[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Polymethyl Aromatic Hydrocarbons. II.[1] The Dehydration and Cyclization of 2-Methyl-5-phenylhexane-2,5-diol[2]

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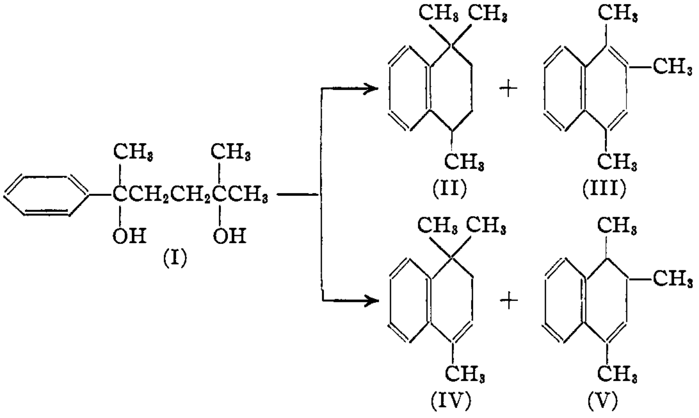
The dehydration and cyclization of 2-methyl-5-phenylhexane-2,5-diol (I) was investigated in order to determine whether hydroaromatic compounds could be synthesized by means of such reactions. Diols of type I may be prepared by the reaction of Grignard reagents with esters of β-aroylpropionic acids and are therefore readily available.

A novel reaction involving the migration of a methyl group occurred when 2-methyl-5-phenylhexane-2,5-diol (I) was treated with hydrogen fluoride or sulfuric acid. Anhydrous hydrogen fluoride acted upon (I) at room temperature to give a mixture of 1,1,4-trimethyltetralin (II) and 1,2,4-trimethylnaphthalene (III); concentrated sulfuric acid acted upon (I) at 0° to give the same mixture of hydrocarbons. In both instances the production of considerable quantities of resinous material indicated the intermediate formation of a polymerizable olefin. In order to ascertain during which process in this complex reaction the rearrangement occurred a milder reagent, phosphoric acid, was employed to effect the dehydration. Even under these conditions the reaction followed two courses, for the prolonged action of hot, 85% phosphoric acid on the diol (I) produced a mixture (A) of 1,1,4-trimethyl-1,2-dihydronaphthalene (IV) and 1,2,4-trimethyl-1,2-dihydronaphthalene (V). It is not unlikely that the reaction of diol (I) with hydrogen fluoride or sulfuric acid proceeds with the intermediate formation of (IV) and (V). This likelihood is suggested by the fact that the mixture (A) of dihydronaphthalenes is converted to a mixture of hydrocarbons (II) and (III) by the action of either hydrogen fluoride or sulfuric acid. It is therefore evident that migration of the methyl group occurred during the cyclodehydration of the diol and not during the subsequent aromatization process. The latter process appears to consist in the intermolecular oxidation–reduction (IV) + (V) → (II) + (III), effected by hydrogen fluoride or sulfuric acid.



The 1,1,4-trimethyltetralin which was obtained from the cyclodehydration reactions was identified by comparison with a synthetic sample. 4-Phenylpentanoic acid[1] was esterified and the ester was treated with methylmagnesium iodide, whereupon 2-methyl-5-phenyl-2-hexanol (VI) was obtained in 95% yield. This alcohol was then cyclized with sulfuric acid following the procedure which was employed by Bogert, Davidson and Apfelbaum[3] to prepare 1,1-dimethyltetralin; 1,1,4-trimethyltetralin (II) was obtained in 86% yield. The structure of this hydrocarbon was ascertained when dehydrogenation of a sample with selenium yielded 1,4-dimethylnaphthalene and the oxidation of a second sample with potassium permanganate yielded α,α-dimethylhomophthalic anhydride (VII). Suitable solid derivatives for the characterization of 1,1,4-trimethyltetralin were obtained when the hydrocarbon was sulfonated and the sulfonic acid was converted into amine salts: the aniline, *p*-toluidine and *p*-nitroaniline salts of 1,1,4-trimethyltetralinsulfonic acid crystallize readily from water and have well-defined melting points. The 1,1,4-trimethyltetralin which was obtained from cyclodehydration of diol (I) yielded amine salts identical with those prepared from synthetic 1,1,4-trimethyltetralin.

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(1) Paper I of this series: THIS JOURNAL, 62, 1708 (1940).

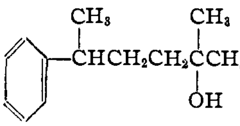
(2) Presented before the Division of Organic Chemistry at the Detroit meeting of The American Chemical Society, September, 1940.

