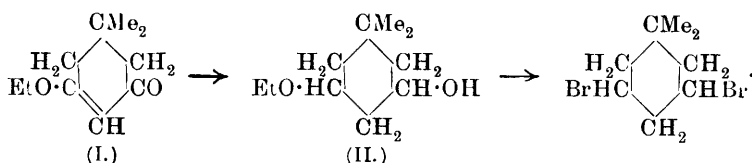


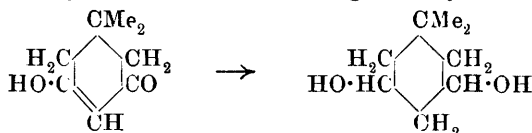
LXII.—*Dihydric Alcohols obtained by the Reduction of Substituted Dihydroresorcins.*

By ARTHUR WILLIAM CROSSLEY and NORA RENOUF.

It has been shown that 1:3-dibromo-derivatives of the saturated *cyclohexane* hydrocarbons may be used for the preparation of substituted *cyclohexadienes* (T., 1908, **93**, 629). In the case referred to, the dibromo-compound was prepared from dimethyldihydroresorcin ethyl ether (I) by reduction, when it gave ethoxydimethyl-*cyclohexanol* (II), which was then treated with fuming hydrobromic acid:

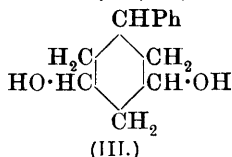


It would appear that a more expeditious method of preparing these substances would be from the dihydric alcohols, which, on theoretical grounds, should be easily obtained by the direct reduction of the dihydroresorcins, but though many attempts have



at various times been made to bring about these reactions, in some cases resulting in the isolation of small quantities of the desired substances, it is only comparatively recently that conditions have been worked out for the preparation of the dihydric alcohols in quantity.

Knoevenagel (*Annalen*, 1895, **289**, 167) obtained small amounts of phenyl-*cyclohexane*-3:5-diol (III) by the reduction of phenyl-

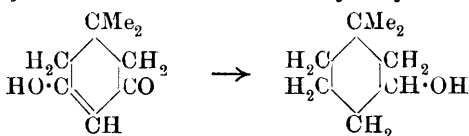


dihydroresorcin with sodium and alcohol, and the only other paper dealing with this subject is one by Zelinski and Uspenski (*Ber.*, 1913, **46**, 1466), who also employed the same reducing agent. Numerous experiments have confirmed the fact that sodium and alcohol give the best results, and the yields are highest when the

reaction is carried out energetically by heating in an oil-bath to 110°, as stated by Zelinski and Uspenski. The amounts of the dihydric alcohols produced vary considerably with different dihydroresorcins, as is seen from the following table:

	Yield per cent.
Methyldihydroresorcin	43
Dimethyldihydroresorcin	66—68
Trimethyldihydroresorcin	20
<i>iso</i> Propyldihydroresorcin	40
Phenyldihydroresorcin	47—50

This is partly due to the nature of the dihydroresorcins themselves, but also to the fact that the reactions are somewhat complicated, and it is interesting to note that in all cases small quantities of the corresponding monohydric alcohols are formed; for example, 1:1-dimethylcyclohexan-3-ol from dimethyldihydroresorcin. Fur-



ther, owing to the unsymmetric structure of all the molecules except that of dimethyldihydroresorcin, isomeric forms of the diols are produced, the separation of which is always tedious and sometimes has been found impracticable; for example, in the reduction of trimethyldihydroresorcin, 70 per cent. of the amount employed was isolated as a solid mixture of diols, but only 20 per cent. of this solid could be obtained as pure diol, owing to the fact that the solubilities of the two forms are so similar as to make their further separation impossible.

The dihydric alcohols are crystalline compounds, neutral to litmus, readily forming dibenzoyl derivatives, and not absorbing bromine in chloroform solution. In many properties they strongly resemble glycols, as they possess a sweet taste, are easily soluble in water, and not readily soluble in ether.

In the preparation of methyldihydroresorcin it has been noticed that when crystallised from water it separates with one molecule of water of crystallisation, and melts at 75—85°, not becoming clear until 94°, despite the fact that Knoevenagel (*Annalen*, 1895, **289**, 170) claims that it melts at 125—126°, after repeated crystallisation from hot water. The melting point is, however, easily raised to 128° by drying the crude substance in a vacuum and crystallising once from ethyl acetate.

