[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

THE SYNTHESIS OF CONDENSED POLYNUCLEAR HYDRO-CARBONS BY THE CYCLODEHYDRATION OF AROMATIC ALCOHOLS. VII. CYCLODEHYDRATION INVOLVING THE WAGNER REARRANGEMENT*

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The continued and increasing activity in the study of polynuclear hydrocarbons because of their tremendous biological significance, renders any investigation which throws light upon the structure or mechanism of formation of polycylic hydroaromatic compounds of considerable importance. The preceding papers of this series¹ have yielded the following rules for the cyclodehydration of phenylated alcohols or olefins². Benzene derivatives with unbranched side-chains of five to seven carbon atoms carrying an hydroxyl group or an olefinic bond will give tetralin or indan derivatives when treated with sulfuric acid except when the hydroxyl group is adjacent to the phenyl nucleus, in which case polymerization takes place. Larger rings than six-membered are not formed. In certain instances tetralins and indans are formed simultaneously. With few exceptions the reaction mechanism involves the intermediate formation of olefins.

The present contribution deals with a study of the case of a phenylated alcohol in which a quaternary carbon atom ajoins the carbinol group. Previous references to the possibility of cyclo dehydration of compounds of this type have been made by Bogert and Davidson³, and by Linstead², but no clear-cut case has so far been reported. In this investigation it has been found that 1-phenyl-4,4-dimethyl-pentanol-3 (I) when treated

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¹ BOGERT AND DAVIDSON, J. Am. Chem. Soc., **56**, 185 (1934); BOGERT, DAVIDSON, AND APFELBAUM, *ibid.*, **56**, 959 (1934); ROBLIN, DAVIDSON, AND BOGERT, *ibid.*, **57**, 151 (1935); PERLMAN, DAVIDSON, AND BOGERT, J. Org. Chem., **1**, 288, 300 (1936); PERLMAN AND BOGERT, J. Am. Chem. Soc., **59**, 2534 (1937).

² LINSTEAD, "Annual Reports on the Progress of Chemistry," Chemical Society (London), **1936**, p. 320.

³ BOGERT AND DAVIDSON, loc. cit.¹, p. 188.

with 90 per cent. sulfuric acid undergoes the Wagner rearrangement⁴, followed by cyclization as shown in Chart I. The structure of the resulting hydrocarbon was confirmed by oxidation to dimethylhomophthalic acid and dehydrogenation to 1,2-dimethylnaphthalene as well as by its synthesis from 1-phenyl-3,4-dimethyl-pentanol-3 (II).



A similar rearrangement was also found to take place in the case of the lower homologue, 1-phenyl-3,3-dimethyl-butanol-2 (IV), which yielded 1,1,2-trimethylindan (V), a cycle which had previously been obtained by Bogert and Davidson (paper I of this series¹) from 1-phenyl-2,3-dimethylbutanol-2.



⁴ Cf. WALLIS, "Molecular Rearrangements," in GILMAN'S "Organic Chemistry," John Wiley & Sons, Inc., New York, **1938**, Vol. I, pp. 720 f. The structure of V was confirmed by oxidation with chromic acid, which yielded VI.



This substance was also obtained in the same manner by oxidation of a sample of the 1,1,2-trimethylindan prepared by Bogert and Davidson¹. The melting points of the oxidation products from both sources agreed within half a degree, and the melting point of a mixture showed no de pression.

EXPERIMENTAL

1-Phenyl-4,4-dimethylpentanol-3, (I).—tert.-Butylmagnesium chloride was prepared according to "Organic Syntheses," Coll. Vol. I, p. 510, from 227 g. (2.5 moles) tert.-butyl chloride. The reaction mixture was cooled to 2° in an ice-salt bath, and 100.6 g. (0.75 mole) of β -phenylpropionic aldehyde, dissolved in an equal volume of ether, was added over a period of 2.5 hours with stirring, the temperature being kept below 10°. The addition compound was decomposed by the addition of ice and 25-30% sulfuric acid in slight excess; the ether layer was shaken out with a solution of sodium bisulfite, washed with sodium carbonate solution, then with water, and finally was dried over sodium sulfate.

The residue, after removal of the ether on the steam bath, was distilled under reduced pressure, and yielded 100.1 g. (70% theoretical) of crude alcohol boiling at 116-126°/6-7 mm. Repeated fractionation failed to yield a product which gave entirely satisfactory analyses. A sample boiling at 90-91°/2 mm. (bath temperature 130-135°) gave the following results.

Anal. Calc'd for C₁₃H₂₀O: C, 81.17; H, 10.49.