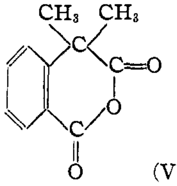
(3) Bogert, Davidson and Apfelbaum, THIS JOURNAL, 56, 962 (1934).

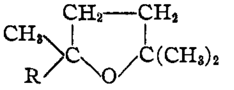
The mixture (A) of dihydronaphthalenes (IV) and (V) instantly decolorized, at 0°, 90% of the bromine calculated for absorption by one double bond; the mixture (A) likewise rapidly absorbed the requisite volume of hydrogen for the saturation of one double bond to give a mixture (B) of the corresponding trimethyltetralins. The presence of 1,2,4-trimethyltetralin in this mixture (B) was ascertained when a sample of the mixture was subjected to selective dehydrogenation with sulfur. Sulfur should readily dehydrogenate 1,2,-4-trimethyltetralin but would not be expected to readily effect the removal of a quaternary methyl group from 1,1,4-trimethyltetralin; 1,2,4-trimethylnaphthalene (III) was indeed the only compound isolated from the dehydrogenation mixture. That 1,2,4-trimethylnaphthalene could not have been produced by the migration of a methyl group during dehydrogenation of 1,1,4-trimethyltetralin with sulfur was demonstrated when a sample of synthetic 1,1,4-trimethyltetralin was dehydrogenated with sulfur under identical conditions: in this instance an 8.9% yield of 1,4-dimethylnaphthalene was obtained and no other picrate-forming hydrocarbon could be isolated. The presence of 1,2,4-trimethyltetralin in the hydrogenated mixture (B) was thereby ascertained, which in turn indicated the presence of 1,2,4-trimethyl-1,2-dihydronaphthalene (V) in the original dehydration mixture (A).

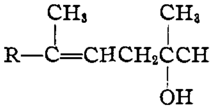
The mixture (B) of trimethyltetralins was next sulfonated and a sample of the characteristic *p*-toluidine salt of 1,1,4-trimethyltetralinsulfonic acid was finally isolated. The presence of 1,1,4-trimethyl-1,2-dihydronaphthalene (IV) in the dehydration mixture (A) was thereby ascertained.

In view of the interesting course taken by the reaction of 2-methyl-5-phenylhexane-2,5-diol (I) with hydrogen fluoride, sulfuric acid and phosphoric acid, further investigation of the reactions of this diol seemed of interest. When the diol (I) was distilled under reduced pressure the elements of water were split out and careful fractionation of the distillate yielded 2,2,5-trimethyl-5-phenyltetrahydrofuran (VIII) and 2-methyl-5-phenylhexen-4-ol-2 (IX) in approximately equal quantities. Under similar conditions 2-methyl-5-(6'-tetralyl)-hexane-2,5-diol (X) yielded a mixture of 2,2,5-trimethyl-5-(6'-tetralyl)-tetrahydrofuran (XI) and 2-methyl-5-(6'-tetralyl)-hexen-4-ol-2 (XII).

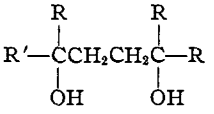

(VI)


(VII)

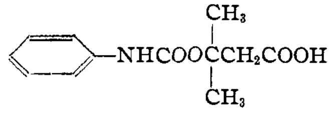

(VIII, R = Phenyl)
(XI, R = 6-Tetralyl)
(XV, R = *p*-Tolyl)


$R-C(CH_3)=CHCH_2C(CH_3)(OH)CH_3$

(IX, R = Phenyl)
(XII, R = 6-Tetralyl)


$R'-C(R)(OH)CH_2CH_2C(R)(OH)-R$

(X, R' = 6-Tetralyl; R = CH$_3$)
(XIV, R' = R = Phenyl)


(XIII)

The isomers (VIII) and (IX) differed considerably in their reactions: (IX) instantly decolorized bromine or aqueous potassium permanganate in the cold and reacted with sodium in ether at room temperature; (VIII) did not decolorize bromine or permanganate nor did it react with sodium. Zerewitinoff analyses indicated that (IX) contained one active hydrogen and that (VIII) contained no active hydrogen. The literature is replete with observations[4] concerning the formation of tetrahydrofuran derivatives from 1,4-diols and the aforementioned reactions leave little doubt concerning the identity of (VIII).

That the hydroxyl group which was eliminated in the dehydration of (I) was the one on the carbon atom carrying the phenyl group was shown when the phenylurethan of (IX) was subjected to ozonization: both acetophenone and the phenylurethan of β-hydroxy-β-methyl-*n*-butyric acid (XIII) were identified in the reaction mixture when the ozonide was reduced. The structure of (IX) was moreover ascertained by synthesis. 4-Phenylpenten-3-oic acid[1] was esterified and the ester was treated with methylmagnesium iodide to give an unsaturated alcohol which proved to be identical with (IX).