Knoevenagel (*ibid.*, p. 167) states that he was only able to obtain a small yield of phenylcyclohexanediol by the reduction of phenyldihydroresorcin, but, if the conditions described in the experimental portion of this communication are adhered to, the yield can be

brought up to 50 per cent. of the dihydroresorcin used, and there are also obtained small quantities of phenylcyclohexanol and of a second variety of phenylcyclohexanediol, probably the *cis*-form. Each form of phenylcyclohexanediol gives one definite dibenzoyl derivative, which on hydrolysis regenerates only the particular form of the diol from which it was made.

EXPERIMENTAL.

Preparation of 1:1-Dimethylcyclohexane-3:5-diol.—Dimethyl-dihydroresorcin in quantities of 10 grams was reduced with sodium in ethyl-alcoholic solution exactly as described by Zelinski and Uspenski (*Ber.*, 1913, **46**, 1466). Instead of crystallising the crude product from a mixture of benzene and acetone, it was first distilled in a current of steam, when a small quantity of liquid, insoluble in water, passed over, which was extracted with ether, etc., and the residue (2.1 grams from three reductions) distilled in a vacuum. The main portion boiled at 102–103°/43 mm. (compare T., 1905, **87**, 1494), and was converted into the *o*-nitrobenzoyl derivative, which melted at 61–62°, nor was this melting point lowered on admixture with the *o*-nitrobenzoyl derivative of 1:1-dimethylcyclohexan-3-ol. This substance has not previously been described. It may be obtained from the alcohol and *o*-nitrobenzoyl chloride in pyridine solution:

0.2915 gave 12.8 c.c. N₂ (moist) at 18° and 759 mm. N=5.06.

C₁₅H₁₉O₄N requires N=5.05 per cent.

It is readily soluble in the cold in benzene, ethyl acetate, chloroform, or acetone, and crystallises from alcohol in radiating clusters of transparent, flattened needles, melting at 62°.

The residue from the above-mentioned steam distillation was salted out with potassium carbonate, the upper layer dissolved in alcohol, the alcoholic solution dried over potassium carbonate, and evaporated. The residue, after one crystallisation from acetone, gave dimethylcyclohexanediol in large, nacreous, scaly plates, melting at 147°, which is slightly higher than the melting point recorded by Zelinski and Uspenski. The yield is 66–68 per cent. of the theoretical, and this has not been improved upon in any of the numerous experiments carried out, despite the fact that Zelinski gives the yield as 90 per cent. A better result could not be anticipated, when it is remembered that 7–10 per cent. of the original material is recovered as dimethylcyclohexanol, and considerable quantities of resin are also formed.

The *dibenzoyl* derivative, prepared in the usual manner, is readily soluble in the cold in chloroform, benzene, or ethyl acetate, readily on warming in acetone or light petroleum (b. p. 60–80°), and

crystallises from alcohol in transparent, flattened needles, melting at 135—136°:

0.1549 gave 0.4259 CO₂ and 0.0956 H₂O. C=74.98; H=6.85.

C₂₂H₂₄O₄ requires C=75.00; H=6.81 per cent.

1-Methylcyclohexane-3:5-diol.

Instead of preparing methyl-dihydroresorcin by the method described by Schilling and Vorländer (*Annalen*, 1899, **308**, 192), the following more expeditious process was adopted.

Twenty-three grams of sodium (one atom) were dissolved in 275 c.c. of alcohol, 136 grams of ethyl acetoacetate (slight excess over 1 molecule) and 114 grams of ethyl crotonate (1 molecule) added, and the whole heated on the water-bath for seven hours. The residue was dissolved in water, the alcohol evaporated, two molecular proportions of potassium hydroxide added, and a sufficient quantity of water to make the solution contain 10 per cent. of alkali, including the atom of sodium originally used. The whole was heated to boiling in an open flask for fifteen minutes, acidified, and boiled until no more carbon dioxide was evolved. This procedure is necessary, as otherwise a poor yield of methyl-dihydroresorcin is obtained, due to the fact that the corresponding resorcylic acid has not been decomposed. On cooling, methyl-dihydroresorcin separated out in aggregates of fern-like crystals, melting at 75—85°, and not becoming clear until 94°. In this form it contains 1H₂O, as was shown by keeping it in a vacuum, when loss in weight took place, and the resulting solid melted sharply at 126—127°:

3.0536 lost 0.3788 H₂O. H₂O=12.40.