Found C, 80.73; H, 9.54.

The *phenylurethane* was prepared by allowing equimolecular proportions of the alcohol and phenyl isocyanate to stand several days at room temperature in a well-stoppered bottle, and then recrystallizing the product repeatedly from Skelly Solvent "D." (petroleum fraction, b.p. 77-115°); microscopic white needles; m.p. 91°.

Anal. Calc'd for C₂₀H₂₅O₂N: C, 77.12; H, 8.10.

Found C, 77.20; H, 8.33.

Cyclodehydration of 1-phenyl-4,4-dimethyl-pentanol-3.—Seventy cc. (64.7 g.) of 1-phenyl-4,4-dimethyl-pentanol-3 was run into 210 cc. of 90% sulfuric acid cooled to 2° in a 500-cc. beaker-flask, with rapid stirring over a period of 2 hours, stirring being continued for 2 hours longer, while the reaction mixture was allowed to warm to room temperature. It was then diluted with ice water, and extracted with 400 cc. of light petroleum ether in three portions; the combined extracts were shaken in a separatory funnel with 30 cc. portions of 90% sulfuric acid until the last was almost colorless.

The solution was washed with water, with dilute sodium carbonate solution, again with water, and was then dried over anhydrous potassium carbonate. Filtra-

tion, and removal of the petroleum ether on the steam bath yielded a water-white product which was carefully distilled through a Widmer column; more than 90% of it passed over at 77-81°/1.5 mm. (bath temperature 135-139°) without change in refractive index. The yield was 55% of the theoretical. Samples redistilled for analysis boiled at 77-77.5°/1 mm. and 242° (uncorr.) at 760 mm.; n_{25}^{25} , 1.5269.

Anal. Calc'd for C₁₃H₁₈: C, 89.58; H, 10.42.

Found: (77-77.5°/1 mm.) C, 89.49; H, 10.59: (242°/760 mm.) C, 89.75; H, 10.66.

Oxidation of 1,1,2-trimethyltetralin.—Two grams of 1,1,2-trimethyltetralin was oxidized by refluxing with 20 g. of potassium permanganate in 500 cc. of water for 10 to 12 hours with good stirring, after which the permanganate color was discharged by the addition of about 25 cc. of ethyl alcohol. The solution was filtered hot, and the manganese dioxide precipitate was washed well with boiling water, the washings being added to the main filtrate which was then evaporated to about 100 cc. and made acid to Congo red with hydrochloric acid.

The white precipitate which separated was dried *in vacuo*, and was found to melt at 123°, the melting-point reported for dimethylhomophthalic acid. Its identity was further established by mixture melting-point determinations with the anhydride of known dimethylhomophthalic acid run in two ways. (1) A sample was mixed with the known anhydride, and the temperature of the mixture was raised above the melting point of the free acid; the sample was then allowed to resolidify; m.p. 82° (m.p. of known anhydride, $82.5-83^{\circ}$) (2). The anhydride was formed by heating a sample to 150° for a short time. A mixture of the product with the known anhydride was found to melt at 82° (corr.).

Dehydrogenation of 1,1,2-trimethyl-tetralin.—One mole equivalent (2.3 g.) of the tetralin and 0.85 g. flowers of sulfur (2 atomic equivalents) were placed in a 10-cc. distilling flask with side-tube set at right angles to the neck. The side-tube was stoppered, the neck was provided with a short reflux condenser, and the reaction mixture was heated over a small flame. When the initial, somewhat vigorous, evolution of hydrogen sulfide had abated, the mixture was refluxed gently for 2.5 hours. The flask was then arranged for downward distillation, and one gram of a fluorescent liquid smelling strongly of hydrogen sulfide was distilled over.

The product was converted to the *picrate* by dissolving it in 10 cc. of boiling alcohol and adding 1.3 g. of picric acid in an equal volume of the same boiling solvent. Upon cooling, the picrate crystallized in orange-red needles and was dried *in vacuuo*; yield, 0.9 g., m.p. 129.8° (corr.). The melting-point of the picrate of 1,2-dimethylnaphthalene is reported in Beilstein as 129.5-130.5°C. A further crop of crystals was obtained from the mother liquor.

1-Phenyl-3, S-dimethylbutanol-2 (IV).—This compound was prepared in the same manner as 1-phenyl-4, 4-dimethylpentanol-3, from 186.0 g. (2 moles) tert.-butyl chloride and 120.1 g. (1 mole) phenylacetaldehyde (b.p. $91-92^{\circ}/20$ mm.), the temperature being kept below 5°. The yield in several experiments amounted to 65% of the theoretical (calculated on the basis of the phenylacetaldehyde used); b.p. 78.5°/2 mm. (bath temperature 125°); n_{2}^{20} , 1.1566.