Dehydration of diol (I) with hydrogen chloride appeared to be the best preparative method for 2,2,5-trimethyl-5-phenyltetrahydrofuran (VIII). Dry hydrogen chloride was simply passed into a benzene solution of the diol (I); an immediate reaction was indicated by the separation of water and the tetrahydrofuran (VIII) was obtained in

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[4] Henry, *Compt. rend.*, **143**, 496 (1906); Pace, *C. A.*, **22**, 3890 (1928); Zalkind and Nedzvetzkii, *ibid.*, **28**, 2707 (1934); Bennett and Wain, *J. Chem. Soc.*, 1114 (1936).

93% yield. When anhydrous formic acid was employed to dehydrate diol (I) a 77% yield of (VIII) was obtained.

1,4-Diols appear to be the normal products in the reaction of excess Grignard reagents with esters of β-aroylpropionic acids. When methyl-β-benzoylpropionate was treated with excess phenylmagnesium bromide the expected 1,1,4,4-tetraphenylbutane-1,4-diol (XIV) was obtained. 2-Methyl-5-phenylhexane-2,5-diol (I) was likewise obtained in 88% yield from the reaction of methylmagnesium iodide with methyl β-benzoylpropionate. Rupe and Schutz[5] reported a 43% yield of 2,2,5-trimethyl-5-(*p*-tolyl)-tetrahydrofuran (XV) from the reaction of methylmagnesium iodide with ethyl β-(*p*-toluyl)-propionate but it is not unlikely that this product was formed by the dehydration of the corresponding diol in the process of working up the reaction mixture.

It will be of interest to examine the behavior of other 1,4-diols containing aromatic nuclei in their reactions with hydrogen fluoride, sulfuric acid and phosphoric acid. A number of such experiments are now in progress.

Experimental

1,1,4,4-Tetraphenylbutane-1,4-diol (XIV).—To the Grignard reagent from 18.8 g. of bromobenzene, 2.9 g. of magnesium and 60 cc. of ether was added a solution of 5.76 g. of methyl β-benzoylpropionate[1] in 25 cc. of ether. A pale green precipitate separated which finally became yellow as the mixture was swirled and refluxed for twenty minutes. After standing for one hour at room temperature the mixture was hydrolyzed with ice and ammonium chloride, biphenyl was removed by steam distillation and the buff-colored residue was crystallized from acetone; yield, 6.4 g. (54%) of colorless needles, m. p. 204° after one crystallization. This diol has been prepared previously in different manners by Valeur,[6] Dilthey and Last[7] and Houben and Hahn[8] who reported the m. p. to be 208°, 202°, and 205–206°, respectively.

2-Methyl-5-phenylhexane-2,5-diol (I).—To the Grignard reagent from 57 g. of methyl iodide, 9.7 g. of magnesium and 150 cc. of ether was added a solution of 19.2 g. of methyl β-benzoylpropionate[1] in 50 cc. of ether at such a rate as to keep the reaction mixture gently refluxing. The solution was refluxed for one additional hour after which it was hydrolyzed with aqueous acetic acid and then extracted with ether. When the neutralized and dried ether extract was allowed to evaporate spontaneously at room temperature there was obtained a colorless, viscous oil which soon crystallized; yield, 18.2 g. (88%) of crystalline product. **2-Methyl-5-phenylhexane-2,5-diol** crystallized from ether–petroleum ether in colorless, hexagonal prisms; m. p. 74–75°.

Anal. Calcd. for $C_{13}H_{20}O_2$: C, 74.9; H, 9.7. Found: C, 74.9; H, 9.6.

The diol is slightly soluble in petroleum ether, moderately soluble in cold ether or water and is very soluble in warm ether. Concentrated sulfuric acid gives a lemon-yellow color with this diol.

Pyrolytic Dehydration of 2-Methyl-5-phenylhexane-2,5-diol.—When 37 g. of the aforementioned diol (I) was distilled under reduced pressure a mixture of water and 29.5 g. of an oil distilled over. By means of three careful fractional distillations in vacuum there was obtained from this oil 9.5 g. of **2,2,5-trimethyl-5-phenyltetrahydrofuran** (VIII) boiling at 71° (0.4 mm.) and 9.2 g. of **2-methyl-5-phenylhexen-4-ol-2** (IX) boiling at 104.5–105° (0.4 mm.). Similar results were obtained when the distillation was carried out at atmospheric pressure in the presence of a trace of iodine; 5 g. of (I) yielded 3.6 g. of (VIII) and 0.8 g. of (IX).