C₇H₁₀O₂.H₂O requires H₂O=12.5 per cent.

The dried substance, after one crystallisation from ethyl acetate, melted at 128°, and was produced in 67 per cent. of the theoretical amount.

Methylcyclohexanediol was prepared by the reduction of methyl-dihydroresorcin exactly as described under dimethyl-dihydroresorcin (see page 604). From the steam distillate methylcyclohexanol was isolated, and identified as the *o*-nitrobenzoyl derivative, melting at 54°.

For the purpose of comparison the *o*-nitrobenzoyl derivative of 1-methylcyclohexan-3-ol was prepared. It is readily soluble in the cold in acetone, ethyl acetate, benzene, or chloroform, and crystallises from light petroleum (b. p. 40—60°) in stout, colourless, transparent rhombs, melting at 54°:

0.2870 gave 13.4 c.c. N₂ (moist) at 18° and 759 mm. N=5.38.

C₁₄H₁₇O₄N requires N=5.32 per cent.

On continuing the preparation and evaporating the dried alco-

holic solution, the residue did not show any sign of solidification after long standing, until sown with a crystal of pure methylcyclohexanediol, obtained by converting the crude material into the benzoyl derivative and hydrolysing the purified product. This process is not, however, of any use for the preparation in quantity of methylcyclohexanediol, as the solid material produced contains so much resinous matter that it will not crystallise readily from any solvent.

These facts are mentioned in order to show that the usual methods of purification were attempted before adopting the following tedious, although satisfactory, process, in which the resinous material, being insoluble in ether, remains dissolved in the aqueous solution.

The residue from the steam distillation was extracted ten times with quantities of 80—100 c.c. of ether, the ethereal solution dried with potassium carbonate and evaporated to about 50 c.c., when on sowing with a crystal of pure methylcyclohexanediol, small, colourless, transparent rhombs (1 gram) separated, melting at 74—75° (mother liquor = A). The process of extraction with ether was continued until no appreciable amount of solid was left on evaporation (five processes each consisting of ten extractions). The total pure material obtained was 4.3 grams (43 per cent. of the theoretical) from 10 grams of crude product:

0.1163 gave 0.2751 CO₂ and 0.1100 H₂O. C = 64.51; H = 10.51.

C₇H₁₄O₂ requires C = 64.61; H = 10.77 per cent.

1-Methylcyclohexane-3:5-diol is readily soluble in the cold in water or alcohol, readily on warming in chloroform, ethyl acetate, or acetone, and crystallises from ethyl acetate in radiating clusters of glistening needles, melting at 75°.

The *dibenzoyl* derivative is readily soluble in the cold in chloroform, benzene, ethyl acetate, or acetone, readily on warming in light petroleum (b. p. 60—80°) or alcohol, and crystallises from aqueous alcohol in small, transparent, six-sided plates, melting at 81°:

0.1893 gave 0.5183 CO₂ and 0.1116 H₂O. C = 74.67; H = 6.55.

C₂₁H₂₂O₄ requires C = 74.55; H = 6.50 per cent.

The mother liquors A (see above) on further evaporation gave a solid (2 grams), which when fractionally extracted with ether yielded further small quantities of the diol, and from the most insoluble portion, a substance crystallising from ethyl acetate in nacreous, flattened needles, melting at 143.5°; these probably consisted of an isomeric form of the diol, as isolated in the case of phenylcyclohexandiol (see page 610), but its amount was too small for complete characterisation.

1:1:2-Trimethylcyclohexane-3:5-diol.

Trimethylcyclohexanediol was obtained by the reduction of trimethyldihydroresorcin (T., 1911, **99**, 1105), employing the conditions already described (see page 604).

Trimethylcyclohexanol is produced, and by fractionating the *o*-nitrobenzoyl derivative prepared from it, there was obtained a substance melting at 114°, which proved to be identical with the *o*-nitrobenzoyl derivative of 1:1:2-trimethylcyclohexan-3-ol (*ibid.*, p. 1109).

