acid solution was extracted with three 75-cc. portions of ether. The combined extracts were washed with 5% potassium carbonate solution, followed by water, and finally dried over anhydrous calcium chloride. On fractionation 4.1 g. of a colorless liquid was obtained; b. p. 175–180° (745 mm.), 75–80° (21 mm.). This liquid absorbed bromine in carbon tetrachloride solution, reduced alkaline potassium permanganate solution, and was found to contain chlorine. The chlorine content corresponded to a dichloride $C_8H_{14}Cl_2$, which would be formed by replacing both hydroxyls of the diol by chlorine.

Anal. Calcd. for $C_8H_{14}Cl_2$: Cl, 39.18. Found: Cl, 38.62, 38.52.

Dehydration of the *trans*-Diol with Sulfuric Acid.—The reagent used was 50% acetic acid to which concd. sulfuric acid was added until the resulting solution was 15% sulfuric acid by weight (42.5% water, 42.5% acetic acid). The diol was quite soluble in this reagent.

A solution of 10 g. of the *trans*-diol in 100 cc. of the above reagent was heated quickly to boiling (103°) and refluxed for three minutes. At this time the reaction was found to be complete and further boiling partially decomposed the products. The originally colorless solution had become deep red in color and a supernatant liquid layer had separated. The solution was quickly cooled and neutralized with 50% sodium hydroxide, while the temperature was kept below 20°. The red color changed to yellow during the neutralization. The product was extracted with two 75-cc. portions of ether, dried over anhydrous calcium chloride, and fractionated in vacuum (since distillation at atmospheric pressure was found to accelerate polymerization). Two products were obtained in about equal amounts (4 g. of each); both compounds were highly unsaturated and polymerized rapidly on standing: (A) b. p. 128° (746 mm.), 34–35° (18 mm.); n^{20}_D 1.4805, n^{25}_D 1.4791; d^{25}_4 0.8211.

Anal. Calcd. for C_8H_{12}: C, 88.99; H, 11.11. Found: C, 87.35, 87.68; H, 9.38, 9.55.

(B) B. p. 145–147° (18 mm.); n^{25}_D 1.5134.

Anal. Calcd. for $C_{16}H_{24}$: C, 88.99; H, 11.11. Found: C, 86.62, 86.70; H, 10.59, 10.78.

The lower boiling compound (A) is undoubtedly identical with the unsaturated hydrocarbon which Bourguel formulated as 2,5-dimethyl-1,3,5-hexatriene and described as follows: b. p. 124–126°, d^{15}_4 0.778, n^{15}_D 1,483, M_D 39.60, calcd. 37.74. The other compound (B) is probably a dimer of it. The lower boiling compound was yellow (possibly due to impurities), while the other was colorless. Both had rather pleasant odors. On refluxing with maleic anhydride in toluene solution for fifteen hours, both gave addition products. Compound A gave a product melting at 135–136°, and B gave a product which began to sublime without melting at about 225°. However, no addition product could be obtained with 1,4-naphthoquinone although various attempts were made. These results, together with those of Bourguel, indicate the lower boiling hydrocarbon is 2,5-dimethyl-1,3,5-hexatriene, presumably the *trans* isomer.

If the solution of the *trans* diol in the dehydrating reagent was allowed to stand at room temperature for two days instead of being boiled, a supernatant layer was observed to separate. After neutralization and extraction, as carried out above, there was obtained: 5 g. of unreacted diol, 3.5 g. of the unsaturated hydrocarbon A, and 0.6 g. of an unsaturated liquid boiling at 145–165°. The last fraction is probably identical with a similar material obtained by Bourguel, which he believed to be the intermediate dehydration product, 2,5-dimethyl-3,5-hexadiene-2-ol. Our material polymerized rapidly on standing, and on heating at atmospheric pressure decomposed with formation of the unsaturated hydrocarbon A and polymers.

Summary

The configurations of the *cis–trans* isomers of 2,5-dimethyl-3-hexene-2,5-diol have been established, and their behavior toward sulfuric and hydrochloric acids has been studied.

The *cis*-isomer undergoes dehydration readily with either reagent to give 2,2,5,5-tetramethyltetrahydrofuran. The structure of this dehydration product has been definitely established.

The *trans*-isomer undergoes dehydration with sulfuric acid to yield an unsaturated hydrocarbon which is probably the *trans*-form of 2,5-dimethyl-1,3,5-hexatriene. A higher boiling fraction was obtained which is a dimer of the triene. The *trans*-isomer is merely converted to a dichloride by the action of cold hydrochloric acid.

These results show a very clear cut difference in the behavior of the isomeric *cis-trans* diols on dehydration. Neither form undergoes rearrangement of the pinacol–pinacolone type.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Sterols. CVII. Steroidal Sapogenins of Aletris, Asparagus and Lilium*

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Steroidal sapogenins have been obtained by the hydrolysis of saponins from plants belonging to the families *Liliaceae*, *Dioscoreaceae* and *Scrophulariaceae*.[1,2]

We have investigated about thirty plants of these families and have now obtained steroidal sapogenins from three of them. The method of isolation was essentially identical with that described previously.[2]

From the roots of *Aletris farinosa* (L.) (*Liliaceae*) a sapogenin was obtained. The analysis of the genin and its acetate and mixed melting point determinations showed that it was diosgenin.

The roots of *Asparagus officinalis* (L.) (*Liliaceae*) gave sarsasapogenin, which gave no depression in melting point with a sample from sarsaparilla root. The identification was confirmed with the acetate.

Japanese lily bulbs purchased from Charles E. Meyer, Inc., New York City, under the name "*Lilium rubrum magnificum*" also gave a sapogenin. The formation of an insoluble digitonide indicated that the substance was steroidal with a hydroxyl group at the 3-position. However, it is not identical with any of the sapogenins which have been described previously. Elementary analysis showed that it was isomeric with gitogenin. It formed a diacetate. Mild oxidation of the new sapogenin with chromic acid gave only acid products. This indicates that the substance has adjacent hydroxyl groups which probably are 2,3 or 3,4. If the hydroxyl groups are 2,3 it may be a structural isomer of gitogenin with the coprostane configuration at C-5 or it may differ from gitogenin in the configuration of the side-chain as sarsasapogenin differs from isosarsasapogenin.[3] It has been shown that gitogenin has the iso-configuration of the side-chain.[4] We propose the name "liligenin" for the new sapogenin.

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Experimental Part

Diosgenin from *Aletris farinosa* (L.).—Dried and powdered aletris roots (25 pounds) were treated as described previously,[2] for *Trillium erectum*, except that the final hydrolysis mixture was extracted with ether. The ethereal solution was washed with water. The residue from the evaporation of the ether was refluxed with hot methanolic potassium hydroxide for fifteen minutes. The alcoholic solution was poured into water and the sapogenin was taken up in ether. The ether was washed with water. The solvent was removed and the residue was refluxed for thirty minutes with 20 cc. of acetic anhydride. The genin separated as the acetate from the cooled solution.

(*) Previous paper, THIS JOURNAL, **62**, 2548 (1940).

(1) Fieser, "Chemistry of Natural Products Related to Phenanthrene," Reinhold Publishing Corp., New York, N. Y., 1937.

(2) Marker, Turner and Ulshafer, THIS JOURNAL, **62**, 2542 (1940).

(3) Marker and Rohrmann, *ibid*, **61**, 846 (1939).

(4) Marker and Rohrmann, *ibid*., **61**, 2724 (1939).