2,2,5-Trimethyl-5-phenyltetrahydrofuran (VIII) is a colorless oil with a characteristic camphoraceous odor; b. p. 233.8–234.2° (769 mm.) or 65° (0.15 mm.); n^{20}_D 1.5002; d^{20}_{20} 0.9573; M_D calcd., 58.12; M_D found, 58.46. Zerewitinoff determinations indicated no active hydrogen. This tetrahydrofuran does not decolorize either bromine water in acetone solution or 1% aqueous potassium permanganate in the cold. With concentrated sulfuric acid a yellow color is produced.

Anal. Calcd. for $C_{13}H_{18}O$: C, 82.0; H, 9.5. Found: C, 82.3; H, 9.3.

2-Methyl-5-phenylhexen-4-ol-2 (IX) was obtained as a pale yellow, practically odorless oil; n^{20}_D 1.5380; d^{20}_{20} 0.9801; M_D calcd., 59.69; M_D found, 60.73 ($\Sigma = 1.04$). Zerewitinoff determinations indicated 0.93 atoms of active hydrogen per molecule. This alcohol instantly decolorized bromine water or 1% aqueous potassium permanganate in the cold and reacted with sodium in ether at 25° to give an orange precipitate. With concentrated sulfuric acid the alcohol gave a yellow color which quickly changed to blood-red.

Anal. Calcd. for $C_{13}H_{18}O$: C, 82.0; H, 9.5. Found: C, 82.4; H, 9.5.

A tightly-stoppered mixture of 1.57 g. of this alcohol and 1.0 g. of phenyl isocyanate became solid after standing for several days at room temperature. Ligroin (70–90°) was added, the hot solution of the phenylurethan was filtered from a small amount of diphenylurea and the solution was concentrated. The **phenylurethan of 2-methyl-5-phenylhexen-4-ol-2** crystallized in clusters of colorless needles; m. p. 103–104° alone and also when mixed with authentic phenylurethan.

Anal. Calcd. for $C_{20}H_{23}O_2N$: N, 4.5. Found: N, 4.8.

A stream of oxygen carrying 0.8 g. of ozone per hour was passed through an ice-cold solution of 1.0 g. of the aforementioned phenylurethan in 25 cc. of pure ethyl acetate until the exit gases colored potassium iodide solution. The ozonide solution then absorbed the requisite volume of hydrogen within ninety minutes (5 lb. pressure; palladium on calcium carbonate catalyst). When the ethyl

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[5] Rupe and Schutz, *Helv. Chim. Acta*, **9**, 994 (1926).

[6] Valeur, *Bull. soc. chim.*, **29**, 683 (1903).

[7] Dilthey and Last, *Ber.*, **37**, 2639 (1904).

[8] Houben and Hahn, *ibid.*, **41**, 1580 (1908).

acetate had evaporated spontaneously the residue was dissolved in ether and was extracted with aqueous sodium carbonate. Residual material from the evaporation of the ether layer was distilled in vacuum (yield, 255 mg.) and was then refluxed for ninety minutes with 320 mg. of semicarbazide hydrochloride and 10 cc. of absolute ethanol containing 0.4 cc. of anhydrous pyridine. **Acetophenone semicarbazone** which was obtained in this manner melted at 202–203° alone and also when mixed with an authentic sample.

The alkaline solution from extraction of the hydrogenated ozonide was clarified with charcoal and upon acidification with dilute sulfuric acid deposited 62 mg. of an acid which crystallized from benzene–ligroin in clusters of narrow, colorless leaflets; m. p. 129–130°. This compound showed the correct analysis for the **phenylurethan of β-hydroxy-β-methyl-*n*-butyric acid** (XIII).

Anal. Calcd. for $C_{12}H_{15}O_4N$: C, 60.7; H, 6.4. Found: C, 60.7; H, 6.3.

Synthesis of the Phenylurethan of 2-Methyl-5-phenylhexen-4-ol-2.—A solution of 7.5 g. of 4-phenylpenten-3-oic acid[1] in 25 cc. of absolute methanol was saturated with dry hydrogen chloride and allowed to stand for three hours at 25°. The solution was refluxed for three hours, most of the methanol was distilled off and water was added to precipitate the ester; yield, 6.6 g. of colorless **methyl 4-phenylpenten-3-oate** which distilled at 106° (0.1 mm.).

A solution of 5.5 g. of this unsaturated ester in 25 cc. of ether was added to the Grignard reagent prepared from 11.2 g. of methyl iodide, 1.9 g. of magnesium and 30 cc. of ether and the mixture was refluxed for thirty minutes. The entire reaction mixture was hydrolyzed with ice and ammonium chloride and the ether layer was evaporated. **2-Methyl-5-phenylhexen-4-ol-2** distilled at 110–112° (0.4 mm.); yield, 3.4 g. of pale yellow oil. The **phenylurethan** was prepared and isolated as previously described; m. p. 103–104°.