As in the case of methylcyclohexanediol, extraction with ether was found to be the best method for isolating trimethylcyclohexanediol, which is, however, more readily soluble, and only requires two processes, each of ten extractions. The yield of pure material is 20 per cent. of the theoretical, for although the total solid from the ethereal extract is about 70 per cent. of the calculated amount, it contains another substance (probably an isomeride) so similar in solubilities that further separation has not, up to the present, been found possible:

0.1165 gave 0.2929 CO₂ and 0.1186 H₂O. C=68.56; H=11.31.

C₉H₁₈O₂ requires C=68.35; H=11.39 per cent.

1:1:2-Trimethylcyclohexane-3:5-diol is readily soluble in the cold in alcohol or acetone, readily on warming in benzene, chloroform, ethyl acetate, or water, and crystallises from either of the latter solvents in nacreous, flattened needles, melting at 150°. The *dibenzoyl* derivative crystallises from alcohol in small clusters of transparent needles, melting at 97°:

0.1340 gave 0.3720 CO₂ and 0.0832 H₂O. C=75.71; H=6.90.

C₂₃H₂₆O₄ requires C=75.41; H=7.10 per cent.

1-isoPropylcyclohexane-3:5-diol.

*iso*Propylcyclohexanediol was obtained by reducing *isopropyl*-dihydroresorcin (this vol., p. 173), using the same conditions as previously described (see p. 604). As the dihydroresorcin crystallises with 1H₂O, it is necessary to remove this water by keeping for some time in a vacuum desiccator.

The viscid, reddish-brown liquid product, possessing a pungent odour, was distilled in a current of steam (residue=B), the distillate extracted with ether, and the residue, amounting to 25 per cent. of the dihydroresorcin used, fractionally distilled in a vacuum. It boiled from 140° to 170°/56 mm., and from the lowest fraction, on treatment with *o*-nitrobenzoyl chloride, there was isolated the *o*-nitrobenzoyl derivative of 1-*isopropyl*cyclohexan-3-ol, melting at

48—49° (this vol., p. 174). The higher fractions of the crude product were investigated, but no definite substance was isolated.

The residue B (see above) of the steam distillation was extracted with ether (in which solvent the diol is appreciably less soluble than the homologues previously mentioned in this communication) as described under methylcyclohexanediol (see p. 606), when 40 per cent. of the theoretical amount of isopropylcyclohexanediol was isolated; but as in the other cases already described, a second substance, probably an isomeride, is also produced, although it could not be obtained in a pure condition:

0.1178 gave 0.2958 CO₂ and 0.1202 H₂O. C=68.48; H=11.34.

C₉H₁₈O₂ requires C=68.35; H=11.39 per cent.

1-isoPropylcyclohexane-3:5-diol is readily soluble in the cold in ethyl alcohol, readily on warming in acetone, ethyl acetate, benzene, chloroform, or water, and crystallises from any of these solvents, preferably ethyl acetate, in radiating clusters of small, flat, transparent needles, melting at 124°.

The dibenzoyl derivative is readily soluble in the cold in the usual organic solvents except light petroleum (b. p. 40—60°) and ethyl alcohol, from which it separates in radiating clusters of transparent needles, melting at 84°:

0.1018 gave 0.2823 CO₂ and 0.0639 H₂O. C=75.62; H=6.97.

C₂₃H₂₆O₄ requires C=75.41; H=7.10 per cent.

1-Phenylcyclohexane-3:5-diol.

Phenylcyclohexanediol was prepared by the reduction of phenyl-dihydroresorcin (Vorländer, *Ber.*, 1894, **27**, 2054; and Michael, *ibid.*, p. 2126), which is most expeditiously obtained in 85 per cent. of the theoretical amount from ethyl malonate and styryl methyl ketone (benzylidenacetone), using the conditions described under the preparation of methyl-dihydroresorcin (see p. 605).

The steam distillate was saturated with potassium carbonate, when a solid separated (0.6 gram from 20 grams of the dihydroresorcin), which crystallised from light petroleum (b. p. 80—100°) in radiating clusters of colourless, transparent needles, melting at 81°, nor was this melting point lowered on admixture with 1-phenylcyclohexan-3-ol* prepared for the purposes of comparison.