Anal. Calc'd for C₁₂H₁₈O: C, 80.85; H, 10.19.

Found: C, 81.02; H, 10.14.

Cyclization of 1-phenyl-3,3-dimethylbutanol-2.—In this procedure, which was the same as for 1-phenyl-4,4-dimethylpentanol-3, except that the reaction mixture was extracted with petroleum ether without dilution, 55 cc. of the alcohol was added to 73 cc. of 90% sulfuric acid at such a rate as to keep the temperature below 5° (3.5

hours). On distillation through a Widmer column, nearly all of the product but a small forerun came over at $55-56^{\circ}/2$ mm. (bath temperature 135°); yield of distilled product, 41% of the theoretical. No further purification for analysis was necessary; n_{27}^{15} , 1.5101. A sample of product distilled at atmospheric pressure, boiled at 208°.

Anal. Calc'd for C₁₂H₁₆: C, 89.94; H, 10.08.

Found: C, 89.97; H, 10.16.

An additional quantity of the cyclic compound was obtained by diluting the extracted reaction mixture with ice and treating the oily layer as above.

Oxidation of 1,1,2-trimethylindan.—One g. of 1,1,2-trimethyl-indan was dissolved in 20 cc. glacial acetic acid, heated to boiling under reflux, and 5 g. of chromium trioxide in 10 cc. of glacial acetic acid and 10 cc. of water was added, little by little, through the top of the condenser, the rather vigorous reaction being allowed to subside before the addition of each fresh portion. The mixture was refluxed for one hour, after which 20 cc. of acetic acid was distilled off, and 100 cc. of water was added. When cool the solution was extracted with four 50-cc. portions of ether; the combined ether extracts were washed several times with water, and dried over anhydrous sodium sulfate. Upon evaporation of the ether, a residue of acetic acid remained, from which the compound was separated by taking up in alcohol and adding water. The product obtained in this manner was quite pure but was further purified for analysis by recrystallization from a mixture of chloroform and heptane; m.p. 157.5° (corr.); yield about 60% of the theoretical.

Anal. Calc'd for C₁₂H₁₄O₃: C, 69.87; H, 6.85.

Found: C, 69.70; H, 6.93.

A second oxidation using chromium trioxide in glacial acetic acid, without the addition of water, gave the same product. A sample of the 1,1,2-trimethylindan prepared by Bogert and Davidson¹ was oxidized by the same procedure, and the product was shown to be identical with the above oxidation product by its melting-point and by a mixture melting-point of the two substances.

1-Phenyl-3,4-dimethylpentanol-3 (II).—The Grignard reagent was prepared in the usual way from 231 g. (1.25 moles) of phenethyl bromide (prepared for us in 84% yield by Mr. Harry G. Steinman, according to the procedure of Roblin⁵), and 30.4 g. (1.25 moles) of magnesium turnings, without external cooling. One hundred grams of methyl isopropyl ketone in an equal volume of ether was added dropwise, the temperature being kept below 7°, and the condensation product worked up as described for the other alcohols.

On distillation under reduced pressure, several low-boiling fractions came over, one of which consisted of styrene. A 50% yield of the crude product was obtained, which on further purification for analysis boiled at 118–119°/3 mm.; $n_{\rm p}^{\rm m}$, 1.5083.

Anal. Calc'd for $C_{13}H_{20}O$: C, 81.18; H, 10.49.

Found: C, 81.37; H, 10.73.

Cyclodehydration of 1-phenyl-3,4-dimethylpentanol-3—The cyclization was carried out exactly as described for 1-phenyl-3,3-dimethylbutanol-3, using 38 g. (40 cc.) of the alcohol and 60 cc. of 90% sulfuric acid. The yield of the product, almost all of which distilled at 94.5°/2 mm., amounted to 86% of the theoretical; b.p., 241-242°/ 760.7 mm.; n_{2}^{25} , 1.5270. Analysis, refractive index, and boiling-point showed this

⁵ ROBLIN, Dissertation, Columbia University, 1934.

compound to be identical with the 1,1,2-trimethyltetralin prepared from 1-phenyl-4,4-dimethylpentanol-3.

Anal. Calc'd for C₁₁H₁₈: C, 89.58; H, 10.42. Found: C, 89.28; H, 10.51.

SUMMARY

In several cases, cyclodehydration of aromatic alcohols having a quaternary carbon atom adjacent to the carbinol group has been found to involve the Wagner rearrangement.