Dehydration of 2-Methyl-5-phenylhexane-2,5-diol with Formic Acid.—A solution of 10 g. of the aforementioned diol (I) in 60 cc. of anhydrous formic acid was refluxed for one hour and was then diluted with 250 cc. of water. Ether was added, the ethereal extract was washed with aqueous sodium bicarbonate and was evaporated. Fractional distillation of the residue in vacuum yielded 7.0 g. (77%) of pure **2,2,5-trimethyl-5-phenyltetrahydrofuran** (VIII). There was in addition a small high-boiling fraction which was not identified.

Dehydration of 2-Methyl-5-phenylhexane-2,5-diol with Hydrogen Chloride.—Dry hydrogen chloride was passed into a solution of 5.8 g. of diol (I) in 35 cc. of benzene for one hour. The solution became cloudy due to the separation of water almost at once. When the neutralized solution was dried and evaporated there remained only **2,2,5-trimethyl-5-phenyltetrahydrofuran** (VIII); yield, 4.9 g. (93%) of vacuum-distilled product; $n^{20}D$ 1.5002.

Reaction of 2-Methyl-5-phenylhexane-2,5-diol with Hydrogen Fluoride.—A finely-powdered sample (10 g.) of the aforementioned diol (I) in a platinum flask was covered with anhydrous hydrogen fluoride and the mixture was allowed to stand at 25° for twenty hours. The small quantity of hydrogen fluoride which still remained was then evaporated on a steam-bath and the oily reaction product was poured into aqueous sodium bicarbonate. Steam distillation separated the volatile reaction products from 3.0 g. of non-volatile resinous material, and by fractional distillation of the volatile portion under reduced pressure there was obtained 2.2 g. of colorless **1,1,4-trimethyltetralin** (b. p. 69° (0.2 mm.)) and 2.4 g. of **1,2,4-trimethylnaphthalene.**

The **1,2,4-trimethylnaphthalene** crystallized from methanol in colorless, nacreous leaflets; m. p. 54–55° alone and also when mixed with an authentic sample.[1]

Anal. Calcd. for $C_{13}H_{14}$: C, 91.71; H, 8.28. Found: C, 91.78; H, 8.22.

The **styphnate** of **1,2,4-trimethylnaphthalene** melted at 123–124° and gave no depression when mixed with an authentic sample.[1] The **picrate** melted at 147.5–148° alone and when mixed with authentic picrate.[1]

Anal. Calcd. for $C_{13}H_{14}\cdot C_6H_3O_7N_8$: N, 10.5. Found: N, 10.4.

The **1,3,5-trinitrobenzene derivative,** m. p. 165.5–166.5°, likewise gave no depression when mixed with an authentic sample.[1]

Anal. Calcd. for $C_{13}H_{14}\cdot C_6H_3O_6N_3$: N, 10.9. Found: N, 10.8.

When the 1,1,4-trimethyltetralin fraction was sulfonated and the sodium salt of the sulfonic acid was treated with hydrochloric acid and *p*-toluidine (details are described in the section concerning synthetic 1,1,4-trimethyltetralin) the ***p*-toluidine salt of 1,1,4-trimethyltetralinsulfonic acid** was obtained; m. p. 195–196° dec. (no depression when mixed with authentic salt).

Reaction of 2-Methyl-5-phenylhexane-2,5-diol with Sulfuric Acid.—Ten grams of finely-powdered diol (I) was added in portions over a period of one hour to 20 cc. of ice-cold, mechanically-stirred, concentrated sulfuric acid. When addition was complete the dark mixture was stirred at 0° for forty minutes and was then poured onto 250 g. of ice. When the product was worked up as previously described for the reaction of the diol with hydrogen fluoride there was obtained 2.3 g. of **1,1,4-trimethyltetralin** (II) and 1.4 g. of **1,2,4-trimethylnaphthalene** (III). The 1,1,4-trimethyltetralin fraction had a b. p. of 69° (0.2 mm.) and did not decolorize aqueous potassium permanganate.

Anal. Calcd. for $C_{13}H_{18}$: C, 89.6; H, 10.4. Found: C, 89.7; H, 10.0.

This fraction likewise yielded the characteristic amine salts of 1,1,4-trimethyltetralinsulfonic acid: **aniline salt,** m. p. 165–166° dec.; ***p*-toluidine salt,** m. p. 195–196° dec.; ***p*-nitroaniline salt,** m. p. 239–240° dec.; all were identified by means of mixed melting point determinations.