The residue from the steam distillation, which contained an insoluble oil, was extracted *once* with ether, when immediately a quantity of white crystals separated from the aqueous liquid, melting sharply at 159°. This was filtered off, and the process of extraction with ether continued as already described (see p. 606). The combined ethereal extracts were evaporated to a small bulk,

* This substance will be described in detail in a future communication.

when further quantities of the substance melting at 159° were obtained, amounting in all to 47—50 per cent. of the phenyldihydroresorcin used. The substance had all the properties of 1-phenylcyclohexane-3:5-diol described by Knoevenagel (*Annalen*, 1895, **289**, 167), except that after crystallisation from ethyl acetate, from which solvent it separated in nacreous leaflets, it melted at 160° instead of 157° .

Benzoyl Derivative.—Knoevenagel (*ibid.*, p. 168) states that he was unable to obtain definite diacetyl or dibenzoyl derivatives, and when the above-prepared substance was benzoylated in the usual manner, slightly more than the theoretical amount of a dibenzoyl derivative was always obtained, which, although crystallising from alcohol, aqueous alcohol, ethyl acetate, a mixture of chloroform and light petroleum, or xylene in glistening, transparent needles, did not possess a sharp melting point. It diminished in bulk at about 95 — 108° , melted at 108 — 111° , and did not become clear until 125 — 127° . Finally, the substance was prepared by allowing the diol and benzoyl chloride to react in pyridine solution. The whole was poured into absolute alcohol, and crystallised from the same solvent, when it again formed glistening, transparent needles, softening at 110 — 114° , melting at 114 — 115° , but not becoming clear until 127° :

0.1494 gave 0.4184 CO_2 and 0.0898 H_2O . $\text{C} = 76.37$; $\text{H} = 6.67$.

$\text{C}_{26}\text{H}_{24}\text{O}_4$ requires $\text{C} = 78.00$; $\text{H} = 6.00$ per cent.

$(\text{C}_{26}\text{H}_{24}\text{O}_4)_2 \cdot \text{C}_2\text{H}_5 \cdot \text{OH}$ requires $\text{C} = 76.59$; $\text{H} = 6.38$ per cent.

The fact that the substance is always produced in rather more than the theoretical amount would indicate that it crystallises with solvent of crystallisation, which supposition is borne out by the above analysis. It was, nevertheless, not found possible to drive off the solvent either by keeping in a vacuum or by heating to 100° for some time. Similar instances of compounds crystallising with solvent of crystallisation, which could not be eliminated, have been recorded by Morgan and Micklethwait (*T.*, 1908, **93**, 615) and by Cain and Micklethwait, (*T.*, 1914, **105**, 1438).

When this benzoyl derivative was hydrolysed with alcoholic potassium hydroxide it gave the original phenylcyclohexanediol (m. p. 160°) in theoretical amount.

The ethereal mother liquors from which the diol (m. p. 160°) had crystallised out were completely evaporated, leaving a reddish-yellow resin, which was boiled with water and filtered while hot, from a small amount of insoluble material, allowed to cool, and extracted ten times with ether. On evaporating to a small bulk a white solid separated, which was crystallised from water (0.7 gram from 20 grams of phenyldihydroresorcin) and analysed:

0.1614 gave 0.4425 CO_2 and 0.1172 H_2O . $\text{C}=74.77$; $\text{H}=8.07$.

$\text{C}_{12}\text{H}_{16}\text{O}_2$ requires $\text{C}=75.00$; $\text{H}=8.33$ per cent.

1-*Phenylcyclohexane-3:5-diol*, probably the *cis*-modification, is sparingly soluble in benzene or chloroform on warming, more soluble in water, and readily soluble in ethyl acetate, acetone, or alcohol; in fact, in these respects it is identical with the variety melting at 160° . It crystallises from ethyl acetate or water in radiating clusters of nacreous, scaly needles, melting at 134° .

The *dibenzoyl* derivative, prepared in the usual manner, crystallises from alcohol in radiating clusters of small, silken needles, melting at 117° :

0.1053 gave 0.3025 CO_2 and 0.0547 H_2O . $\text{C}=78.34$; $\text{H}=5.77$.

$\text{C}_{26}\text{H}_{24}\text{O}_4$ requires $\text{C}=78.00$; $\text{H}=6.00$ per cent.

This benzoyl derivative is produced in theoretical amount, and when hydrolysed regenerates quantitatively the *phenylcyclohexane-diol*, melting at 134° .

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[Received April 12th, 1915.]