The **1,2,4-trimethylnaphthalene** obtained in the cyclodehydration reaction melted at 54–55°: **picrate,** m. p. 148–148.5°; **styphnate,** m. p. 123–124°; **1,3,5-trinitrobenzene derivative,** m. p. 166–167°; all gave no depression of m. p. when mixed with authentic samples.[1]

Synthesis of 1,1,4-Trimethyltetralin.—A solution of 45.4 g. of 4-phenylpentanoic acid[1] and 5.5 cc. of concentrated sulfuric acid in 135 cc. of absolute methanol was refluxed for fifteen hours, excess methanol was distilled off and water was added to the residue. The **methyl 4-phenylpentanoate** which was extracted with ether distilled at 143–144° (25 mm.); yield, 44.8 g. (92%). A solution of this ester

(44.8 g.) in 180 cc. of ether was added to the Grignard reagent from 100 g. of methyl iodide, 17 g. of magnesium and 285 cc. of ether at such a rate that the reaction mixture refluxed gently. After the first vigorous reaction the mixture was refluxed for forty minutes and was hydrolyzed with ice and ammonium chloride. The residue obtained by evaporation of the dried ethereal extract was distilled, yielding 42.5 g. (95%) of **2-methyl-5-phenyl-2-hexanol** (VI); b. p. 106° (0.4 mm.).

To 42 g. of the aforementioned alcohol, cooled in ice and mechanically stirred, was added dropwise over a period of one hour 42 cc. of concentrated sulfuric acid. Stirring and cooling were continued for fifteen minutes and the orange emulsion was poured onto 400 g. of ice. Extraction of the reaction mixture with ether yielded **1,1,4-trimethyltetralin** which was purified by distillation over sodium; b. p. 68° (0.2 mm.); yield, 32.7 g. (86%). The hydrocarbon has a pungent camphoraceous odor; $n^{20}{}_{D}$ 1.5243; $d^{20}{}_{20}$ 0.9381; M_D found, 56.82 (calcd., 56.43).

Anal. Calcd. for $C_{13}H_{18}$: C, 89.6; H, 10.4. Found: C, 89.3; H, 10.7.

Sulfonation of 1,1,4-Trimethyltetralin.—A mixture of 5.0 g. of 1,1,4-trimethyltetralin and 7 cc. of concentrated sulfuric acid was stirred violently at 60–70° until a test sample of the mixture was entirely soluble in water (one hour). To the cooled mixture was added 9 g. of sodium bicarbonate, 16 g. of sodium chloride and enough water to give a clear solution at the boiling point. For purposes of characterization the crude, gelatinous sodium sulfonate which separated upon cooling the hot solution was converted[9] into several amine salts of the corresponding sulfonic acid. The **aniline salt** of **1,1,4-trimethyltetralinsulfonic acid** crystallized from water, in which it is moderately soluble, in thin, colorless leaflets; m. p. 168–170° dec. (after four recrystallizations).

Anal. Calcd. for $C_{13}H_{18}O_3S \cdot C_6H_7N$: N, 4.0. Found: N, 4.1.

The ***p*-toluidine salt** of **1,1,4-trimethyltetralinsulfonic acid** was obtained similarly in colorless, nacreous leaflets from water; m. p. 195–196° dec. (after three recrystallizations).

Anal. Calcd. for $C_{13}H_{18}O_3S \cdot C_7H_9N$: N, 3.9. Found: N, 3.7.

The ***p*-nitroaniline salt of 1,1,4-trimethyltetralinsulfonic acid** separated from water in thin, colorless leaflets; m. p. 240–241° dec. (after three recrystallizations). When this salt is dissolved in water it dissociates to give a yellow solution.

Anal. Calcd. for $C_{13}H_{18}O_3S \cdot C_6H_6N_2O_2$: N, 7.1. Found: N, 7.0.

Dehydrogenation of 1,1,4-Trimethyltetralin.—When 5.0 g. of 1,1,4-trimethyltetralin was heated to 270° for seventy hours with 5.0 g. of selenium in a nitrogen atmosphere and the resulting melt was extracted with ether there was obtained 1.8 g. (40% yield) of **1,4-dimethylnaphthalene; picrate,** m. p. 143–144°; **styphnate,** orange rectangular prisms, m. p. 125°; neither derivative showed a depression of m. p. when mixed with an authentic sample.[1]

When 2.9 g. of 1,1,4-trimethyltetralin was heated to 240° for one hour with 1.07 g. of sulfur and the reaction mixture was worked up as previously described there was obtained 0.23 g. (8.9% yield) of **1,4-dimethylnaphthalene** which would not solidify at 0°; **picrate,** m. p. 142–143° alone and 142–144° when mixed with an authentic sample. No other picrate-forming compound was found in the dehydrogenation melt.

Oxidation of 1,1,4-trimethyltetralin was accomplished when 2.61 g. of the hydrocarbon was refluxed (with mechanical stirring) for six hours with a solution of 17.4 g. of potassium permanganate in 500 cc. of water Ethanol was added to discharge the remaining permanganate color, manganese dioxide was filtered off and the colorless filtrate was concentrated to a volume of 75 cc. Acidification of the hot solution with 20 cc. of concentrated hydrochloric acid resulted in the deposition of a colorless precipitate which was extracted with ether and finally distilled at 0.4 mm. pressure; yield, 600 mg. (21%) of **α,α-dimethylhomophthalic anhydride** (VII)[10] which formed colorless needles or thin plates from 30–60° petroleum ether; m. p. 80–81°.

Anal. Calcd. for $C_{11}H_{10}O_3$: C, 69.5; H, 5.3. Found: C, 69.4; H, 5.4.

Reaction of 2-Methyl-5-phenylhexane-2,5-diol with Phosphoric Acid.—When a mixture of 30 g. of diol (I) and 70 cc. of 85% phosphoric acid was vigorously refluxed for forty hours and the product was subjected to steam distillation, 21.5 g. (87%) of a pale yellow oil distilled with the steam. This product, which was shown to be a mixture (A) of **1,1,4-trimethyl-1,2-dihydronaphthalene** (IV) and **1,2,4-trimethyl-1,2-dihydronaphthalene** (V) by means of subsequent reactions, distilled at 70–76° (0.2 mm.). The mixture of isomers, which had a sweet pungent odor, reduced 1% aqueous potassium permanganate in the cold and gave a red-brown color with concentrated sulfuric acid.

Anal. Calcd. for $C_{13}H_{16}$: C, 90.6; H, 9.4. Found: C, 90.3; H, 9.4.

A sample of the aforementioned mixture (A) instantly decolorized bromine in carbon tetrachloride solution at 0° until 90% of the requisite quantity, calculated for the saturation of one double bond, had been absorbed. No crystalline dibromide could be isolated.

When a 10-g. sample of the mixture (A) of dihydronaphthalenes was treated with anhydrous hydrogen fluoride as previously described for the cyclodehydration of diol (I) there was obtained 2.3 g. of **1,1,4-trimethyltetralin** (II) and 1.6 g. of **1,2,4-trimethylnaphthalene** (III): when concentrated sulfuric acid was substituted for hydrogen fluoride the yield of 1,1,4-trimethyltetralin was 2.8 g. and of 1,2,4-trimethylnaphthalene 2.0 g.

Ten-gram samples of the dihydronaphthalene mixture (A) were subjected to catalytic hydrogenation employing Adams catalyst. When ethyl acetate was used as the solvent the requisite volume of hydrogen for the saturation of one double bond was absorbed in thirteen hours: when glacial acetic acid was used absorption was complete within one and three-quarters hours. The solvent was removed under reduced pressure and the colorless residual oil was

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[9] Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., N. Y., 1935, p. 140.

[10] Gabriel, *Ber.*, **19**, 2366 (1886); Bogert, Davidson and Apfelbaum, THIS JOURNAL, **56**, 962 (1934).

distilled over sodium; yield, 87%; b. p. 66–67° (0.3 mm.). The distillate, which was found to be a mixture (B) of **1,1,4-trimethyltetralin** and **1,2,4-trimethyltetralin**, had a faintly pungent, camphoraceous odor, and would not reduce 1% aqueous potassium permanganate at 25°.

When 2.2 g. of the aforementioned mixture (B) was heated to 240° with 0.81 g. of sulfur, hydrogen sulfide was smoothly liberated during the course of one hour. The volatile product was then distilled off under reduced pressure and was treated with the theoretical quantity of picric acid in methanol. When a benzene solution of the crystalline picrate was filtered through a column of activated alumina there was regenerated 0.173 g. of crystalline **1,2,4-trimethylnaphthalene**; m. p. 51–53° after being twice recrystallized from methanol; mixed with authentic 1,2,4-trimethylnaphthalene[1] (m. p. 54–55°) the m. p. was 52.5–55°.

When a sample of the mixture (B) of trimethyltetralins was sulfonated (as described for the sulfonation of 1,1,4-trimethyltetralin) and the resulting mixture of sulfonic acid salts was treated with hydrochloric acid and *p*-toluidine, a mixture of *p*-toluidine salts was produced; fractional crystallization finally yielded the ***p*-toluidine salt** of **1,1,4-trimethyltetralinsulfonic** acid; m. p. 193–194° dec. There was no depression of m. p. when this sample was mixed with authentic salt.

β-(6-Tetroyl)-propionic acid has been prepared previously in 34% yield by Krollpfeiffer and Schaefer[11]: the acid may, however, be prepared in 77% yield in the following manner. To a solution of 60 g. of succinic anhydride and 133 g. of anhydrous aluminum chloride in 660 cc. of dry nitrobenzene, cooled in an ice–salt mixture, was added dropwise over a period of fifteen minutes 66 g. of freshly-distilled tetralin. The mixture was shaken at 0° during the entire addition and it was then allowed to stand for seventeen hours, whereupon the ice melted and the reaction mixture came to room temperature. The mixture was worked up in the usual manner and the crude acid was precipitated from a clarified sodium carbonate solution and crystallized from benzene; yield, 89 g. (77%); m. p. 120–121°.

The **methyl ester** of **β-(6-tetroyl)-propionic acid** was prepared in 98% yield when an absolute methanol solution of the keto acid containing a little sulfuric acid was refluxed for five hours. The ester was usually obtained as a colorless oil, b. p. 165–166° (0.2 mm.), although it can be crystallized from 30–60° petroleum ether containing a little benzene; colorless, hexagonal prisms; m. p. 31–32°. The compound is soluble in most organic solvents.

Anal. Calcd. for $C_{15}H_{18}O_3$: C, 73.1; H, 7.4. Found: C, 73.4; H, 7.7.

The keto ester **semicarbazone** forms clusters of colorless needles from 95% ethanol; m. p. 144°.

Anal. Calcd. for $C_{15}H_{21}O_3N_3$: N, 13.8. Found: N, 13.7.

The ***p*-nitrophenylhydrazone** of **methyl β-(6-tetroyl)-propionate** was obtained in silky yellow needles from 95% ethanol; m. p. 123–124°.

Anal. Calcd. for $C_{21}H_{23}O_4N_3$: N, 11.0. Found: N, 10.8.

2-Methyl-5-(6′-tetralyl)-hexane-2,5-diol (X) was prepared from methyl β-(6-tetroyl)-propionate and excess methylmagnesium iodide in the manner previously described for the preparation of 2-methyl-5-phenylhexane-2,5-diol, and crystallized from ether–petroleum ether in colorless, prismatic needles; m. p. 89–90°. The diol is slightly soluble in petroleum ether or water, moderately soluble in cold ether and very soluble in warm ether. With concentrated sulfuric acid the diol gives a red-orange color.

Anal. Calcd. for $C_{17}H_{26}O_2$: C, 77.8; H, 10.0. Found: C, 77.4; H, 10.1.

Dehydration of the diol (X) was accomplished by distillation in vacuum in the same manner as described previously for the dehydration of diol (I). After four careful fractional distillations in vacuum there were finally obtained (from 52 g. of X) two fractions with reasonably constant properties: 12 g. of **2,2,5-trimethyl-5-(6′-tetralyl)-tetrahydrofuran** (XI) distilled at 128–129° (0.2 mm.) and 14 g. of **2-methyl-5-(6′-tetralyl)-hexen-4-ol-2** (XII) distilled at 152–153° (0.2 mm.). The high viscosity of these isomers rendered their separation extremely difficult.

2,2,5-Trimethyl-5-(6′-tetralyl)-tetrahydrofuran (XI) is a colorless viscous liquid with a faintly sweet odor; Zerewitinoff determinations indicated no active hydrogen; the tetrahydrofuran did not reduce potassium permanganate solution in the cold and did not react with sodium in ether at 25°; concentrated sulfuric acid gave a yellow-brown color.

Anal. Calcd. for $C_{17}H_{24}O$: C, 83.5; H, 9.9. Found: C, 83.4; H, 10.1.

2-Methyl-5-(6′-tetralyl)-hexen-4-ol-2 (XII) was obtained as a pale yellow, very viscous, odorless oil which gave a yellow-brown color with concentrated sulfuric acid. Zerewitinoff determinations indicated 1.01 atoms of active hydrogen per molecule. The unsaturated alcohol instantly reduced 1% aqueous potassium permanganate at 25° and reacted with sodium in ether at 25° to give a colorless precipitate.

Anal. Calcd. for $C_{17}H_{24}O$: C, 83.5; H, 9.9. Found: C, 83.4; H, 10.2.

Summary

The reaction of 2-methyl-5-phenylhexane-2,5-diol with certain dehydrating agents is accompanied by the migration of a methyl group: with anhydrous hydrogen fluoride or sulfuric acid a mixture of 1,1,4-trimethyltetralin and 1,2,4-trimethylnaphthalene is produced; with phosphoric acid the products are 1,1,4-trimethyl-1,2-dihydronaphthalene and 1,2,4-trimethyl-1,2-dihydronaphthalene. Pyrolytic dehydration of the aforementioned diol gives a mixture of 2,2,5-trimethyl-5-phenyltetrahydrofuran and 2-methyl-5-phenylhexen-4-ol-2. If the dehydration is effected with anhydrous hydrogen chloride, 2,2,5-trimethyl-5-phenyltetrahydrofuran is the sole product.

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[11] Krollpfeiffer and Schaefer, *Ber.*, **56**, 628 (1923).